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DESENVOLVIMENTO DE PROCESSOS QUÍMICOS**

**Simulação e otimização de reator de formaldeído,
processo prata, usando técnicas de
inteligência artificial**

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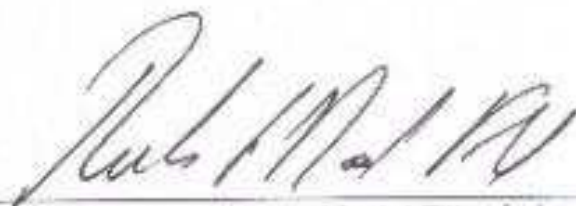
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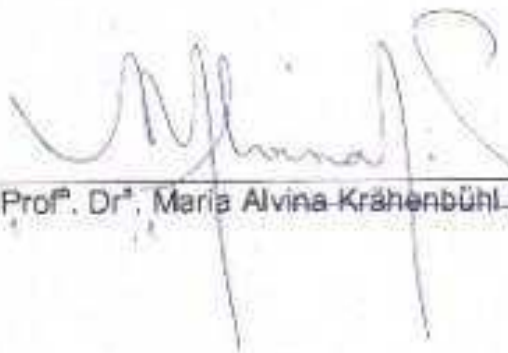
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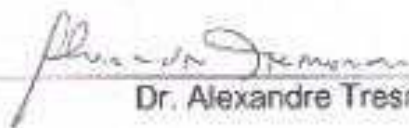
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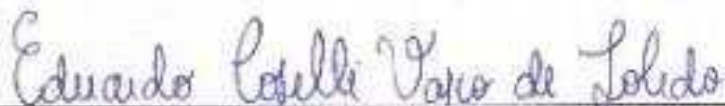
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que chegou para alegrar minha
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RESUMO

Essa tese encontra-se focada na simulação e otimização de um reator de leito fixo com catalisador de prata para oxidação do metanol a formaldeído, utilizando técnicas de inteligência artificial (algoritmo genético e redes neurais artificiais).

O formaldeído é um importante intermediário químico utilizado principalmente na produção de adesivos ou resinas empregados em vários segmentos de mercado. A sua produção pelo processo “Prata” encontra-se em desvantagem frente às novas plantas construídas com o moderno processo “Formox”, catalisado por óxido de ferro-molibdênio, por apresentar menor desempenho e possuir poucas ferramentas que permitam melhorar o processo. Poucos modelos cinéticos são encontrados na literatura para o processo Prata, inadequados para a simulação do reator sob condições industriais. Há falta de dados cinéticos de qualidade para o desenvolvimento de equações da taxa e existem dificuldades experimentais em obtê-los sob condições industrialmente relevantes.

Um simulador híbrido foi desenvolvido para o reator de formaldeído, empregando-se um modelo determinístico baseado na equação diferencial de balanço de massa aplicado sobre o leito fixo e uma rede neural artificial para modelar a cinética da reação, implementada como uma sub-rotina no simulador. Como dados cinéticos não se encontravam disponíveis para o ajuste da rede neural (treinamento), essa operação foi realizada através de três abordagens, usando uma associação de algoritmos genéticos e métodos de treinamento tradicionais para a rede neural, de modo a utilizar dados de processo (conversão e seletividades), amplamente disponíveis na literatura e facilmente mensuráveis em operações industriais.

Tendo a rede neural sido treinada através das três abordagens apresentadas, o simulador foi capaz de estimar adequadamente o desempenho do reator, validado em comparação com dados experimentais obtidos da literatura e dados industriais. Várias simulações foram realizadas para determinar as influências de importantes variáveis operacionais no desempenho do reator, como temperatura, vazão de ar, vazão de metanol, vazão de água e tempo de residência, apresentando de forma gráfica informações fundamentais para a comunidade industrial e científica. Os resultados obtidos foram discutidos com base no mecanismo da reação e trabalhos publicados na literatura.

A otimização do reator, utilizando-se o simulador validado, foi realizada através de dois métodos: algoritmo genético e SQP. O SQP foi empregado como referência nessa comparação, tratando-se de um método clássico de otimização, baseado em gradientes. Demonstrou-se que, dependendo da estimativa inicial, o SQP pode convergir para um ótimo local, muito distante do global e que o algoritmo genético sempre convergiu para o ótimo global, não dependendo de estimativas iniciais. A melhor abordagem, no entanto, mostrou ser a associação dos dois métodos para obter maior precisão com menor tempo computacional.

As técnicas de inteligência artificial (redes neurais e algoritmo genético) foram perfeitamente empregadas em conjunto com equações determinísticas, gerando modelos híbridos. A modelagem da cinética da reação, bem como do reator de formaldeído foi bem sucedida, validada em diversas situações. Vários casos foram estudados, indicando a condição de operação otimizada para cada, o que permitirá às plantas de prata definir as melhores políticas operacionais para minimizarem os custos com o consumo de matéria-prima.

ABSTRACT

The focus of this Thesis is the simulation and optimization of a silver catalyzed fixed-bed reactor for the oxidation of methanol to formaldehyde, using artificial intelligence techniques (genetic algorithm and artificial neural networks).

Formaldehyde is a key chemical intermediate used mainly in the production of adhesives and resins for several market segments. Its production by the “Silver” process is behind new plants operated with the modern “Formox” process, catalyzed by iron-molybdenum oxide, as far as performance and optimization tools are concerned. A few kinetic models are found in literature for the Silver process but they are inadequate to simulate the reactor at industrial conditions. Lack of good quality available kinetic data makes difficult the development of rate equations and new data is not easily obtained due to constraints to run experiments at relevant industrial conditions.

A hybrid simulator was developed for the formaldehyde reactor, using a deterministic model based on differential mass balance equation over the fixed-bed, and a neural network to model the reaction kinetics, implemented as a sub-routine in the simulator. As kinetic data were not available for the neural network fit (training), this operation was performed through three approaches, using an association of genetic algorithms and classical training methods, employing process information (conversion and selectivity), widely available in literature and easily measured by industrial plants.

After training the neural network through the three presented approaches, the simulator was able to properly estimate the reactor performance, which was validated by comparison with literature experimental data and industrial data. Many simulations were run in order to clarify the influences of important operational variables (temperature, air flowrate, methanol flowrate, water flowrate and residence time) on the reactor performance, presenting the results in graphic format. The discussion was carried out based on the reaction mechanism and literature work, adding value to the industrial and scientific community.

The reactor optimization, using the validated simulator, was made by two methods: genetic algorithm and SQP. SQP was used as a reference, consisting in a classical optimization method, gradient-based. It was demonstrated that SQP may reach a local optimum, far from the global one, depending on the initial estimate. The genetic algorithm,

differently, always converged to the global optimum, not depending on initial estimates. The best approach, however, was the association of both methods in order to obtain best precision with shorter computing times.

The artificial intelligence techniques (neural network and genetic algorithm) were perfectly employed here together with deterministic equations, producing hybrid models. The kinetic modeling of the chemical reaction, as well as the reactor modeling, was successful, validated in several situations. Many cases were studied, indicating the optimized conditions for each one, whose conclusions will allow Silver plants to define the best operational policies to minimize costs with raw material consumption.

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CAPÍTULO 1 INTRODUÇÃO

O formaldeído é um importante intermediário químico utilizado na produção de adesivos para vários setores produtivos, como construção civil, automotivo, fundição e naval (WANG ET AL., 2005). Duas rotas de produção são comercialmente empregadas para a manufatura desse produto: o processo Prata, desenvolvido no início do século XX e o processo Formox, desenvolvido na década de 50. Esse último apresenta desempenho muito superior ao primeiro, traduzindo-se em um menor custo operacional, o que explica por que as novas plantas de formol construídas nas últimas décadas empregam massivamente o processo Formox. No entanto, de 30 a 50% da capacidade instalada no mundo ainda depende de plantas Prata, as quais sofrem com a falta de assistência técnica especializada e estudos publicados que permitam otimizar a sua operação, diminuindo assim a desvantagem para as plantas mais modernas.

Nesse trabalho, foi desenvolvido um simulador para o reator de formaldeído com catalisador de prata, empregando uma rede neural para o cálculo da taxa de reação química. Três abordagens foram apresentadas para o treinamento (ajuste) da rede neural, todas baseadas em dados de processo, uma vez que dados cinéticos não se encontravam disponíveis.

Várias simulações foram realizadas com o intuito de estabelecer as relações entre as variáveis operacionais e o desempenho do reator. Com o simulador validado, o reator foi otimizado em uma série de cenários, representando situações possíveis em uma planta industrial.

As ferramentas desenvolvidas, bem como os resultados reportados nessa tese, permitem a melhor compreensão desse processo e a otimização das plantas Prata, apresentando-se como uma importante contribuição para a comunidade industrial e científica. Uma vez que os principais subprodutos desse processo são o dióxido de carbono e o monóxido de carbono, esse trabalho permitirá a redução das emissões de carbono dessas plantas, enquadrando-se nos esforços mundiais contra o aquecimento global.

1.1. Objetivos

O objetivo dessa tese é apresentar novas ferramentas e novas abordagens para a simulação e otimização de um reator de formaldeído por processo Prata, representando uma vantagem competitiva para as plantas com essa tecnologia frente às modernas plantas Formox.

É importante destacar que as metodologias apresentadas nesse trabalho podem ser facilmente adaptadas a outros sistemas químicos, trazendo importantes contribuições a esses processos no que tange à redução de custo, minimização na emissão de poluentes ou melhoria nas condições de segurança.

As principais contribuições dessa tese são:

- Desenvolvimento de um simulador para o reator de Prata, utilizando uma abordagem híbrida baseada em modelos determinísticos para o leito fixo e redes neurais para a cinética de reação, com solução numérica das equações realizada pelo método Crank-Nicholson;
- Apresentação de uma nova abordagem para a obtenção de dados de taxa de reação a partir de dados de operação do reator facilmente mensuráveis (conversão e seletividades) e sua utilização para treinamento da rede neural (modelagem da cinética de reação);
- Apresentação de uma abordagem híbrida para treinamento da rede neural, associando-se o clássico método de retro-propagação com algoritmo genético;
- Apresentação de uma nova abordagem “acoplada” para treinamento da rede neural, utilizando-se algoritmo genético para ajuste dos pesos;
- Definição de melhores políticas operacionais, possibilitando a otimização do reator de Prata;
- Apresentação de comparação entre o desempenho de dois diferentes métodos de busca - algoritmo genético e programação quadrática sucessiva (SQP) - na otimização do reator de Prata.
- Desenvolvimento de “softwares” abertos para a comunidade acadêmica:
 - ✓ “Software” de treinamento da rede neural, baseado apenas em retro-propagação (NEURAL.FOR);

- ✓ “Software” de treinamento da rede neural, baseado em uma associação de algoritmo genético e retro-propagação (GARNA.FOR);
- ✓ “Software” de treinamento da rede neural considerando-a uma “caixa-preta” dentro do simulador, baseado em algoritmo genético (GAFIT.FOR);
- ✓ Simulador do reator de formaldeído, utilizando método numérico de Crank-Nicholson para solução das equações diferenciais (HCHOPRATA.FOR);
- ✓ Otimizador do reator de formaldeído, baseado em algoritmo genético e SQP (OTIGA.FOR).

Esses “softwares” encontram-se configurados para os sistemas estudados nessa Tese, porém, podem ser facilmente adaptados para simulação de reatores de leito fixo de outros sistemas e otimização de processos mais variados.

As inovações apresentadas nesta tese são:

- Desenvolvimento de um modelo da cinética da reação de oxidação do metanol a formaldeído sobre o catalisador de prata baseado em Redes Neurais Artificiais, mais abrangente e exato que os modelos determinísticos encontrados na literatura e mais direcionado às condições industriais reais.
- Criação de um software de treinamento para Redes Neurais, usando Algoritmo Genético de modo a encontrar o conjunto ótimo de pesos para cálculo da taxa de reação através das Redes Neurais, mas minimizando o erro entre a conversão e seletividades do reator calculadas e reais.

1.2. Organização da tese

Essa tese possui grande inter-relação entre os capítulos, como mostra a Figura I. Para efeito de apresentação, optou-se por iniciar a tese pela descrição dos trabalhos de treinamento da RNA (Capítulos 3 a 5), definindo a cinética de reação, onde o simulador do reator foi empregado para desenvolvimento do método e validação dos resultados. O simulador foi descrito em detalhes apenas no Capítulo 6, porém seu desenvolvimento é referenciado a partir do Capítulo 3.

O Capítulo 2 apresenta informações sobre o formaldeído, incluindo capacidades produtivas, métodos de obtenção, descrição dos processos industriais e as reações envolvidas, bem como uma discussão sobre os limites de flamabilidade frente às condições

de operação. Também apresenta uma análise do equilíbrio químico desse sistema, demonstrando que a produção do formaldeído não é favorecida pelo equilíbrio termodinâmico, reforçando a necessidade de estudos cinéticos para otimização desse processo.

Os Capítulos 3 a 5 apresentam diferentes abordagens para treinamento da rede neural. O Capítulo 3 apresenta a nova abordagem para obtenção de dados de taxa de reação a partir de dados de processo do reator (conversão e seletividades) e o treinamento clássico da rede neural através de retro-propagação. O Capítulo 4 utiliza os dados de taxa de reação obtidos no Capítulo anterior para realizar o treinamento da rede neural através de um método híbrido que emprega algoritmo genético e retro-propagação. O Capítulo 5 apresenta uma nova abordagem para o treinamento da rede neural, onde essa é considerada “acoplada” ao simulador e apenas dados de processo (conversão e seletividades) são utilizados no treinamento, ao invés de dados de taxa de reação.

O Capítulo 6 apresenta simulações realizadas para diferentes casos com o “software” contendo a rede neural treinada, bem como uma discussão baseada em resultados de artigos publicados na literatura e mecanismo da reação. Os resultados permitem compreender a relação entre variáveis de processo e o desempenho do reator. O simulador, desenvolvido nesse trabalho e apresentado em detalhes no Capítulo 6, foi utilizado no desenvolvimento dos Capítulos 3 e 4 para obtenção dos dados de taxa de reação com uma cinética simplificada, e especialmente utilizada no Capítulo 5, onde o simulador foi o modelo para o treinamento da RNA (essa importante inter-relação entre os Capítulos 5 e 6 está ilustrada na Figura I).

O Capítulo 7 traz um estudo de otimização do reator, utilizando o simulador validado nos capítulos anteriores, considerando-se vários cenários condizentes com a realidade industrial. A otimização é realizada através de dois métodos de busca: algoritmo genético e SQP, mostrando as vantagens e desvantagens de cada um, bem como de sua associação. Uma análise econômica é apresentada, mostrando a redução no custo de produção entre a condição normal de operação industrial e as condições otimizadas reportadas nesse trabalho.

O Apêndice A apresenta uma descrição detalhada do algoritmo genético, ilustrado com exemplos. O Apêndice B contém a descrição do método numérico de Crank-Nicholson, utilizado para a solução das equações diferenciais no simulador do reator.

A descrição detalhada das redes neurais, com exemplos, pode ser encontrada na dissertação de mestrado de Papes Filho (1999).

O Apêndice C apresenta o conceito de Engenharia Co-Corrente (Concurrent Engineering) aplicado a um reator de acetaldeído, também simulado com a aplicação de uma RNA para cálculo das taxas de reação. O conceito baseia-se na integração de diferentes “softwares” ou grupos de trabalho para que informações geradas por cada parte sejam agrupadas e harmonizadas, maximizando o desempenho do sistema e fornecendo resultados de forma ágil e prática. No caso apresentado, “softwares” de treinamento da RNA e simulador do reator de acetaldeído são integrados por um Sistema Especialista (Expert System) que coordena a entrada de dados do usuário, a simulação automática de diferentes casos e realiza cálculos termodinâmicos, apresentando resultados na forma de gráficos ou relatórios, facilmente compreensíveis pela equipe operacional da planta. O Sistema Especialista também emite alarmes e fornece sugestões de alterações nas condições operacionais permitindo aos operadores agir rapidamente frente a situações inesperadas, mantendo a planta nas condições ideais de desempenho (conversão e seletividade) e segurança (limites de flamabilidade). O conceito pode ser aplicado igualmente para uma planta de formaldeído, integrando-se os “softwares” desenvolvidos nessa tese (treinamento da RNA, simulação e otimização do reator de Prata) para auxiliar equipe operacional na sua utilização diária.

O Apêndice D apresenta um compêndio das equações mais relevantes, propriedades físicas, pesos da Rede Neural e “sites” de referência.

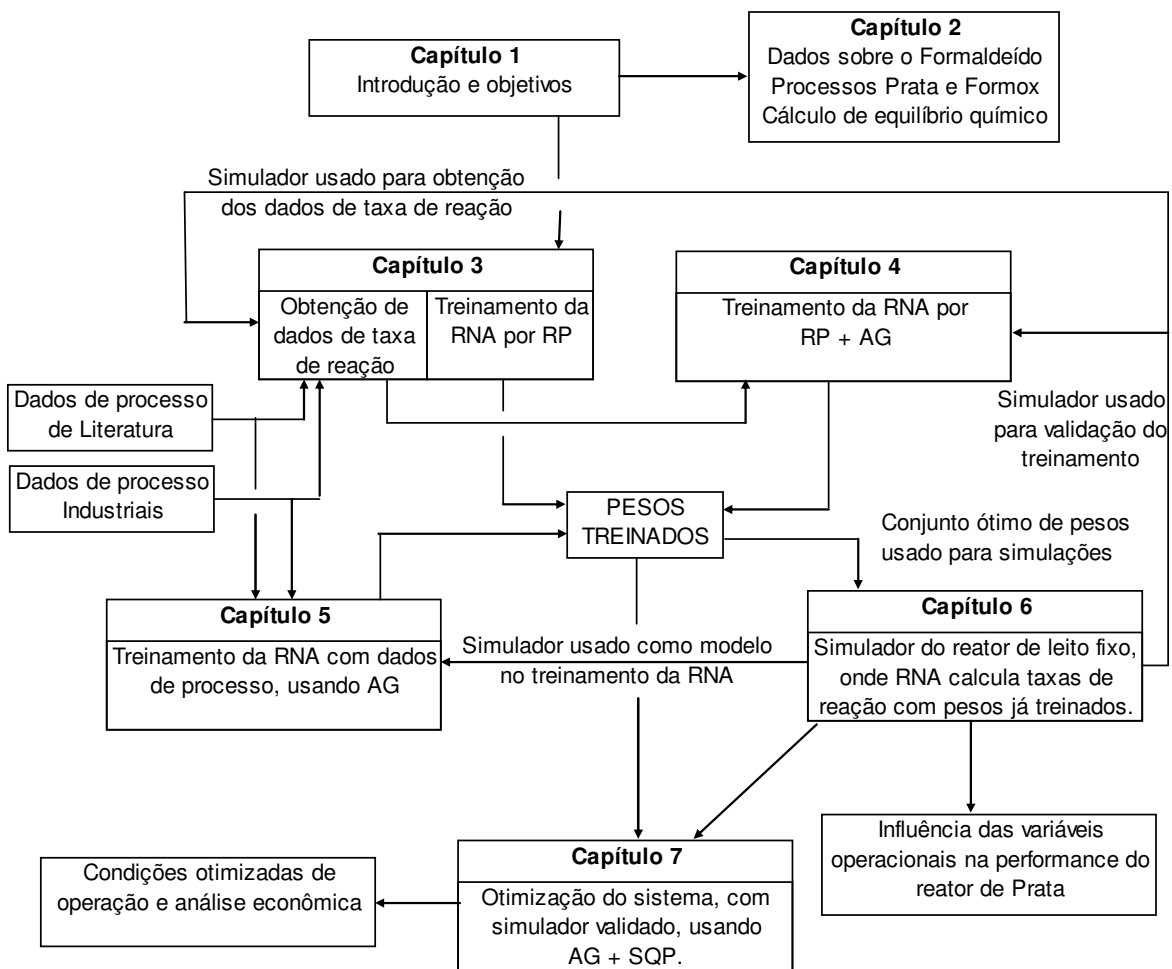


Figura I: Inter-relações entre os Capítulos da tese

CAPÍTULO 2

AVALIAÇÃO DE PROCESSOS COMERCIAIS PARA PRODUÇÃO DE FORMALDEÍDO

2.1. Introdução

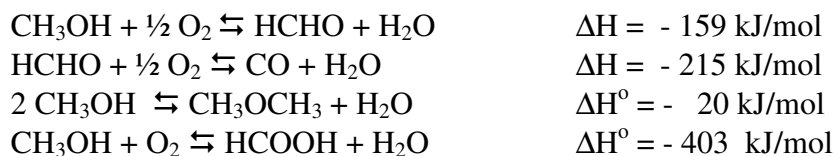
O formaldeído é um importante intermediário orgânico, sintetizado pela primeira vez em 1868 por August Wilhelm von Hofmann e ainda hoje tem posição de destaque na indústria química figurando como matéria-prima para a produção principalmente de resinas uréia-formaldeído e fenólicas, empregadas em vastas aplicações nos setores de construção civil, automotivo, fundição e naval.

A produção mundial desse monômero saltou de 15 milhões de toneladas em 1996 para 32 milhões de toneladas em 2004 (base solução 37%). A China assumiu recentemente a liderança na produção de formaldeído, com pelo menos 500 plantas com capacidade para 11 milhões de toneladas/ano.

No Brasil, a demanda em 2005 foi de 687.000 toneladas (base 37%). A produção mais que dobrou entre 1995 e 2004, encontrando-se distribuída entre 9 produtores.

O principal método de produção do formaldeído baseia-se na oxidação catalítica do metanol em corrente de ar. Duas rotas são comercialmente usadas na indústria química: o processo Prata e o Formox.

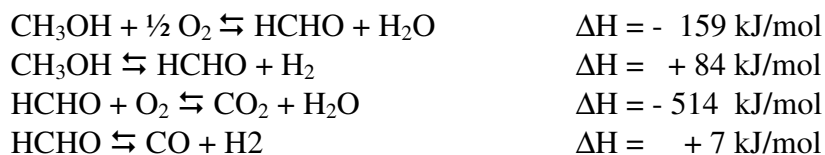
O processo Formox (FALIKS ET AL., 2001) é o mais novo, utilizado industrialmente a partir da década de 50. Esse método consiste na oxidação do metanol em excesso de ar, em um reator multitubular preenchido com catalisador de óxido de ferro-molibdênio. A temperatura de reação está na faixa de 250 – 400 °C, atingindo-se conversões típicas de metanol de 98 – 99% e rendimento para formaldeído na faixa de 88 – 93 %. As equações químicas envolvidas nesse processo são:



onde o monóxido de carbono é o principal subproduto.

O processo Prata data do início do século XX e consiste na alimentação de uma corrente de metanol e ar, rica no combustível, em um leito fixo simples de partículas de

prata eletrolítica. A temperatura de operação encontra-se na faixa de 600 – 700 °C, e a reação é extremamente exotérmica, ocorrendo em condições adiabáticas. Aproximadamente 50 – 60% do formaldeído é gerado na reação de oxidação do metanol e o restante na reação de desidrogenação. Os principais subprodutos são o dióxido de carbono, gerado pela oxidação do formaldeído; e o monóxido de carbono, gerado pela decomposição do formaldeído na fase gasosa, a altas temperaturas (MATSUBAYASI E NAKAHARA, 2005). As equações químicas são:



Várias versões do processo Prata foram desenvolvidas, mas duas são utilizadas comercialmente:

- O Processo Metanol, onde apenas metanol e ar são alimentados no reator, com conversão incompleta, requerendo posterior destilação.
- O Processo BASF, onde água é acrescentada à mistura metanol-ar, possibilitando atingir altas conversões (98 – 99%) com boa seletividade para formaldeído (85 – 90%). A adição de água é limitada pela especificação de concentração do produto final. O efeito benéfico da água na seletividade desse processo deve-se principalmente à sua alta capacidade calorífica, removendo calor da reação (o leito não é resfriado), prevenindo superaquecimento do reator e consequentemente sinterização do catalisador. A água também auxilia na queima do coque na superfície do catalisador, expondo seus sítios ativos, e participa do mecanismo de reação, reduzindo a formação de subprodutos.

Mesmo após um século de produção industrial, ainda não há uma perfeita compreensão da síntese do formaldeído em catalisador de prata. Considerando-se que as plantas operando com esse processo encontram-se em desvantagem com relação às plantas Formox e o preço do metanol mais que dobrou desde a década de 1980, representando hoje parcela superior a 80% do custo de fabricação do formaldeído, é claro o interesse em melhorar a seletividade das plantas de prata: um aumento de 1 ponto percentual na seletividade para formaldeído em uma planta de médio porte representa uma economia da

ordem de US\$ 200.000 por ano em compras de metanol, o que justifica o grande esforço da comunidade científica para esse sistema.

Qualquer estudo no sentido de melhorar a seletividade das plantas de formaldeído vai ao encontro da mobilização mundial para redução das emissões de carbono, freando o aquecimento global, uma vez que os óxidos de carbono são os sub-produtos deste processo.

Nesse capítulo também é apresentada uma discussão sobre os limites de flamabilidade (PERRY E CHILTON, 1980) do sistema químico, comparando-se com as condições típicas de operação para os processos Prata e Formox.

Cálculos de equilíbrio para o processo Prata foram realizados, demonstrando que a formação do formaldeído não é favorecida pelo equilíbrio termodinâmico, o que deixa evidente a importância dos estudos cinéticos para esse sistema.

2.2. Desenvolvimento

O desenvolvimento desse capítulo é descrito no artigo intitulado “Evaluation of Commercial Processes for Formaldehyde Production”, apresentado a seguir, que será submetido para publicação em revista indexada internacional.

Evaluation of Commercial Processes for Formaldehyde Production

Antonio Carlos Papes Filho^{1*} and Rubens Maciel Filho¹

1. Introduction

Formaldehyde is one of the world's most important chemicals, basic building unit for a wide variety of substances. It is the simplest aldehyde, synthesized for the first time in a lab during the nineteenth century (1868) by August Wilhelm von Hofmann (Walker, 1975) and still today plays an important role on the chemical industry, found in many objects used in our daily life. In 1992, formaldehyde ranked the 22nd place among the top 50 chemicals produced in United States.

It is also produced by nature, in small concentrations, as a result of the metabolic process of plants and animals, including the human being (the human blood contains 2 to 3 ppm of formaldehyde). Incomplete combustion of organic compounds also generates formaldehyde, thus it can be found on the off gas from automobiles, thermal power plants, boilers and cigarettes.

The metanal (IUPAC name) is a gas at room temperature and normally is commercialized in aqueous solution, known as formalin, safer and more practical to be handled. Some physical properties of the pure formaldehyde are shown in Figure 1.

Formaldehyde is very reactive, even in aqueous solutions. It polymerizes by itself, forming a polymer of formaldehyde, known as paraformaldehyde. This reaction takes places at higher formaldehyde concentrations or lower temperatures. In this sense, formalin is commercialized in solutions containing about 25 to 56 % formaldehyde by weight (the standard solution has concentration of 37 %), and it must be kept warm to prevent polymerization. Methanol acts as a stabilizer for formalin solutions and industrial products may be manufactured with 4 to 12% methanol in order to increase shelf life and reduce storage temperature requirements to economical levels. The physical properties of many formalin solutions may be found in literature (Walker, 1975).

Figure 1: Physical properties of pure formaldehyde

Odor:	pungent, irritating to eyes, nose and throat
Molecular weight:	30,03 g/mol
Boiling point (1 atm):	- 19 °C
Freezing point (1 atm):	- 118 °C
Flammable limits:	7 % to 72 % (formaldehyde/air, v/v)

2. Production and capacities

The world's production of this monomer has jumped from 15 million of metric tons per year in 1996 (Kirk Othmer, 1986) to 32 Mtons in 2004 (ABRAF, 2004), in a 37% solution basis. Its manufacture was begun in the United States on a limited scale in 1901. At this time, it was only used as a disinfectant and embalming agent. However, the development of the synthetic resin industry, initiated by the discoveries of Dr. Leo Baekeland in 1909 soon resulted in an increasing commercial demand on the infant industry (Walker, 1975).

Nowadays, formaldehyde is produced all over the world, as shown in Tables 1 and 2. Table 1 presents the total production with Silver and Formox processes as well as the total installed capacity, as of 1986. Table 2 shows the total demand by continent in 2005.

Table 1: Worldwide formaldehyde production capacities in 1986 (Ullman, 1988)

Country	Production Silver Process^(a)	Production Fe-MO Process^(a)	Total Capacity^(a)
United States	1,052	385	1,437
Germany	697	135	832
Japan	461	86	640
Russia	-	51	421
Italy	-	311	318
Canada	111	74	185
France	155	26	181
Great Britain	118	15	179
Indonesia	10	33	172
Sweden	-	124	124
Yugoslavia	44	56	122
North Korea	47	-	116
Taiwan	47	-	105
Brazil	58	23	102
China	-	-	74
Mexico	12	20	74
Australia	54	-	54
Argentina	21	11	45
Poland	37	-	37
Turkey	13	13	35
South Africa	26	-	33
Other			
Europe	293	312	572
East Europe	4	61	86
East Asia	78	14	159
Africa / W.Asia	39	22	98
Latin America	14	31	46

^(a) thousands of metric tons per year – 100% base

Table 2: Worldwide formaldehyde demand in 2005 (ABRAF, 2004)

Country/region	Demand (kt/yr)
<i>Asia</i>	<i>14,890</i>
<i>European Union</i>	<i>8,308</i>
<i>North America</i>	<i>5,772</i>
<i>East Europe</i>	<i>2,423</i>
Latin America and Africa	1,317

^(b) thousands of metric tons per year – 37% base

Current Eastern European and Russian formaldehyde markets are expected to grow by 5% per year, driven mostly by the wood panel manufacturing, favored by cheap local raw materials. Western European market should remain stable as costs are higher in this region. Germany still figures as the main formaldehyde user in Europe. China has assumed the leading producing country in the world, with at least 500 formaldehyde plants with total capacity of 11 million tones per year (GRFT, 2007).

Formaldehyde demand in Brazil was reported as 687,000 metric tons (37% basis) in 2005 (ABRAF, 2004). Production capacity more than doubled from 1995 to 2004 as shown in Table 3. In 2005, the capacity was distributed among 9 producers (ABIQUIM, 2006):

- Synteko (facilities in Gravatai-RS, Araucaria-PR and Uberaba-MG)
- Copenor (Camacari-BA and Sorocaba-SP)
- Hexion (Curitiba-PR)
- Elekeiroz (Varzea Paulista-SP)
- Dynea (Araucaria-PR)
- Georgia-Pacific (Jundiai-SP)
- Schenectady (Rio Claro-SP)
- Royalplas (Guarulhos-SP)
- Sulana (Maringa-PR)

Table 3: Production capacity of formaldehyde in Brazil (ABRAF, 2004)

Year	Capacity, k_ton/yr (37% basis)
1995	322
1996	328
1997	424
1998	454
1999	462
2000	514
2001	587
2002	793
2003	794
2004	850
2005	850

As of 1998, three manufacturers were responsible for 50% of the formaldehyde capacity in USA: Georgia-Pacific, Hoechst Celanese Corp, and Hexion.

3. Production Processes

The partial oxidation of gaseous methanol on air stream is the major method to manufacture formaldehyde. Two important routes are used in the industrial production: the first synthesis route is performed over an electrolytic silver catalyst at air-lean condition, which has been commercialized at the beginning of the twentieth century (classical method); the second route, industrialized since the 1950s, is by the oxidation in excess air over a ferric molybdate catalyst. Other routes have not been commercialized yet, like the sodium catalyzed dehydrogenation of methanol to anhydrous formaldehyde and the partial oxidation of methane over silica catalyst (Qian et al., 2003).

Nowadays, new formaldehyde plants are built using the Formox process, but 30 - 50% of the current world's capacity rely on plants that use silver process (Van Veen et al., 2002; Qian et al., 2003; Waterhouse et al., 2004a; Silver Institute, 2006). Its advantages are low investment cost, high yield and stable process.

The Formox process consists in methanol oxidation on excess air, over an iron-molybdenum catalyst at 250 – 400 °C (Santacesaria and Morbidelli, 1981; Piccoli, 1992; Belmar, 1995; Kim et al., 2004; Soares et al., 2005). Typical conversion is 98-99 % and yield on 88-93% range. All formaldehyde is formed by the exothermic oxidation (Eq 1) and the higher the temperature, the higher the secondary reaction of combustion (Eq 2), reducing the selectivity towards the desired product. Other side reactions are the formation of dimethyl ether (Eq 3) and formic acid (Eq 4).



In the Silver process, two parallel reactions take place to form formaldehyde: methanol oxidation (Eq 5) and methanol dehydrogenation (Eq 6), on air stream and excess methanol, over a silver catalyst at 600 – 700 °C. The reaction is extremely exothermic and is carried out under adiabatic conditions. Approximately 50-60% of the formaldehyde is produced by oxidation and the remaining by dehydrogenation. Formaldehyde may also react with oxygen over the silver catalyst, forming carbon dioxide (Eq 7). At high temperature, formaldehyde decomposes to carbon monoxide on the gas phase (Eq 8). Reactions 7 and 8 reduce the selectivity towards the desired product.



Oxidation reactions supply heat to make the process self-sustaining and are also believed to keep the catalyst active and displace the dehydrogenation equilibrium towards the products (Walker, 1975).

Various versions of the conventional silver-catalyzed process are described in many different patents, but two main variations are used industrially:

Methanol Ballast Process: only air and pure methanol are fed to the silver bed, featuring incomplete methanol conversion (77 – 87 %) and requiring a distillation recovery of the raw material.

Water Ballast Process: firstly employed on an industrial scale by BASF in 1905, this process remains unchanged and it is still in use today; advances in process design have made yields as high as 91-92%. Extra water is fed with the reactant mixture, achieving almost complete conversion of methanol (98-100%). However, water is limited by the requirement on the concentration specs of the final product. Due to the high heat capacity, water vapor removes a great deal of reaction heat, thereby preventing detrimental overheating as well as sintering of catalyst. It also helps to burn away the coke of catalyst surface to expose active sites (the shelf-life of silver on this process is significantly longer than that in the methanol ballast process), blocks specific surface sites or displaces the reaction mechanism reducing the formation of undesirable by products (Bartean and Madix, 1984; Qian et al, 2003; Andreasen et al., 2003). Typical selectivity is found on 85 – 90% range.

Qian et al. (2003) compared Methanol Ballast to Water Ballast processes and concluded that the later performs higher conversion of methanol and selectivity to formaldehyde.

Despite a century of industrial production, there is no comprehensive insight into the silver-catalyzed formaldehyde synthesis available. Considering the potential market demand for formaldehyde and strong competition, even small improvements are economically attractive. Current methanol prices are higher than twice of 1988 figures and methanol cost represents today more than 80% of the production cost of formaldehyde, thus, there is crescent economical pressure to improve the process selectivity towards formaldehyde. An improvement of 1 percentage point on the selectivity towards formaldehyde in an average size plant means saving about 200,000 US\$ per year on methanol purchasing. This is certainly one of the reasons that quite some research work is devoted to this system (Van Veen et al., 2002).

Any attempt towards improving the formaldehyde selectivity will contribute to world's efforts to reduce carbon emission to prevent global warming, once carbon oxides are the by-products of this process.

Formaldehyde is only formed in the presence of oxygen. The oxygen interaction with silver catalyst plays an important role on the mechanism of the reaction. It is supposed to be responsible for keeping the catalyst active (Bhattacharyya et al., 1971). Electronic microscopy reveals that the morphology of silver catalyst changes strongly during the reaction, observing pinholes firstly predominantly in the vicinity of initial surface defects and spread gradually from the region of defects to the entire silver surface. This reaction-induced morphological restructuring reinforces the formation of grain boundary defects over the catalyst, which enables more oxygen to penetrate into the silver lattice and, in turn, to intensify the reaction. Many articles explore this subject under the surface science perspective (Wachs and Madix, 1978; Bazilio et al., 1985; Pestryakov and Davydo, 1994; Nagy and Mestl, 1999; Van Veen et al., 2002; Qian et al., 2003; Waterhouse et al., 2004a).

This is a very clean process, where most of the streams can be recycled to recover raw materials and products. The main waste stream is the off-gas, containing mostly nitrogen, hydrogen, water and carbon dioxide.

3.1. Formox Process

Compressed air, fresh and recycled methanol are fed to an evaporator, heated with steam. The gaseous stream with excess air goes to the top of a multitubular reactor, composed by 3,000 to 10,000 tubes (length: 1.0 – 1.5 m; diameter: 1 inch) filled with iron and molybdenum oxides mixture. Reaction takes place at 250 – 400 °C and the tubes are cooled with thermal fluid, controlling reaction temperature (the heat extracted from the reactor is used to produce steam).

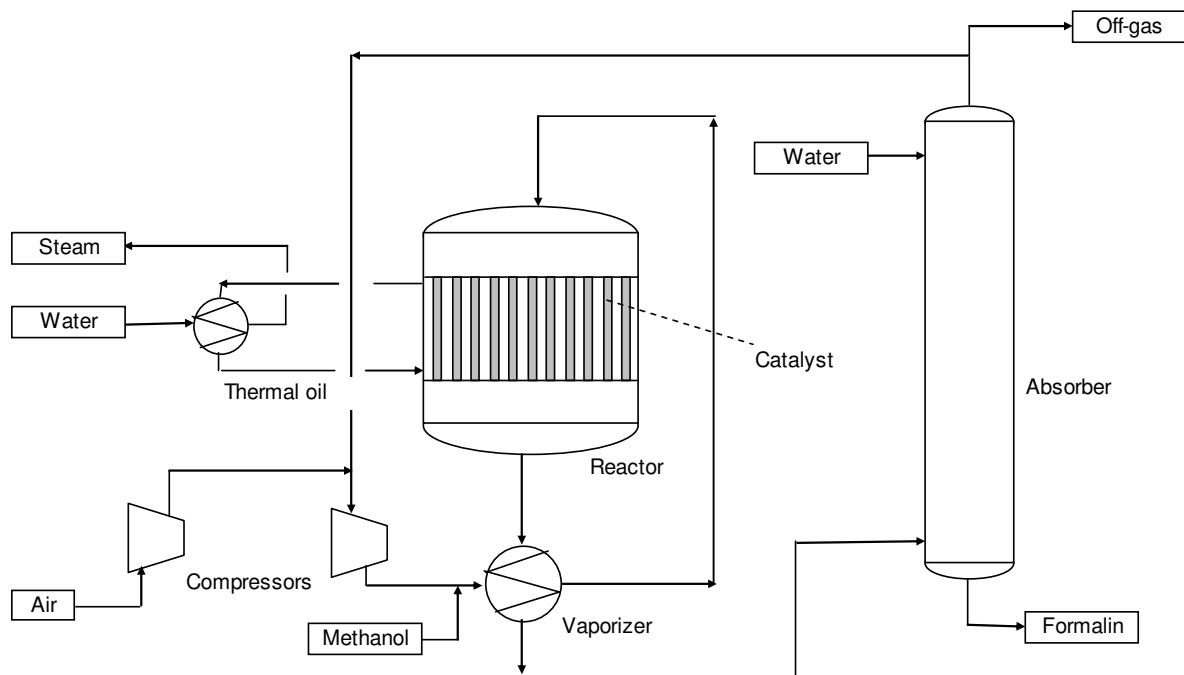


Figure 2: Flowchart of Formox process (Ullmann, 1988)

The reacted stream is promptly cooled and fed to an absorber, where the gas containing poor air, methanol and products flows countercurrent to cold water. Formaldehyde is absorbed into the water and the bottom stream is the desired product (formalin), pumped to storage tanks. The top stream contains nitrogen, water, carbon monoxide, carbon dioxide and small amount of formaldehyde and methanol. Part of the off-gas stream can be recycled to the evaporator in order to recycle methanol and dilute the reactor feed (nitrogen). Most of the off-gas is directed to a scrubber to remove traces of formaldehyde and methanol. The scrubbed off-gas is the nitrogen purge and is released to the atmosphere.

Normally, further distillation of formalin is unnecessary due to high conversion rates. Eventually, the absorption tower may be fed with a urea-water solution, instead of only water. In this case, the plant produces the urea-formaldehyde concentrate (UFC), a pre-polymer used for urea-formaldehyde resin production.

A Formox plant operated with yield of 93% (without distillation) has a methanol cost of about US\$ 148 per metric ton of formalin 37% produced.

3.2. Silver process

Compressed air, fresh and recycled methanol are fed to an evaporator, heated with steam. In the water ballast process, additional liquid water is fed to the evaporator and/or water steam is fed to the pipe before the reactor.

The gaseous stream from the evaporator is pre-heated to 100 – 200 °C and goes to the top of the reactor, composed by a single thin bed of silver catalyst (thickness: 1 – 30 mm; diameter: 1 – 2 m; particle size: 0.1 – 2.0 mm), sandwiched between a silver gauze. The feed is quickly heated to the bed set-point temperature by radiation and high thermal conductivity through the silver catalyst. There is no cooling or heating at the silver bed itself and the high net heat generated by the reactions is enough to increase feed temperature.

The catalyst bed operates in the range of 620 – 700 °C, depending on the plant process. Reactor outlet temperature is monitored by thermocouples installed below the catalyst bed. Bed temperature is maintained at set-point by controlling the inlet temperature with a pre-heater. According to industrial measurements, the fixed-bed operates adiabatically and isothermally; very small pressure drop and delta temperature are observed in practice.

Gases from the bottom of the reactor bed are quickly cooled. Normally, the bed is installed on the top of a heat exchanger, and the gases exiting the bed are fed immediately to the tubes of the exchanger, being cooled to 100 - 150 °C, with water. Steam is produced on this cooling operation, and the recovered energy is used to pre-heat the reactor inlet stream.

Right after being cooled, the stream is fed to the absorbing packed tower. Water is fed to the top of the tower and runs counter-current with the reacted stream, containing nitrogen, formaldehyde, non-reacted methanol, carbon dioxide, carbon monoxide, hydrogen and water. Formaldehyde is absorbed into the water and the bottom stream is the desired product (formalin). The top stream contains nitrogen, water, hydrogen, carbon dioxide, carbon monoxide, non-absorbed formaldehyde and methanol.

In some plants, the process can either produce formalin or UFC in the absorbing tower. In this case, instead of only water, a urea-water solution is fed to the tower and the plant produces the urea-formaldehyde concentrate (UFC). Other facilities use two absorbers: the first absorber, right after the reactor, is fed with water and produces formalin; the gas from the first absorber is fed to a second tower, counter-current with a urea solution, and produces UFC, recovering the formaldehyde not absorbed on the first tower.

The produced UFC is pumped directly to storage tanks. The produced formalin may either be pumped to storage tanks or be distilled to reduce methanol content. When distillation is used, the bottom stream is the final formalin, pumped to storage tanks, and the top stream, methanol rich, is condensed and recycled to the evaporator.

Some end-uses of formaldehyde require low methanol content, once this alcohol inhibits its reactivity. When catalyst is aged, conversion decreases and methanol content on final

product increases. Generally, the plants start operating with fresh silver turning off the distillation tower; as catalyst gets old and conversion decreases, the distillation is started.

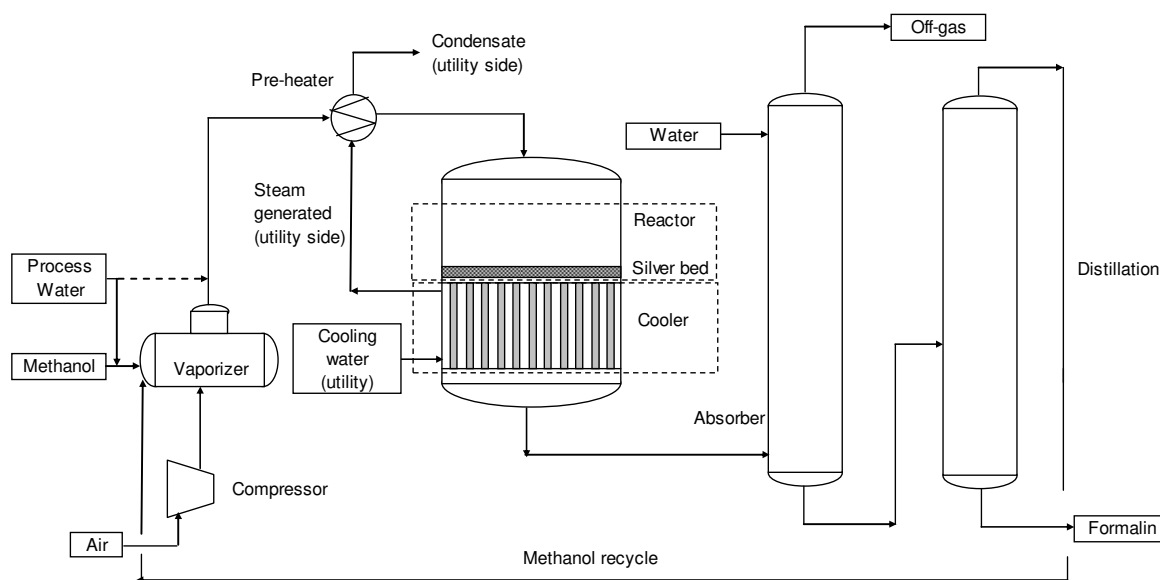


Figure 3: Flowchart of Silver process (Ullmann, 1988)

The off-gas stream from the absorption tower is directed to a scrubber to remove traces of formaldehyde and methanol. The scrubbed off-gas is the nitrogen purge (75 %, mole basis) and is released to the atmosphere, containing also water, carbon dioxide (5 %), carbon monoxide (0.3 %) and hydrogen (15 - 20 %) (Walker, 1975). Part of the off-gas stream may be recycled to the evaporator in order to dilute the reactor feed (nitrogen). The saturated water from the scrubber may be fed to the evaporator on the water ballast process.

Numerous modifications in the classical process are covered by patents. These include a two phase process in which the gases from a silver catalyst reactor are cooled, blended with additional air and then passed through a second reactor.

A Silver plant operated with formaldehyde selectivity of 85% has a methanol cost of about US\$ 162 per metric ton of formalin 37% produced, which consists in 86% of formalin variable cost, according to table 4.

3.3. Catalysts

Iron molybdenum catalyst is composed by a blend of iron oxide and molybdenum oxides, as $\text{Fe}_2(\text{MoO}_4)_3$, MoO_3 and Fe_2O_3 (molar ratio Mo:Fe from 1.5 to 3.0). Small amounts of other oxides may be present, as vanadium, copper, chromium, cobalt or phosphorous. The life time of Fe-Mo catalysts ranges from 6 to 18 months, influenced principally by mechanical destruction of the catalyst during process.

The classical process to manufacture formaldehyde by the oxidation of methanol employs silver or copper catalysts at approximately 600 °C and 725 °C respectively (Walker, 1975). The characteristics of these two catalysts were compared in the early development of the process and silver showed to be slightly more selective toward the formation of

formaldehyde, having almost completely replaced copper as a catalyst in commercial processes (Wachs and Madix, 1978; Su et al., 1994).

Table 4: Estimative of variable cost of formalin 37% production.

	Consumption ^(a)	Material price	Cost (US\$/ton) ^(b)
Methanol	0.464 ton/ton ^(c)	350 US\$/ton	162.4
Process water	1.4 ton/ton	1 US\$/ton	1.4
Catalyst losses	0.07 g/ton	0.5 US\$/g	0.035
Regenerated catalyst	0.02 kg/ton	30 US\$/kg	0.6
Electrical power	50 kW.h/ton	0.5 US\$/kW.h	25
Cooling water	40 m ³ /ton	0.01 US\$/m ³	0.4
		Variable cost	189.8

(a) Raw material consumption per ton of formaldehyde 37% basis; (b) material cost per ton of formaldehyde 37% basis; (c) Formaldehyde selectivity of 85%. Sources for consumption: Ullmann (1988), SRI International (1978) and estimations based on a Silver plant in operation. Sources for material price: international commodity indexes for methanol, market prices for silver and local estimations for other materials.

Nowadays, the dominant commercial silver catalyst used throughout the world in the methanol oxidation process is electrolytic silver (Sauer and Emig, 1995; Dai et al., 2004). Although supported catalysts exhibits longer lifetimes, the potential of application of this catalyst system is limited by its low formaldehyde yield.

Silver catalyst life time varies depending on its quality and process. The catalyst cycle varies from 2 to 6 months, and regularly the plant must be shut-down to change the bed. Some consequences of catalyst aging are decreasing conversion, decreasing selectivity towards formaldehyde, and increasing formic acid formation. The short lifetime strongly restricts its wide use in industry and results in the relatively high price of formaldehyde (Dai et al., 2004).

Lower conversion means higher methanol concentration on the final product. When methanol is higher than specification, the distillation tower must be used. When distillation cost is high or methanol specification cannot be reached, catalyst must be changed. Lower selectivity means more methanol consumption for the same formaldehyde throughput. When specific consumption is high, production costs increase and catalyst must be changed. Increased formic acid selectivity means higher concentrations on the process and on the final product. As it is a strongly corrosive by-product and undesired contaminant on formalin, plant must be shut-down for catalyst substitution.

Methanol and air must be filtered to remove particles that could poison or plug the catalyst bed. Methanol specs should be controlled to avoid introducing impurities that could poison the catalyst or the final product, as iron pentacarbonyl, ethanol, sulfur and chlorine.

Despite all chemical consequences of catalyst deactivation stated above, the main reasons for catalyst substitution are from mechanical nature: catalyst sintering (Van Veen et al., 2002; Dai et al., 2004), crush, bed cracks and catalyst blocking. If the reactor is run at high temperatures (close to 700 °C), the silver particles may melt causing catalyst sintering. Pressure drop increases and air compressor loses capacity, decreasing productivity. During reactor operation, the high gas flow through the bed agitates the silver particles that collides

one to each other, breaking the crystals and generating finer particles that blocks the voids in the bed, increasing pressure drop. In case of operational problems where bed temperature changes abruptly, the silver bed might crack, and gas may flow directly through fissures, decreasing conversion and increasing methanol concentration on final product. Lastly, impurities from methanol or from air may poison the catalyst or block its voids, reducing conversion and increasing pressure drop.

Used catalyst is regenerated by electrolytic process and may be reused in other cycle. The silver surface structure is very important to formaldehyde reaction, but it is also a very difficult parameter to be measured. The efficiency of the silver catalyst depends on the quality of the electrolytic regeneration. In this sense, silver performance as catalyst may vary from plant to plant and from one silver batch to other, in the same plant (Waterhouse et al., 2004b).

Studies show that an initialization phase is needed to properly activate the silver catalyst. This is observed in industrial plants and can take some hours to several days (Nagy et al., 1998; Van Veen et al., 2002; Qian et al., 2003; Cao and Gavriilidis, 2005).

3.4. Flammability

Flammability refers to the ability of a mixture of fuel and air to sustain combustion when ignited. If the mixture contains too few fuel molecules, the released heat will not be enough and burning will not progress. If the mixture contains too few oxygen molecules, only a few fuel molecules will react and the released heat will not be enough to burn the material as well. In this sense, there is a composition range where the mixture fuel-air is flammable.

Almost all published flammability values are measured using a fuel/air mixture at room temperature. If the mixture temperature is higher, the flammability range increases. As a practical rule, an increase of 100°C on the mixture temperature decreases the lower flammability limit by 8% and increases the upper limit by the same extent. The expression below is used for this calculation, using the flammability limits at room temperature and the temperature in Celsius (Coward and Jones, 1939; Affens, 1966).

$$LIMIT(T) = 1.02 \cdot LIMIT(25^\circ c) \cdot (1 \pm 7.75 \cdot 10^{-4} \cdot T)$$

The flammability limits for methanol at room temperature is reported to be 6 – 36 % v/v (NFPA, 1978). The reported lower limit varies from 6 to 8% and the upper varies from 25 to 37% (Walker, 1975). Figure 4 shows the influence of temperature on the flammability limits of methanol.

The presence of water in the mixture changes the flammability limits. Figure 4 presents the approximate upper flammability limit, as a function of temperature, for a mixture with 85% methanol and 15% water, molar basis. The lower flammability limit is not greatly affected with this water concentration.

Considering a feed composition to a Silver reactor with molar ratio methanol/oxygen of 2.6 and the molar ratio water/methanol of 18%, the stream can be seen as a solution water-methanol with 39% molar concentration in a solution-air mixture. The solution contains

85% methanol and 15% water, molar basis. In this sense, the dot at the right of Figure 4 indicates the operation condition for a Silver reactor, which is clearly inside flammability limits, but close to the upper edge.

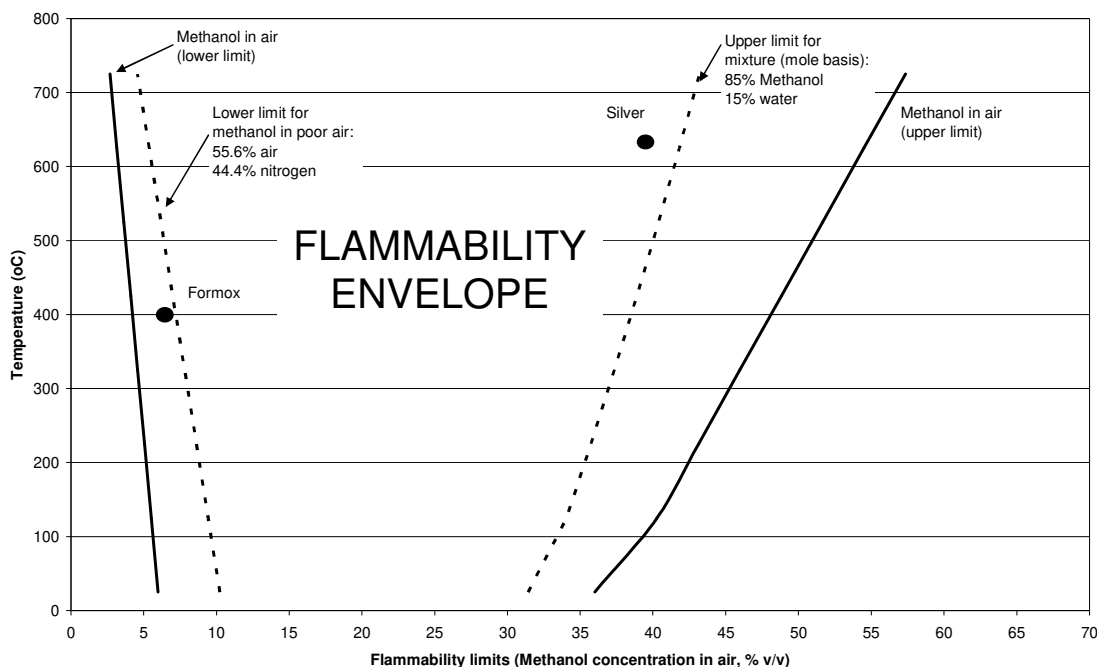


Figure 4: Flammability limits for methanol in a formaldehyde reactor

The feed to the Formox reactors are normally diluted with off-gas from the absorber. Considering the off-gas recycle as nitrogen, one example of Formox feed composition is 6% methanol, 11% oxygen and 83% nitrogen (mole basis). This system can be seen as methanol in a gas solution with 55.6% air and 44.4% nitrogen. In this case, the lower flammability limit, including the inert gas with air, is higher than that for pure air, as plotted with dashed lines in Figure 4. The operational condition for this Formox plant is represented by the left dot, which is practically at the lower flammability limit.

The error associated to the flammability limits is big due to lack of experimental data at higher temperatures and different dilutions with water and nitrogen. The expressions used here to estimate the limits at these conditions are not validated and the dashed lines may be somewhat deviated from the true position. Besides, the operational conditions for both processes presented in this example may change due to process variations.

In this sense, both processes operate at the edge of the flammability envelope for methanol and their feed mixture may be flammable, at least occasionally. This fact is reported in literature (SRI International, 1978; Ullmann, 1988) and it is well known in industrial plants. The explosion risk is low due to the high gas flowrate, fed at lower temperature to the catalyst bed: if a flame begins, it cannot propagate upstream. For safety reasons, all formaldehyde reactors are equipped with flame arrestors and rupture disks, in case of the flame is able to propagate upstream.

Formaldehyde has flammable limits between 7 – 73% (v/v) at room temperature. The hazard for this substance is negligible in a formaldehyde reactor, once the remaining

oxygen in the reactor outlet is not enough to burn the formaldehyde, as well as the hydrogen formed.

4. Thermodynamic chemical equilibrium calculations

The thermodynamic chemical equilibrium calculations were based on the equilibrium constant “ K_{eq} ” (Sandler, 1989), defined by the relation (Eq.9):

$$K_{eq}(T) = \exp\left(-\frac{\Delta G_R^o}{RT}\right) \quad (9)$$

In this equation, “ R ” is the ideal gas constant (8.314 J/mol.K), “ T ” is the reference temperature (usually 298.15 K) and “ ΔG_R^o ” is the Gibbs free energy change on the reaction, considering the species at the standard state (1 atm, 25 °C), calculated by Eq 10.

$$\Delta G_R^o(T) = \sum_i \nu_i \cdot \Delta G_{f,i}^o(T) \quad (10)$$

Where, “ ν_i ” is the stoichiometric coefficient of component “ i ”, “ $\Delta G_{f,i}^o$ ” is the Gibbs free energy of formation for component “ i ” at reference temperature “ T ”, normally 25 °C, obtained from literature (Sandler, 1989).

According to Eqs 9 and 10, K_{eq} is calculated at 25 °C. The integration of Van’t Hoff (Eq 11) computes the equilibrium constant at other temperatures, where “ ΔH_R^o ” is the heat of reaction, calculated by Eq 12.

$$\ln\left(\frac{K_{eq}(T_2)}{K_{eq}(T_1)}\right) = \int_{T_1}^{T_2} \frac{\Delta H_R^o(T)}{RT^2} dT \quad (11)$$

$$\Delta H_R^o(T) = \Delta H_R^o(25^\circ C) + \int_{298.15K}^T \Delta C_p^o(T) \cdot dT \quad (12)$$

With $\Delta C_p^o(T) = \sum_i \nu_i \cdot \Delta C_{p,i}^o(T)$, where “ C_p^o ” is the heat capacity of species “ i ” in its standard state, written as a function of temperature, generally a polynomial, in the form of Eq 13.

$$C_p = a + b.T + c.T^2 + d.T^3 \quad (13)$$

The thermodynamic data for the species involved in the formaldehyde reactions are stated on Table 5.

For calculating the equilibrium composition, the equilibrium constant may be written as function of the species’ fugacities “ f_i ”, as in Eq 14.

$$K_{eq} = \prod_i (\hat{f}_i)^{v_i} \quad (14)$$

Table 5: Thermodynamic data for the species involved in Silver process (Sandler, 1989)

Specie	Coefficients for C _p equation ¹				Energies of formation ²	
	a	b	c	d	ΔG _f ⁰	ΔH _f ⁰
CO ₂	5.316	1.429E-02	-8.362E-06	1.784E-09	-94,26	-94,052
CO	6.726	4.001E-04	1.283E-06	-5.307E-10	-32,808	-26,416
H ₂ O	7.700	4.594E-04	2.021E-06	-8.587E-10	-54,6351	-57,7979
H ₂	6.952	-4.576E-04	9.563E-07	-2.079E-10	0,00	0,00
O ₂	6.085	3.631E-03	-1.709E-06	3.133E-10	0,00	0,00
HCHO	5.447	9.739E-03	1.703E-06	-2.078E-09	-26,88	-28,29
CH ₃ OH	4.550	2.186E-02	-2.910E-06	-1.920E-09	-38,62	-48,08

¹ C_p values in cal/mol.K; ² energies in kcal/mol.

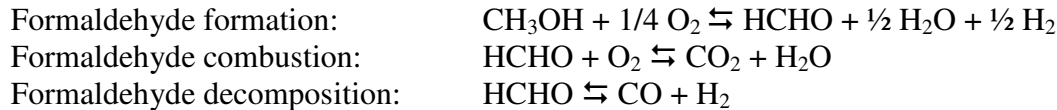
As the reaction pressure for the Silver process is low, the hypothesis of ideal gas is feasible and the fugacity may be written as Eq 15. Substituting Eq.15 in Eq 14, a simpler equation is defined (Eq 16), based on the total pressure “P” (atm), stoichiometric coefficients (v_i) and mole fractions (y_i).

$$\hat{f}_i = y_i \cdot P / 1.atm \quad (15)$$

$$K_{eq} = \left(\frac{P}{1.atm} \right)^{\sum v_i} \cdot \prod_i (y_i)^{v_i} \quad (16)$$

4.1. Equilibrium calculations for the Silver process

Considering that Eqs 5 and 6 may be joined to form a single reaction for formaldehyde formation, there are three reactions involved in this process:



Using the stoichiometric coefficients as on reaction equations above, ΔH_R and ΔG_R were calculated at 25 °C. The equilibrium constants at 25 °C for each reaction were calculated by Eq 9. Table 6 shows the calculated values.

Considering a reaction temperature of 630 °C, at 1.2 atm, the equilibrium constants are corrected according to Eq 11. Values are shown on Table 6.

Table 6: Equilibrium constants, enthalpy and free Gibbs energy

Reaction	ΔH _R ⁰ (25 °C)	ΔG _R ⁰ (25 °C)	K _{eq} (25 °C)	K _{eq} (630 °C)
Formation	-9,109	-15,578	2,625E+11	1,401E+07
Combustion	-123,560	-122,015	2,771E+89	7,302E+28
Decomposition	1,874	-5,928	2,216E+04	4,451E+05

Based to a standard industrial condition, with methanol to oxygen molar ratio of 2.6 and a water to methanol molar ratio of 0.18, the mole balance is defined as in Table 7, provided that “ ξ_F ”, “ ξ_C ” and “ ξ_D ” are the advancement of the reactions of formation, combustion and decomposition, respectively, at equilibrium condition.

Writing Eq 16 for the three reactions, as a function of the mole fractions (y_i), Eqs 17 – 19 are defined.

$$K_{eq,F} = \frac{y_{H_2}^{0.5} \cdot y_{H_2O}^{0.5} \cdot y_{HCHO}}{y_{MeOH} \cdot y_{O_2}^{0.25}} \cdot P^{0.75} \quad (17)$$

$$K_{eq,C} = \frac{y_{CO_2} \cdot y_{H_2O}}{y_{HCHO} \cdot y_{O_2}} \quad (18)$$

$$K_{eq,D} = \frac{y_{CO} \cdot y_{H_2}}{y_{HCHO}} \cdot P \quad (19)$$

Using a “Solver” tool, the equilibrium advancement of the three reactions (ξ_F , ξ_C , ξ_D) were found in order to make the results of Eqs 17-19 match the corresponding values shown on Table 6, at reaction temperature. Using the equilibrium advancements at equilibrium, obtained by solving the equations, it is possible to calculate the conversion and selectivity at the equilibrium condition. The results are shown on Table 8.

Two reactions (combustion and decomposition) eliminate formaldehyde from the media, displacing the equilibrium of the methanol oxidation towards the products (Le Chatellier principle). The consequence is the practically complete methanol conversion at equilibrium condition.

Table 7: Mole balance at equilibrium condition

Specie	Reactor feed (kmol/h)	Reactor outlet (kmol/h)	Outlet mole fraction (y_i)
CH ₃ OH	260	260 - ξ_F	$(260 - \xi_F) / (782.8 + 0.75 \cdot \xi_F + \xi_D)$
H ₂ O	46.8	46.8 + 0.5 · ξ_F + ξ_C	$(46.8 + 0.5 \cdot \xi_F + \xi_C) / (782.8 + 0.75 \cdot \xi_F + \xi_D)$
N ₂	376	376	$376 / (782.8 + 0.75 \cdot \xi_F + \xi_D)$
O ₂	100	100 - 0.25 ξ_F - ξ_C	$(100 - 0.25 \xi_F - \xi_C) / (782.8 + 0.75 \cdot \xi_F + \xi_D)$
HCHO	0	ξ_F - ξ_C - ξ_D	$(\xi_F - \xi_C - \xi_D) / (782.8 + 0.75 \cdot \xi_F + \xi_D)$
H ₂	0	0.5 ξ_F + ξ_D	$(0.5 \xi_F + \xi_D) / (782.8 + 0.75 \cdot \xi_F + \xi_D)$
CO ₂	0	ξ_C	$\xi_C / (782.8 + 0.75 \cdot \xi_F + \xi_D)$
CO	0	ξ_D	$\xi_D / (782.8 + 0.75 \cdot \xi_F + \xi_D)$
TOTAL	782.8	782.8 + 0.75 · ξ_F + ξ_D	1

The combustion to CO₂ is very shifted to the “products” side, but the equilibrium conversion is limited by the remained oxygen available. The constant for the decomposition of formaldehyde is the lower one, but as there is much formaldehyde in the media, the equilibrium is shifted to the “products”, CO in this case.

It is clear that the equilibrium does not favor the formation of formaldehyde, but its reaction products (carbon monoxide and carbon dioxide). This is the reason why the kinetic study of this process is essential for improving the selectivity towards formaldehyde.

Table 8: Reactor performance at equilibrium (630 °C, 1.2 atm) and industrial condition

Parameter	Equilibrium condition	Industrial condition
Conversion	100.0 %	94.0 %
Selectivity to HCHO	0.0 %	86.8 %
Selectivity to CO ₂	13.5 %	13.2 %
Selectivity to CO	86.5 %	0.0 %

5. End Uses

Formaldehyde is the building block of many important production chains. Table 9 shows the main uses in the world.

Table 9: Formaldehyde demand by segment (Kirk Othmer, 1991)

Applications	Formaldehyde demand in 1989
Urea-formaldehyde resins	25 %
Phenolic resins	22 %
Butanediol	11 %
Acetal resins	9 %
Pentaerythritol	7 %
Urea-formaldehyde concentrates	6 %
Hexamethylenetetramine	6 %
Methyl diisocyanate	5 %
Melamine resins	4 %
Other	5 %

Urea-formaldehyde resins are essential on building and furniture markets. The reaction of formaldehyde with urea produces a series of wood adhesives for the manufacture of furniture, OSB (oriented strand board), MDF (medium density fiber), particleboard and ureic plywood. The use of boards instead of wood for building and furniture increases year by year, due to the pressure against deforestation of native trees.

Phenol-formaldehyde resins are present in a huge variety of markets. The reaction of formaldehyde with phenol produces phenolic resins, used as a bonding agent for many industrial segments as automotive (brake pads, brake linings, clutches), building materials (phenolic plywood, grinding and cutting wheels, sandpaper, flooring laminates, glass wool and rock wool insulation for houses and industry), engineering materials (molding compounds, fiber reinforced plastic), foundry (sand molds for shell process), refractory materials, surface coatings (varnishes and paints for naval, automotive and metallurgical industries). Many objects around us contain phenolic resins, as cars, pans, houses, furniture, building tools, flooring and ships. Besides phenolic resin is one of the first plastic substances to be discovered, new applications are developed every year. Fiberglass reinforced plastics (FRP) have been produced with phenolic resin for replacing steel on offshore oil platforms and underground mines: gratings and pipes manufacture with FRP have more resistance on fire and does not generate toxic smoke, which could be a deadly

trap at these places. New coatings based on phenolic resins were developed to improve chemical resistance on metal pieces for automotive and naval industries.

Melamine resins are specialty chemicals for building and furniture markets. Produced by the reaction of melamine with formaldehyde, it is used for paper impregnation on flooring and laminates manufacture. Most of laminate flooring and furniture contains a transparent melamine overlay paper that resists to water, chemical substances and mechanical abrasion.

Formaldehyde is also used as a monomer for specialty resins, as acetal resins, furanic resins, and chemical intermediates, as butanediol, pentaerythritol, hexamethylenetetramine (hexa), methyl-di-isocyanate (MDI) and EDTA.

Known for its anti-bacterial action, it has been used in many formulations of anti-bacterial, household cleaning products, dish-wash liquids, fabric softeners, shoe-care agents, car shampoos and waxes.

6. Conclusion

Formaldehyde, the simplest aldehyde, plays an important role on the present chemical industry, being manufactured by big companies all over the world. After more than a century since the first formaldehyde plant, much work is still devoted to understand the mechanisms of reaction and develop high performance processes for its manufacture.

The first application of the formaldehyde, phenolic resins, was discovered almost a century ago, but this monomer has continued to be used for new innovative end uses. Despite many efforts to replace the formaldehyde or formaldehyde-based compounds for new substances, there is no perspective for the decline of formaldehyde market in the horizon, as it is the simplest and most economic viable solution for the segments where it is used.

The main commercial technologies for formaldehyde production – Silver and Formox - were compared in this work, explaining the differences on the reactions involved, operational conditions, catalysts, chemical process and methanol costs. The Formox process is a new technology, using an iron-molybdenum catalyst operated at much lower temperature than the silver catalyzed process. The different reaction mechanism and the lower temperature allow better selectivity towards formaldehyde and consequently a lower methanol specific consumption, translated as smaller production cost.

Both processes operate at the edge of the flammability limits and may, at least occasionally, be inside the flammable envelope. High air flowrate to the bed, with low temperature, normal for both processes, minimizes the explosion risk once eventual flames, generated in the vicinity of the catalyst, are not propagated upstream. Reactors are equipped with flame arrestors and rupture disks, which prevent severe accidents.

Equilibrium calculations for the Silver process showed that the formation of formaldehyde is not favored by equilibrium thermodynamics. In this sense, the understanding of the kinetics is essential for maximizing the formation of the valuable product. Economical and environmental drivers do exist to improve the performance of Silver plants, in order to guarantee the competitiveness against Formox plants and reduce carbon emissions to the

atmosphere (Papes Filho and Maciel Filho, 2007ab). Simulators and optimization tools are essential for aiding operators and engineers in pursuing this goal (Papes Filho, 2007), once Silver plants generally do not count on technical assistance of licensors, as Formox plants do.

References

- ABIQUIM (Brazilian Association of Chemical Industry), "The Brazilian Chemical Industry Directory", www.abiquim.org.br, 2006.
- ABRAF (Brazilian Association of Formaldehyde Manufacturers) report; Panorama da cadeia produtiva, www.abraf.com.br, 2004.
- Affens, W.A.; "Flammability properties of hydrocarbon fuels", *Journal of Chemical Engineering Data*, v.11, n.2, 1966.
- Andreasen, A.; Lynggaard, H.; Stegelmann, C. and Stoltze, P.; "A microkinetic model of the methanol oxidation over silver", *Surface Science*, 544, pp.5-23, 2003.
- Barteau, M and Madix, R.J.; *Surf. Sci*, 40, p.108, 1984.
- Bazilio, C.A.; Thomas, W.J.; Ullah, U. and Hayes, K.E.; "The catalytic oxidation of methanol", *Proc. R. Soc. Lond. A*, 399, pp.181-194, 1985.
- Belmar, C.Y.C., "Análisis y modelación del reactor de formaldehído de químicos Coronel", Informe de habilitación profesional, Concepción University, Chile, 1995.
- Bhattacharyya, S.K.; Nag, N.K. and Ganguly, N.D.; "Kinetics of vapor-phase oxidation of methanol on reduced silver catalyst", *J. of Catalysis*, v.23, i.2, pp.158-167, 1971.
- Cao, E; Gavriilidis, A.; "Oxidative dehydrogenation of methanol in a microstructured reactor"; *Catalysis Today*, 110, pp.154-163, 2005.
- Coward, H.F and Jones, G.W., "Limits of Inflammability of Gases and Vapors", *Bull.*, 279, 81-82, US Bureau of Mines, US Government Printing Office, Washington, 1939.
- Dai, W.L., Cao, Y, Ren, L.P., Yang, X.L., Xu, J.H., Li, H.X., He, H.Y. and Fan, K.N.; "Ag-SiO₂-Al₂O₃ composite as highly active catalyst for the formation of formaldehyde from the partial oxidation of methanol", *Journal of Catalysis*, 228, pp. 80-91, 2004.
- GFRT - Global Formaldehyde & Resin Technologies, Formaldehyde Industry Newsletter, v.1, i.2, March 2007.
- Kim, T.H.; Ramachandra, B.; Choi, J.S.; Saidutta, M.B.; Choo, K.Y.; Song, S.D. and Rhee, Y.W.; "Selective oxidation of methanol to formaldehyde using modified iron-molybdate catalysts", *Catalysis Letters*, v. 98, n. 2-3, pp. 161-165, 2004.
- Kirk Othmer, *Encyclopedia of Chemical Technology*, 4th ed., Wiley & Sons, 1991.
- Kirk Othmer, *Encyclopedia of Chemical Technology*, Wiley & Sons, 1996.
- Nagy, A. and Mestl, G.; "High temperature partial oxidation reactions over silver catalysts", *Applied Catalysis A: General*, 188, pp.337-353, 1999.
- Nagy, A.; Mestl, G.; Ruhle, T.; Weinberg, G. and Schlogl, R.; "The dynamic restructuring of electrolytic silver during the formaldehyde synthesis reaction", *J. of Catalysis*, 179, pp.548-559, 1998.
- NFPA, National Fire Protection Association, Hazardous Chemicals Data, 1978.
- Papes Filho, A.C.; "Simulation and optimization of a silver formaldehyde reactor, using artificial intelligence techniques", PhD thesis (in English) , UNICAMP – University of Campinas, Brazil, 2007.
- Papes Filho, A.C. and Maciel Filho, R.; "Hybrid simulation of a fixed-bed formaldehyde silver-catalyzed reactor using artificial neural networks", to be published, 2007a.
- Papes Filho, A.C. and Maciel Filho, R.; "Optimization of a Fixed-bed Formaldehyde Silver Reactor using Genetic Algorithms and Sequential Quadratic Programming", to be published, 2007b.

- Pestryakov, A.N. and Davydo, A.A.; “Active electronic states of silver catalyst for methanol selective oxidation”; *Applied Catalysis*, v.120, n.1, 1994, pp.7-15.
- Piccoli, R.L.; “Kinetic study of methanol selective oxidation to formaldehyde on iron molybdate catalyst”, Master dissertation, Rijksuniversiteit Gent, Belgium, 1992.
- Qian, M.; Liauw, M.A. and Emig, G.; “Formaldehyde synthesis from methanol over silver catalysts”, *Applied Catalysis A: General*, 238, pp.211-222, 2003.
- Santacesaria, E.; Morbidelli, M.; “Kinetics of the catalytic oxidation of methanol to formaldehyde”, *Chem. Engng. Sci.*, v.36, pp.909-918, 1981.
- Sauer, J. and Emig, G.; “The catalyzed dehydrogenation of methanol to formaldehyde at high temperatures”, *Chem. Eng. Technol.*, 18, pp.284-291, 1995.
- Silver Institute, www.silverinstitute.org, 2006.
- Soares, A.P.V.; Portela, M.F. and Kiennemann, A.; “Methanol selective oxidation to formaldehyde over iron-molybdate catalysts”, *Catalysis reviews*, v. 47, pp.125-174, 2005.
- SRI International; “Formaldehyde”, Report n° 23A, Menlo Park, 1978.
- Su, S; Zaza, P. and Renken, A.; “Catalytic dehydrogenation of methanol to water-free formaldehyde”, *Chem. Eng. Technol.*, 17, pp.34-40, 1994.
- Ullmann’s Encyclopedia of Industrial Chemistry, v.A11, 5th ed., VHC Publishers, New York, 1988.
- Van Veen, A.C, Hinrichsen, O. and Muhler, M.; “Mechanistic studies on the oxidative dehydrogenation of methanol over polycrystalline silver using the temporal-analysis-of-products approach”, *J. of Catalysis*, 210, pp. 53-56. 2002.
- Wachs, I.E. and Madix, R.; “The oxidation of methanol on a silver (110) catalyst”, *Surface Science*, 76, pp. 531-558, 1978.
- Walker, J.F; “Formaldehyde”; 3rd Ed.; Robert E. Krieger Publishing Company, New York, 1975.
- Waterhouse, G., Bowmaker, G. and Metson, J.; “Mechanism and active sites for the partial oxidation of methanol to formaldehyde over an electrolytic silver catalyst”; *Applied Catalysis A*, 265, pp.85-101; 2004a.
- Waterhouse, G., Bowmaker, G. and Metson, J.; “Influence of catalyst morphology on performance of electrolytic silver catalysts for the partial oxidation of methanol to formaldehyde”, *Applied Catalysis A*, 266, pp.257-273, 2004b.

2.3. Conclusões

O formaldeído, o mais simples dos aldeídos, tem posição de destaque como intermediário orgânico na indústria química. Ele é manufaturado por grandes empresas em todo o mundo, através de duas rotas: Prata e Formox. Mesmo após um século desde a construção da primeira planta de formaldeído, ainda há muito trabalho para entender os mecanismos de reação e desenvolver processos de alto desempenho.

A primeira aplicação do formaldeído foi para a produção de resinas fenólicas, no início do século XX, mas esse monômero ainda continua a ser usado em novas e inovadoras aplicações (PARK E WANG, 2005). Apesar dos esforços para substituir o formaldeído por novas substâncias, ainda não há perspectiva para o declínio na produção, uma vez que esse aldeído ainda é a solução economicamente mais viável.

As duas rotas de produção do formaldeído foram comparadas nesse capítulo, destacando as diferenças nas reações envolvidas, condições operacionais, catalisadores, processo químico e custo de metanol. O processo Formox é uma nova tecnologia à base de catalisador de ferro-molibdênio, operada à temperatura mais baixa que o leito de prata. A diferença nos mecanismos de reação e a menor temperatura do leito permitem que processo Formox tenha melhor seletividade para formaldeído e, conseqüentemente, menor consumo específico de metanol, traduzindo-se como menor custo de produção.

Ambos os processos operam nos limites de inflamabilidade e podem, pelo menos ocasionalmente, encontrar-se dentro do envelope inflamável. Altas vazões de alimentação com baixas temperaturas (condições normais desses processos) minimizam os riscos de explosão, uma vez que eventuais chamas formadas nas vizinhanças do catalisador não são propagadas à montante. Os reatores são equipados com dispositivos corta-chamas e discos de ruptura, que previnem acidentes graves.

Cálculos de equilíbrio para o processo Prata mostram que a formação do formaldeído não é favorecida pelo equilíbrio. Dessa forma, a compreensão da cinética de reação é essencial para maximizar a formação do produto comercializado. Fortes motivações econômicas e ambientais existem para melhorar o desempenho das plantas Prata, de modo a garantir sua competitividade frente às plantas Formox e reduzir emissões atmosféricas. Simuladores e ferramentas de otimização são essenciais para auxiliar operadores e engenheiros nessa tarefa, uma vez que as plantas Prata geralmente não contam

com assistência técnica de licenciadores de tecnologia, como ocorre com as plantas Formox.

CAPÍTULO 3

NOVA ABORDAGEM PARA OBTENÇÃO DE TAXAS DE REAÇÃO A PARTIR DE DADOS DE PROCESSO PARA TREINAMENTO DE REDES NEURAIIS: APLICAÇÃO A UM REATOR INDUSTRIAL PARA OXIDAÇÃO DO METANOL A FORMALDEÍDO COM CATALISADOR DE PRATA.

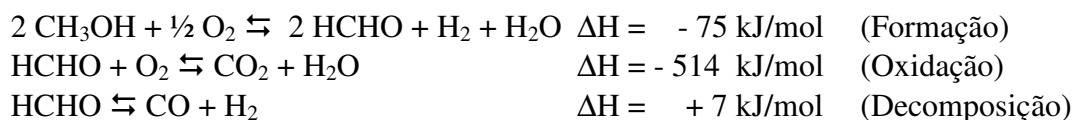
3.1. Introdução

Vários pesquisadores propuseram modelos cinéticos e equações da taxa para a síntese do formaldeído, porém, eles apresentam grandes deficiências, pois não consideram a formação de subprodutos ou são somente aplicáveis a condições específicas, distantes das condições reais encontradas nos processos industriais. Alguns simuladores para o reator de Prata foram reportados, mas estão baseados nas equações cinéticas incompletas e falham ao prever situações industriais reais.

Nessa tese, apresenta-se um simulador para o reator de Prata onde a taxa de reação é calculada com o auxílio de uma rede neural artificial (RNA), sistema descrito em detalhes no Capítulo 6. No entanto, para o perfeito funcionamento da RNA na predição de taxas de reação, ela deve ser primeiramente ajustada, ou treinada, com base em dados experimentais correlacionando as taxas de reação com condições de processo (temperatura, pressão e pressões parciais das substâncias presentes).

Nesse ponto os pesquisadores deparam-se com um obstáculo, pois dados experimentais de taxa de reação não se encontram disponíveis na literatura e são muito difíceis de serem obtidos devido às dificuldades em controlar as limitações da transferência de massa, não-isotermia do reator, envelhecimento e desativação do catalisador. Sem dados experimentais de taxa de reação, é impossível treinar a rede neural pelos métodos convencionais.

Uma nova abordagem é proposta nesse capítulo, utilizando-se equações da taxa aproximadas para as três reações de interesse nesse processo: formação do formaldeído, oxidação do formaldeído e decomposição na fase gasosa.



As equações aproximadas foram baseadas nas equações da taxa propostas por ANDREASEN ET AL. (2003), em um trabalho considerado como o mais completo

encontrado na literatura, e implementadas no simulador do reator descrito no Capítulo 6. As equações modificadas encontram-se definidas a seguir para a formação do formaldeído (r_5) e combustão do formaldeído (r_{10}).

Formação do formaldeído:

$$r_5 = \frac{k_5 \cdot K_A \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/4} \cdot \frac{P_{CH_3OH}}{P_\theta} \cdot \left(\frac{P_{H_2O}}{P_\theta}\right)^{-x}}{\left(1 + K_C^{1/2} \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/2}\right)^2}$$

Combustão do formaldeído:

$$r_{10} = \frac{k_{10} \cdot K_B \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/2} \cdot \frac{P_{HCHO}}{P_\theta} \cdot \left(\frac{P_{H_2O}}{P_\theta}\right)^{-x}}{\left(1 + K_C^{1/2} \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/2}\right)^2}$$

Os trabalhos de Andreasen et al. não consideram a decomposição do formaldeído na fase gasosa. Como esta reação tem impacto significativo na seletividade do reator de Prata, uma nova equação foi incluída, baseada na cinética de decomposição do acetaldeído (FOGLER, 1992), levantando a hipótese de que a decomposição do formaldeído é irreversível e depende apenas da temperatura e da concentração do reagente:

$$r_{CO} = k_{CO} \cdot P_{HCHO}^\alpha$$

O processo de obtenção baseia-se na seqüência descrita a seguir, ilustrada na Fig 3.1.

- i. Focando-se em um único ponto experimental, os parâmetros ajustáveis das equações da taxa simplificadas (“ k_5 ”, “ k_{10} ”, “ x ”, “ k_{CO} ” e “ α ”) são variados até que a conversão e seletividades calculadas pelo simulador sejam iguais aos valores referentes ao dado experimental em questão. Nesse caso, apenas encontram-se disponíveis as condições experimentais (temperatura, pressão e vazões de reagentes), conversão e seletividades medidas a partir da composição da corrente de saída do reator. Não há informação experimental acerca das taxas de reação ou pressões parciais dos componentes ao longo do reator.
- ii. O ajuste dos parâmetros das equações simplificadas foi realizado utilizando-se o algoritmo genético como método de busca.

- iii. Ao encontrar os parâmetros corretos nas equações simplificadas que permitem ao simulador calcular corretamente a conversão e seletividades, o “software” escreve em um arquivo de dados o perfil de pressões parciais ao longo do reator associado ao perfil de taxas para cada uma das três reações, conforme calculado pelas equações simplificadas. Dessa forma, obtém-se um conjunto de pontos correlacionando temperatura, pressões parciais e taxas de reação.
- iv. O procedimento é repetido para cada ponto experimental, salvando-se o perfil de taxas de reação para cada caso.
- v. Ao final do processo, obtém-se um grande conjunto de dados de taxa de reação, agrupando-se os conjuntos obtidos para cada ponto experimental, com as respectivas condições operacionais locais (pressões parciais).

As taxas de reação calculadas foram utilizadas para treinar a RNA, cujos parâmetros de entrada são a temperatura e as pressões parciais de todos os componentes. Os dados de saída são as três taxas de reação.

O treinamento da RNA foi feito utilizando-se o método clássico de retro-propagação. Dois conjuntos de dados experimentais obtidos da literatura (ROBB E HARRIOT, 1974; WATERHOUSE ET AL., 2004b) foram usados para validação do método.

Boa correlação foi encontrada comparando-se as taxas de reação calculadas pela RNA e as taxas extraídas dos dados experimentais, demonstrando sucesso no treinamento da rede. Simulações foram realizadas nas mesmas condições dos dados experimentais e o simulador do reator de Prata, equipado com a RNA, foi capaz de prever adequadamente a conversão e seletividades experimentais, validando o método de obtenção das taxas de reação.

3.2. Desenvolvimento

O desenvolvimento desse capítulo é descrito no artigo intitulado “Novel Approach for Acquiring Rate of Reaction Data from Process Information for Neural Network Training: Application to an Industrial Reactor for Methanol Oxidation to Formaldehyde over Silver Catalyst Process”, apresentado a seguir, que será submetido para publicação em periódico indexado internacional.

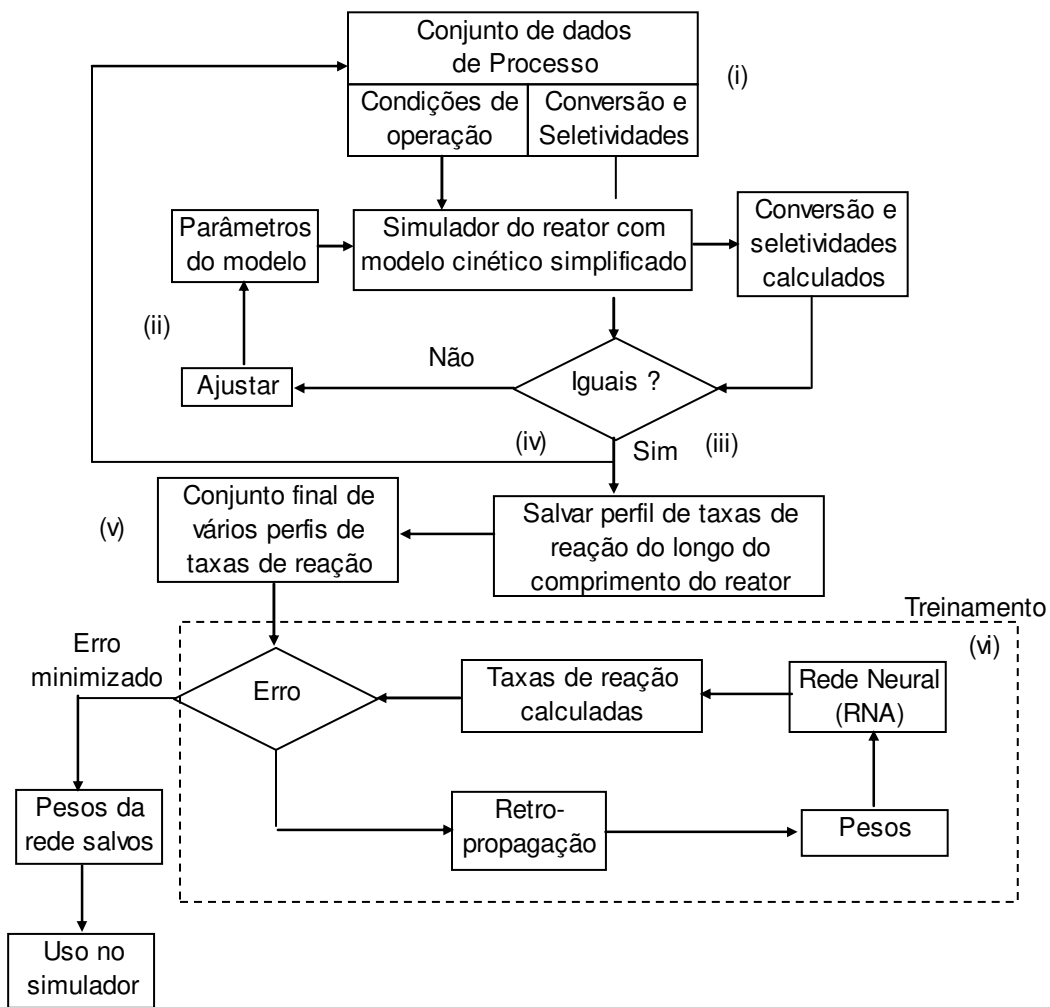


Figura 3.1: Fluxograma do procedimento de obtenção de dados de taxa de reação a partir de informações de processo.

Novel Approach for Acquiring Rate of Reaction Data from Process Information for Neural Network Training: Application to an Industrial Reactor for Methanol Oxidation to Formaldehyde over Silver Catalyst Process

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Abstract

A simple procedure for acquiring the rate of the reaction from process data has been formulated in order to train an artificial neural network used to simulate the methanol oxidation to formaldehyde over silver catalyst. Most of the available experimental data rely on process information as reactor conversion, selectivity, raw material consumption or exit stream composition, but such information cannot be readily used for training a neural network to predict the rate of the reaction. New experimental work for measuring the rate of the reaction is costly and any approach that allows extracting it from existing process data is essential for reducing research time, once literature is filled with process information. Rate of reaction data was extracted from process conditions for methanol oxidation to formaldehyde using a novel approach presented in this paper. The best kinetic model in literature was employed as a base reference to develop a modified model, used together with a reactor simulator in order to fit experimental data. For every data point, the parameters of the modified model were adjusted, until the conversion and selectivity matched the experimental values for a given process condition. The Neural Network was successfully trained with the extracted data and the net was used for simulating process conditions, achieving good results when compared to experimental data. The procedure can be applied to industrial data allowing the extraction of reaction rate.

Key words: formaldehyde, silver, artificial neural networks, methanol oxidation, kinetic modeling.

1. Introduction

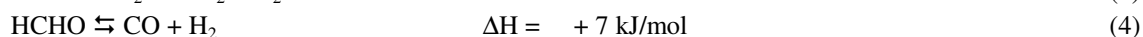
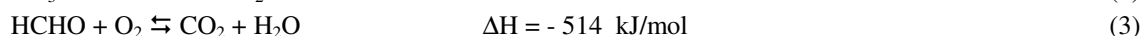
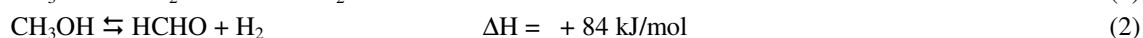
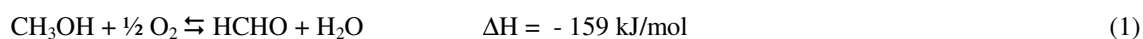
Formaldehyde is one of the world's most important chemicals, basic building unit for a wide variety of substances, such as phenolic resins, urea-formaldehyde resins, butanediol and pentaerythritol. It is the simplest aldehyde, synthesized for the first time in a lab during the nineteenth century (1868) by August Wilhelm von Hofmann (Walker, 1975) and still today plays an important role on the chemical industry, found in many objects used in our daily life. Formaldehyde is ranked among the top 50 products of industrial organic chemistry, which produces worldwide about 32 million metric tones of formalin, 37% solution basis, per year (ABRAF, 2004). The consumption has grown steadily over the past two decades due to increasing demand in the construction and automotive sectors for engineered products manufactured using formaldehyde-based resins.

More than 90% of the world's formaldehyde is produced by catalytic oxidation of methanol (Cancho et al., 1989). Two processes are commonly employed: the Silver process and the Formox process (Santacesaria and Morbidelli, 1981; Piccoli, 1992). In the former, methanol-rich methanol-air stream mixture is passed through a simple silver catalyst bed at 600 – 700 °C. The Formox process differs in the nature of the catalyst (iron-molybdenum oxides), methanol concentration (oxygen-rich), bed temperature (300 – 400 °C) and bed configuration (multitubular reactor). In both processes, aqueous solutions are obtained and commercialized as final products.

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Nowadays, new formaldehyde plants are built using the Formox technology, but 30 - 50% of the current world's capacity rely on Silver plants (Van Veen et al, 2002; Qian et al., 2003; Waterhouse et al., 2004b). Its advantages are low investment cost, high yield and stable process.

In the silver process, two parallel reactions take place to form formaldehyde: methanol oxidation (Eq. 1) and methanol dehydrogenation (Eq. 2), over a silver catalyst. The reaction is extremely exothermic and it is carried out under adiabatic conditions. Approximately 50-60% of the formaldehyde is produced by oxidation and the remaining by dehydrogenation. Formaldehyde may also react with oxygen on the silver surface, forming carbon dioxide (Eq. 3). The higher the temperature, the higher the rate of gas phase decomposition of formaldehyde (Eq. 4). Reactions 3 and 4 reduce the selectivity towards the desired product.



Oxidation reactions supply heat to make the process self-sustaining and are also believed to keep the catalyst active and displace the dehydrogenation equilibrium towards the products (Walker, 1975). Various versions of the conventional silver-catalyzed process are described in many different patents, but two main variations are used industrially:

Methanol Ballast Process: only air and pure methanol are fed to the silver bed, featuring incomplete methanol conversion and requiring a distillation recovery of the raw material.

Water Ballast Process: firstly employed on an industrial scale by BASF in 1905, this process remains unchanged and it is still in use today; advances in process design have made yields as high as 91-92%. Extra water is fed with the reactant mixture, achieving almost complete conversion of methanol (98-100%). However, water is limited by the requirement of the final product concentration specs. Due to the high heat capacity, water vapor removes a great deal of reaction heat, thereby preventing detrimental overheating as well as sintering of catalyst. Water helps to burn away the coke of catalyst surface to expose active sites (the shelf-life of silver on this process is significantly longer than that in the methanol ballast process), blocks specific surface sites and displaces the reaction mechanism, reducing the formation of undesirable by-products (Barteau and Madix, 1984; Qian et al, 2003; Andreasen et al., 2003). Typical selectivity is found on 85 – 90% range.

Qian et al. (2003) compared Methanol Ballast to Water Ballast processes and concluded that the later performs higher conversion of methanol and higher selectivity to formaldehyde.

Formaldehyde is only formed in the presence of oxygen. The oxygen interaction with silver catalyst plays an important role on the mechanism of the reaction, as it is supposed to be responsible for keeping the catalyst active (Bhattacharyya et al., 1971). Electronic microscopy reveals that the morphology of silver catalyst changes strongly during the reaction, observing pinholes firstly predominantly in the vicinity of initial surface defects and spread gradually from the region of defects to the entire silver surface. This reaction-induced morphological restructuring reinforces the formation of grain boundary defects over the catalyst, which enables more oxygen to penetrate into the silver lattice and, in turn, to intensify the reaction. Many articles explore this subject under the surface science perspective (Nagy and Mestl, 1999; Qian et al., 2002; Waterhouse et al., 2004a).

Despite of the fact that the formaldehyde synthesis has existed for more than a century and a substantial research effort has been devoted to the reaction, the mechanism remains controversial (Bazilio et al., 1985; Van Veen et al., 2002; Andreasen et al., 2003) and the kinetics of the reaction at industrially relevant reaction temperature is not available (Cao and Gavriilidis, 2005). Some authors postulate that a change in the mechanism occurs at 650 °C (Gravilin and Popov, 1965; Ullman, 1988). Studies showed that HOCH₂ and HO₂ radicals are formed by a heterogeneous mechanism in the range 500 – 620 °C and a homogeneous

mechanism is predominant at 620 – 730 °C, while CH₃O radicals are formed as well as other radicals (SRI, 1978).

In only a few reported studies in literature, attention has been paid to the way that by-products are formed. No single study covers the influence of temperature and concentrations of methanol, oxygen and water under near industrial conditions (temperature: 600 – 700 °C; methanol/oxygen molar ratio: 2.3 – 3.0 and water/methanol molar ratio: 0.15 – 0.75). Because of differences in the catalysts and operational conditions used in the various studies, it is not clear how the process takes place (Lefferts et al., 1986). Lack of good quality kinetic experiments is caused by difficulties in avoiding mass transfer limitations, non-isothermicity, deactivation and aging of silver catalyst in conventional reactors (Cao and Gavriilidis, 2005).

It has been pointed out for the methanol oxidation that the high yields and high selectivities may seem to render superfluous any attempt to study the reaction with the aim to improve it, but considering the potential market demand for formaldehyde and strong competition, even small improvements are economically attractive. Methanol cost represents more than 80% of the production cost of formaldehyde after strong price increase in the recent years and there is always economical pressure to improve the process selectivity towards formaldehyde. The methanol cost to produce one metric ton of formaldehyde 37% basis is US\$ 162, in a Silver plant operated with 85% selectivity. An improvement of 1 percentage point on the selectivity in an average size plant means saving about 200,000 US\$ per year on methanol purchasing. This is certainly one of the reasons that significant research effort is devoted to this system (Qian et al., 2003), including experimental work and development of reactor simulators. Besides, any improvement on the formaldehyde selectivity automatically means a reduction on the carbon emissions, in line with the world's efforts against global warming.

Complete kinetic models valid for actual industrial conditions are not available and costly experimental work is required for developing new models and therefore simulators. However, much process data is available from literature as well as from industrial plants, as reactor conversion, selectivity, raw material consumption, inlet and outlet stream compositions. Any attempt to convert this available process data into kinetic data and furthermore model the kinetic data in a quick fashion would be a powerful tool for understanding and optimizing this process. In these cases, novel approaches like neural networks are useful for predicting the rate of reaction, based on available data.

Artificial Neural Networks (ANNs) have been effectively used for process simulation in cases where deterministic models are not available or fail to represent kinetic data (Psichogios and Ungar, 1992; Papes Filho and Maciel Filho, 2005). Its foundation relies on mind psychology, based on theories of Freud, William James and other psychologists of XIX century (Berne and Levy, 1990). In practice it is a complex mathematical model based on the biological studies on brain function.

At a first view, ANN may be compared to simple regression or data fit, but they are much more powerful once: they can manage multiple outputs and multiple inputs (MIMO system), a regression model is not necessary, they use less parameters than polynomial regression and they tolerate hardware failures and data noise. Once the ANN is a generic model (Lennox et al, 2001), it needs to be configured to the studied data set in a process named “training”, where, as in statistical regression, many data rows [input/output] are presented to the net until it captures the pattern of data. Mathematically, it “learns” from data set, adjusting its internal parameters until the error between predicted output and experimental output is minimized. Most of the researchers consider the training or fitting step as a “learning” process, in other words, they say that the net is able to learn the data pattern and store the knowledge into its internal parameters, as a memory. This is the reason why ANN is considered part of the Artificial Intelligence field (Wasserman, 1989; Davis, 1991; Pham and Pham, 1999).

In this work, kinetic models were searched on literature for the methanol oxidation to formaldehyde over silver catalyst. The available models showed to be incomplete to predict the rate of reaction under actual industrial conditions and some modifications had to be introduced to the best model found in literature. The

modified model was used in a reactor simulator in order to back-calculate the rate of reaction by changing model parameters until the simulated conversion and selectivity matched the available experimental values for a given process condition. The procedure was repeated to generate a series of rate of reaction data, associated with process conditions.

The rate of reaction data obtained were used to train an ANN in order to have a unique kinetic model for a given formaldehyde silver process, valid for all industrial operation range of this process. The trained ANN was included in a reactor simulator to calculate the reaction rate. This hybrid model (simulator with ANN) was used for many cases with successful results, proven to be an effective tool for the simulation of this process.

2. Methods

2.1. Models available in literature

Many researchers studied reaction mechanisms and kinetic equations for the formaldehyde silver process. The most important works found in literature were summarized below.

Bhattacharyya and al. (1971), suggested a mechanism based on four reactions (Eqs 5-8), at low conversion level, in the temperature range of 264-290 °C and atmospheric pressure. The paper presents a rate expression (Eq. 9), by applying a modified Hinshelwood mechanism, where “R” is the total rate of methanol oxidation (considering the formation of formaldehyde and carbon dioxide, in mol/h.g-cat), “p_m” and “p_o” are the partial pressures of methanol and oxygen (atm), respectively. They state that it is very difficult to define the course of formation of CO₂. It may be formed by the reaction of HCHO with adsorbed oxygen on the catalyst, by direct reaction of gaseous methanol with adsorbed O₂ on catalyst or by gas phase reaction of HCHO and O₂.



$$R = \frac{2.k_m.k_o.p_m.p_o^{0.5}}{(k_m.p_m + 2.k_o.p_o^{0.5})} \quad (9)$$

Robb and Harriott (1974) performed kinetic investigations in a fixed-bed differential reactor, using a porous alumina supported silver catalyst at 420 °C and observed almost zero order dependence on oxygen, less than first order dependence on methanol and inhibition by the products. Feed contained CH₃OH/O₂/He of molar composition 1.0/1.45/100. They assumed that the controlling step of the mechanism is the surface reaction and proposed the following relative rate expression (Eq 10), based on Langmuir-Hinshelwood model, where “P_o”, “P_m” and “P_p” are the partial pressures (atm) of oxygen, methanol and formaldehyde, respectively. They suggest that water inhibits the reaction. At the studied conversion range (< 70%), they proposed that carbon dioxide is formed by methanol or formaldehyde oxidation.

$$R = \left(\frac{k_3.K_m.P_M}{1 + K_m.P_M + K_p.P_P} \right) \left(\frac{K_o.P_o^{0.5}}{1 + K_o.P_o^{0.5}} \right) \quad (10)$$

Bazilio et al. (1985) proposed a kinetic model based on the methanol oxidation to formaldehyde. Experimental data covered the temperature range of 250 – 350 °C, 1 bar pressure and residence time of 20 msec. They presented a rate expression for the oxidation of methanol (Eq 11), where “p_o”, “p_m” and “p_w” are the partial pressures (atm) of oxygen, methanol and water, respectively; and “R” is the rate of reaction (mol/s.g-cat). They concluded that this equation provides a prediction of conversion within 25% of actual

values. Studied range varied from 0.1 to 0.6 conversions, which are much smaller than industrial figures (> 90%).

$$R = \frac{k_m \cdot k_o \cdot p_m \cdot p_o^{0.5}}{(0.5 \cdot k_m \cdot p_m + k_o \cdot p_o^{0.5}) \cdot (1 + K_w \cdot p_w)} \quad (11)$$

Mao and Vannice (1995) studied the oxidation of formaldehyde with silver powder. They reported that few kinetic data were historically obtained and limited information about surface species under reaction conditions is available. They concluded that only CO₂ is formed during HCHO oxidation on silver powder and proposed a reaction mechanism and a rate equation (Eq 12), where “r” is the rate of reaction (mol/s.g-cat), “P_{O₂}” is the oxygen partial pressure and “P_{HCHO}” is the formaldehyde partial pressure (Torr).

$$r = \frac{k'_{O_2} \cdot P_{O_2}}{[1 + K' \cdot P_{O_2}^{0.4} \cdot P_{HCHO}^{-0.4}]^2} \quad (12)$$

Based on silver surface studies, Wachs and Madix (1978) proposed a mechanism for methanol oxidation (Figure 1) with only one kind of active oxygen, based on a Langmuir-Hinshelwood mechanism, kept as simple as possible by ignoring known elementary reactions involving carbonate, adsorbed OH, HCOOH formation and oxidative decomposition of formate. The authors explain the reasons for this simplification and guarantee the precision of the mechanism for practical ends (Andreasen et al, 2003). According to this mechanism, the oxidation of methanol to formaldehyde goes through a methoxy intermediate that is formed by a reaction between methanol and an atomic surface oxygen, decomposing to formaldehyde and hydrogen. The formaldehyde may be oxidized to carbon dioxide through a formate intermediate in a consecutive reaction path. They showed no indication of a direct oxidation from methanol to carbon dioxide, as proposed by some investigators.

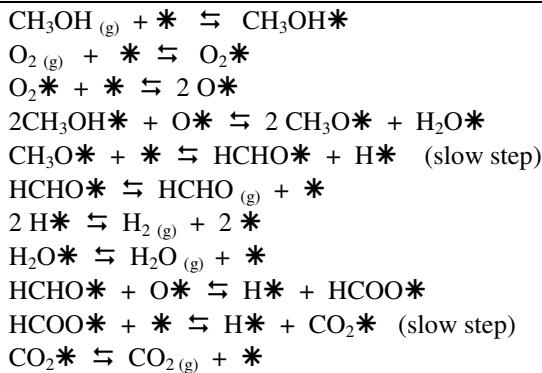


Figure 1: Mechanism of Wachs and Madix
 (“*” denotes the active site or a molecule adsorbed on the catalyst)

According to this mechanism, the formaldehyde synthesis cannot be divided into separate dehydrogenation and oxidation steps. Secondly, carbon dioxide is considered formed by the further oxidation of formaldehyde through the formate intermediate and not by direct combustion of methanol. If the reaction steps are grouped, the proposed mechanism would result in the global reactions (Eqs 13 and 14):



In other words, this mechanism considers that 50% of the formaldehyde is formed by dehydrogenation route and 50% by oxidation route. It is believed that the balance between these two routes changes according to temperature (Nagy et al., 1998; Nagy and Mestl, 1999), deviating from this ideal 50/50 model. The methoxy

decomposition (5th step) and formate decomposition (10th step) were shown to be rate limiting reactions for formaldehyde and carbon dioxide formation, respectively (Andreasen et al., 2003). All the other elementary reactions are equilibrated. Other simplification on the mechanism is related to the exclusion of the reactions involving OH formation:

- The model does not properly describe the water formation and the mechanism predicts a 1:1 H₂/H₂O molar ratio, while in industrial conditions slightly more water is produced than hydrogen. This issue is not relevant for practical ends, once the focus of simulation is on formaldehyde production and decomposition and not on water or hydrogen formation.
- These excluded reactions involve the removal of available oxygen from the reacting media. The authors suggest that the stability of OH* is low and the oxygen uptake is assumed to be equilibrated, so the oxygen scavenger effect would be negligible.

The production of formic acid has also been ignored in the model. This reaction seems to be unimportant in steady-state kinetics, as showed by literature (Schubert et al., 1994; Qian et al., 2003; Waterhouse et al., 2004b) and industrial observations (low formic acid concentrations are found on final product).

Andreasen et al. (2003) proposed a microkinetic model based on Wachs and Madix mechanism with only one kind of active oxygen. Surface science calculations indicate that their mechanistic scheme is general for oxidation of alcohols on silver and other metal surfaces (Andreasen et al., 2003). According to their paper, the formation of carbon dioxide is favored at low temperatures (much lower than industrial processes) and the formation of carbon monoxide is favored at high temperatures (above 625 °C) due to the pyrolytic gas phase reaction. Using the microkinetic model, the authors showed that the activation enthalpy for oxidation of methanol to formaldehyde was always larger than that for CO₂, hence the rate of formaldehyde formation increased more rapidly than formaldehyde combustion at increasing temperature. The same authors wrote a second paper (Andreasen et al., 2005) where a simplified model was developed (Lynggaard et al., 2004). These papers present the most complete kinetic equations for methanol oxidation on silver found in literature.

The 5th step on Figure 1 is the rate limiting reaction for the methanol oxidation, therefore “r₅” is the rate of formaldehyde formation and “k₅” is the rate constant, with Arrhenius form, having prefactor of 4.2x10¹⁰ s⁻¹ and activation enthalpy of 60 kJ/mol. The 10th step is the rate limiting reaction for the formaldehyde oxidation to carbon dioxide, therefore “r₁₀” is the rate of formaldehyde oxidation and “k₁₀” is the rate constant, with Arrhenius form, having prefactor of 9.8x10⁹ s⁻¹ and activation enthalpy of 77 kJ/mol. The rate equations “r₅” and “r₁₀” are stated below, on Eqs 15 and 16.

$$r_5 = \frac{k_5 \cdot K_A \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/4} \cdot \frac{P_{CH_3OH}}{P_\theta} \cdot \left(\frac{P_{H_2O}}{P_\theta}\right)^{-1/2}}{\left(1 + K_C^{1/2} \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/2}\right)^2} \quad (15)$$

$$r_{10} = \frac{k_{10} \cdot K_B \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/2} \cdot \frac{P_{HCHO}}{P_\theta} \cdot \left(\frac{P_{H_2}}{P_\theta}\right)^{-1/2}}{\left(1 + K_C^{1/2} \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/2}\right)^2} \quad (16)$$

Where “P_{O₂}”, “P_{CH₃OH}”, “P_{H₂O}”, “P_{HCHO}” and “P_{H₂}” are the partial pressures of oxygen, water, formaldehyde and hydrogen, respectively; “P_θ” is the atmospheric pressure, at the unit used for partial pressures; “K_A” is the equilibrium constant for the formation of CH₃OH*; “K_B” is the equilibrium constant for the formation of HCOO*; “K_C” the equilibrium constant for the dissociation of oxygen. The equilibrium constants can be calculated from thermodynamic parameters found in Table 1, using Eq 17 (Andreasen et al. 2005).

Table 1: Thermodynamic parameters for Andreasen's (2005) kinetic equations

Equilibrium constants	ΔS (J/mol.K)	ΔH (kJ/mol)
K_A	-117	-18
K_B	-171	-80
K_C	-165	-121

$$K_r = \exp\left(\frac{\Delta S_r}{R}\right) \cdot \exp\left(-\frac{\Delta H_r}{RT}\right) \quad (17)$$

The kinetic model based on the proposed mechanism showed good agreement with data obtained from formaldehyde process without water at the reactor feed, even with all simplifications explained above. When used to simulate data from water ballast process the model failed in estimating the influence of water added to the reaction. Water plays an important role in some steps of the mechanism, not considered by current literature. It certainly does not act merely as a competitor for active sites, reducing the oxygen availability at the silver surface, but it participates directly on the mechanism.

The model also fails in predicting the formaldehyde selectivity at higher temperatures, once this mechanism does not consider the decomposition of formaldehyde to carbon monoxide (Andreasen et al., 2003) by pyrolytic gas phase decomposition. Qian (2003) experiments show the carbon monoxide formation at high rates above 650 °C. Waterhouse (2004a) also presents experimental data with carbon monoxide formation between 675 and 725 °C. At industrial conditions, with operating temperatures in the range 620 – 700 °C, the selectivity towards formaldehyde clearly decreases with increasing temperature. The microkinetic model simulates perfectly the selectivity to formaldehyde at lower temperatures (< 620 °C), but at the industrial operation range, it cannot predict the decrease of formaldehyde selectivity with increasing temperature. The reason is that most of the experiments in literature were carried out at conditions where formaldehyde gas-phase decomposition is negligible, but when temperatures goes above 620 °C, this undesirable reaction (Eq. 18) cannot be neglected.



Irdam et al. (1993) studied the formaldehyde decomposition mechanism for the reaction in high-radical combustion and pyrolysis environments over very high temperature ranges (1700 to 2700 °C). According to Su et al. (1994), the formation of formaldehyde is favored at high temperatures in excess of 477 °C and the temperature must be above 577 °C to obtain conversion higher than 95 %. Low pressures would favor methanol dehydrogenation. Normally, formaldehyde is decomposed almost exclusively to carbon monoxide and hydrogen. Residence time should be short and fast cooling of reaction products must be ensured to minimize subsequent decomposition of formaldehyde. Equation rate for the decomposition of formaldehyde was not found in literature. Fogler (1992) reports the rate of reaction for the vapor-phase decomposition of acetaldehyde involving free radicals at temperatures of about 500 °C (Eq. 19):

$$-r_{\text{CH}_3\text{CHO}} = k \cdot C_{\text{CH}_3\text{CHO}}^{3/2} \quad (19)$$

2.2. Formaldehyde reactor simulator

A formaldehyde reactor simulator was built in this work to obtain rate of reaction data from process information and also to implement the artificial neural network for validation of the novel approach.

The formaldehyde reactor was simulated based on mass balance (Eq. 20), derived from the equation of continuity (Welty, 1984) for the bidimensional flow on cylindrical coordinates, considering plug-flow tubular model, molecular diffusion and steady-state operation (Treybal, 1981). Calculations and industrial observations indicated that, for practical ends, the reactor (fixed-bed) operates isothermally and adiabatically

(Nagy et al., 1998; Nagy and Mestl, 1999; Papes Filho, 2007; Papes Filho and Maciel Filho, 2007). Figure 2 shows a scheme of a typical silver reactor.

$$D_L \cdot \frac{\partial^2 C}{\partial z^2} + D_R \cdot \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial C}{\partial r} \right) - V_z \cdot \frac{\partial C}{\partial z} + v_A \cdot R_V = 0 \quad (20)$$

where: “C” is the substance concentration (kg/m³); “r” is the distance from the reactor central line – radius on cylindrical coordinates (m); “z” is the distance from the reactor inlet – axial distance on cylindrical coordinates (m); “D_L” is the axial diffusion coefficient (m²/s); “D_R” is the radial diffusion coefficient (m²/s); “V_z” is the axial velocity (m/s); “v_A” is the stoichiometric coefficient for the studied substance (dimensionless) and “R_V” is the rate of the reaction per reaction volume (kg/m³.s).

The mass balance differential equation was solved numerically using the Crank-Nicholson algorithm, described in literature (Crank and Nicholson, 1947; Press et al., 1992), a semi-implicit method known to be intrinsically stable. The physical properties of pure substances and mixtures were calculated (Reid et al., 1987) at each step of Crank-Nicholson method, according to the actual local conditions.

Two simulators were built by the authors, using Fortran code. The first contains modified kinetic equations from literature in order to obtain the rate of reaction data, using process information. A second simulator contains the trained ANN for calculating the rate of reaction, able to predict new process conditions for desired inputs (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007).

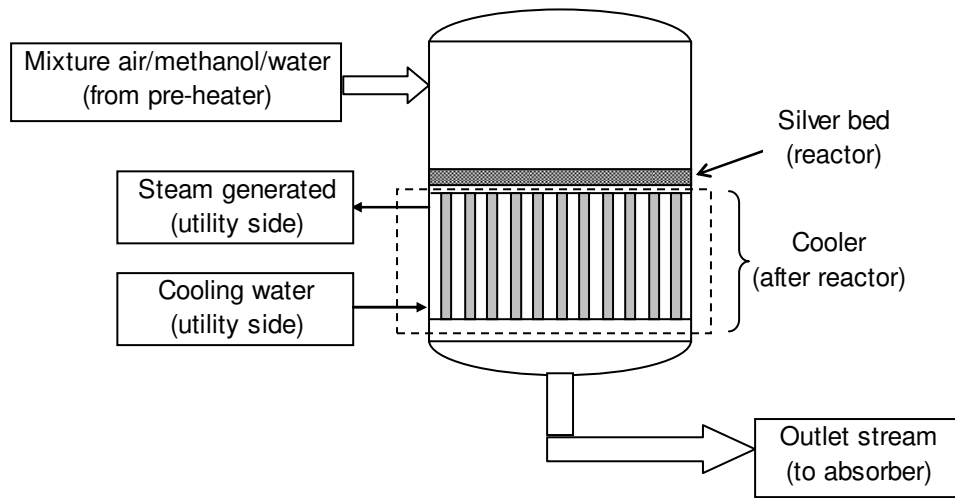


Figure 2: Scheme of a typical silver reactor, showing the fixed-bed, where reaction takes place, and the downstream cooler.

2.3. Modified kinetic equations

For acquiring rate of reaction data, the simulator was implemented using modified kinetic equations based on the best kinetic model obtained from literature (Andreasen et al., 2005). Despite the simplifications on Andreasen’s microkinetic model, failing in simulating the conditions of water addition at feed and formaldehyde decomposition at industrial reactor temperatures, it is the best model for formaldehyde silver process reported in literature. It can perfectly simulate the influence of oxygen pressure, methanol pressure and residence time on selectivity and conversion. The model also simulates well the relationship between selectivity and temperature below 600 °C. Using this model as a reference, we observed that if the rate constant (k_5 and k_{10}) and the exponential factor of the term associated with the water partial pressure (x) were changed for the rate of methanol formation (r_5) and formaldehyde combustion (r_{10}), the model is able to perfectly simulate the influence of the water and temperature on selectivity.

It was also necessary to include the formaldehyde gas-phase decomposition (Eq. 18) on the simulator, once the reaction takes place at high temperatures (> 600 °C) at industrial conditions, and this reaction will play an important role in predicting the selectivity.

A kinetic equation for the gas-phase decomposition of formaldehyde was not found in literature. Besides some authors mention this reaction, they did not include it in their works. A kinetic model for the gas-phase decomposition of acetaldehyde was found (Fogler, 1992) and it was used as a base for the modified model for formaldehyde pyrolytic reaction. The hypothesis is that this reaction is irreversible and it depends only on temperature and reagent concentration. In this sense, the rate constant (k_{CO}) and the order of the reaction (α) were changed to fit the Eq.19 for the formaldehyde process data (Eq. 23).

Equations 21, 22 and 23 show the modified kinetic equations for formaldehyde formation, formaldehyde combustion and formaldehyde decomposition, respectively.

$$r_5 = \frac{k_5 \cdot K_A \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/4} \cdot \frac{P_{CH_3OH}}{P_\theta} \cdot \left(\frac{P_{H_2O}}{P_\theta}\right)^{-x}}{\left(1 + K_C^{1/2} \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/2}\right)^2} \quad (21)$$

$$r_{10} = \frac{k_{10} \cdot K_B \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/2} \cdot \frac{P_{HCHO}}{P_\theta} \cdot \left(\frac{P_{H_2O}}{P_\theta}\right)^{-x}}{\left(1 + K_C^{1/2} \cdot \left(\frac{P_{O_2}}{P_\theta}\right)^{1/2}\right)^2} \quad (22)$$

$$r_{CO} = k_{CO} \cdot P_{HCHO}^\alpha \quad (23)$$

In these equations, “ r_5 ” is the rate of formaldehyde formation, “ r_{10} ” is the rate of formaldehyde combustion and “ r_{CO} ” is the rate of gas-phase decomposition of formaldehyde (the other terms have been previously defined).

2.4. Method for acquiring rate of reaction data

The modified kinetic equations were implemented in the reactor simulator in order to calculate the rate of formaldehyde formation, formaldehyde combustion and formaldehyde gas-phase decomposition at every point of the silver bed.

Many process conditions are available in literature and from industry, correlating input process variables (temperature, pressure, reagents flow) to output process variables (conversion, selectivity towards formaldehyde, carbon dioxide and carbon monoxide). For every available data, the adjustable terms of the kinetic equations were varied until the simulator was able to predict the output variables for the associated input variables at a specific data point. The five adjustable terms are: “ k_5 ”, “ k_{10} ”, “ x ”, “ k_{CO} ” and “ α ”.

The same adjustment is not supposed to fit all data points, once this modified and simplified model cannot be better than the original complete kinetic models, but it is able to fit one data point at a time, supplying a profile of rate of reaction throughout the catalyst bed. Every point of the bed has a particular process condition, characterized by the partial pressures of all species present in the reactor, plus the temperature and total pressure. As the reactor simulator calculates these partial pressures and the corresponding rate of reaction, once the particular data point is fit, a set of data rows is obtained for rate of reaction.

The adjustment of “ k_5 ”, “ k_{10} ”, “ x ”, “ k_{CO} ” and “ α ” was performed using Genetic Algorithms (GA) as a search method (Goldberg, 1989; Davis, 1991; Carrol, 1996). According to GA operators, these terms were adjusted in order to minimize the difference between the conversion and selectivity calculated by the simulator equipped with the modified kinetics and the experimental values associated with the considered data point.

If the procedure is repeated for many process data points available for one particular reactor, a huge set of rate of reaction data is obtained. Different reactors may be filled with particular silver catalyst, whose activity may vary from one to another. In this sense, the procedure should not be used mixing process data from different reactors. Special attention must be given for data points from the same reactor avoiding the use of information at different cycle times (fresh and aged catalysts have different activity). Industrial data used in this work refer to fresh catalyst only. The conversion and selectivity trends obtained for one reactor may apply to other silver reactors, however precise values may be somewhat different.

The data set obtained was used for training the neural net and then the reactor was simulated again with the trained ANN to validate the procedure, comparing the output variables calculated by the simulator with the experimental output variables.

2.5. Artificial Neural Networks

The rate of reaction was calculated by a neural network sub-routine inside the reactor simulator. An ANN with three layers and bias neurons was used in this work, as described in Figure 3.

The inputs to the network were chosen to be the same as the ones encountered on the modified model, plus the partial pressures of hydrogen, carbon monoxide and carbon dioxide that could possibly influence the rate of the three parallel reactions. Total pressure was also included. The input parameters are bed temperature (K); total pressure (atm); partial pressures of methanol, oxygen, water, hydrogen, formaldehyde, carbon dioxide and carbon monoxide, as well as the bias neuron (input = 1).

The number of neurons at hidden layer was varied to obtain the optimum configuration. A bias neuron connected to “1” was included to this layer. Three neurons compose the output layer, calculating:

- The rate of methanol oxidation (r_5), kmol/m³.h
- The rate of formaldehyde oxidation (r_{10}), kmol/m³.h
- The rate of gas phase decomposition of formaldehyde (r_{CO}), kmol/m³.h

Equation 24 shows the calculation performed by each virtual neuron, where “ x_j^s ” is the value from the neuron “j” at layer “s”, “ w_{ji}^s ” is the weight associated to link between the neuron “j” at layer “s” and the neuron “i” at layer “s-1” and “ x_i^{s-1} ” is the value from the neuron “i” at layer “s-1”

$$x_j^s = f\left(\sum_i (w_{ji}^s \cdot x_i^{s-1})\right) = f(I_j) \quad (24)$$

The function “f” is a transfer function, typically a sigmoid, as in equation 25.

$$f(I_j) = \frac{1}{1 + \exp(-I_j)} \quad (25)$$

The training algorithm used in this work was the back-propagation. The ANN was trained until the net error (E) at output layer is minimized, according to Eq 26, where “ d_m ” is the experimental rate for reaction “m”, “ o_m ” is the calculated rate for reaction “m” and “N” is the number of data points. In this process, the internal parameters of the ANN (weights) are adjusted to minimize “E”. Experimental inputs and outputs were normalized before being used by the training process.

$$E = \frac{1}{N} \cdot \sum_{i=1}^N \left(\sum_{m=1}^3 ((d_m - o_m)^2) \right) \quad (26)$$

When the training process is finished, the optimum set of weights is stored in a data file and the ANN is then able to predict new outputs. Running with the reactor simulator, the local conditions at every step of the simulation are calculated and fed to the ANN, which generates the rate of the three reactions, using the trained weights stored in the data file. The rates are used back in the simulator, which calculates the advancement of the reactions and the new conditions at the next simulation step.

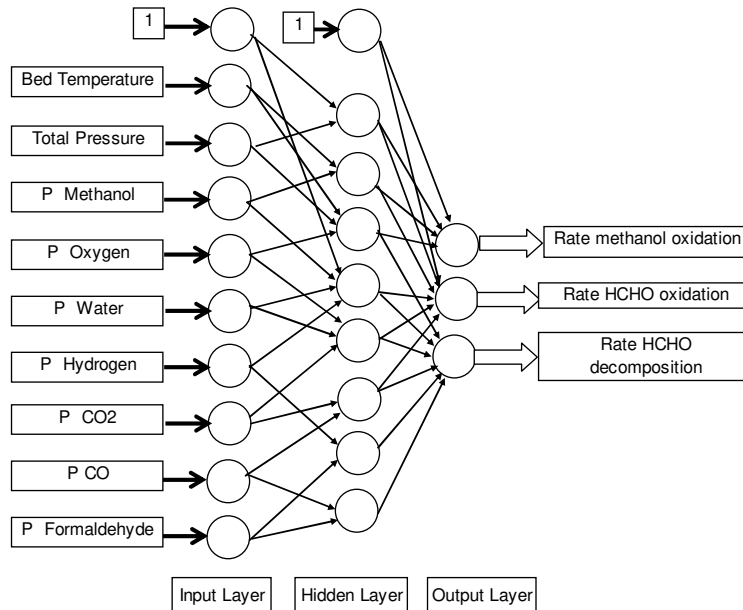


Figure 3: Schematic of the ANN used (not all arrows were drawn, in order to make the picture clear)

Details about the neural network algorithm calculations and training process may be found in Rumelhart et al. (1986), Wasserman (1989), Bhagat (1990) and Papes Filho (2007). The ANN code inside the reactor simulator and the ANN training program were written in Fortran code by the authors.

3. Results and Discussion

The procedure for obtaining the rate of reactions was applied for cases reported in literature, and the trained ANN was used for simulating experimental conditions in order to validate the method.

Robb and Harriot (1974) ran important experiments, used as reference by Andreasen et al. (2003) for their studies. The experiments were run at 422 °C, total pressure of 1.22 atm, partial pressure of methanol in feed of 0.011 atm, partial pressure of oxygen in feed of 0.016 atm (molar ratio oxygen to methanol of 1.45), using helium as carrier gas. Different conditions were investigated by changing the total gas flow (or residence time), obtaining curves that correlate the conversion to the formaldehyde and carbon dioxide yields. The reported curves are shown on Figure 7.

Seven data points from Robb and Harriot's study were fit by the simulator described in this work, using the modified kinetic equations. The chosen data points covered the whole range of data reported by Robb and Harriot (conversions from zero to 70%). For every data point, the procedure was:

- simulate the reactor, using the kinetic parameters reported by Andreasen et al. (2005) for Equations 21 and 22, as a reference, with the basic process condition reported by Robb and Harriot;
- change kinetic parameters "k₅", "k₁₀", "x", "k_{CO}" and "α" on equations 21, 22 and 23 until formaldehyde, carbon dioxide and carbon monoxide yields match the particular data point conversion and yields (fine tuning procedure, using genetic algorithm approach for searching the optimum parameter values);

- c. when the simulator is able to predict the correct conversion and selectivity for the particular data point, the rate of reaction profile is supposed to be true for the three reactions involved;
- d. the simulator saves the rate of reaction profile or, in other words, it saves the rate values for the three reactions at every simulation step, associating with the local process conditions (temperature and partial pressures);
- e. the total flowrate (or residence time) is changed in order to simulate another data point with a different conversion;
- f. steps “b” to “e” are repeated until all data points are fit, individually;
- g. the rate of reaction profiles generated by all data points are grouped into a single file.

Table 2 shows a sample of the rate of reaction data generated by the simulator (except temperature and total pressure, which are constant). The whole set of data, in this case containing 144 points, was used for training the ANN. The internal weights of the net were adjusted to minimize the error between the calculated and experimental rate of reactions, using the back-propagation algorithm, and the optimized set of weights was stored in a data file.

Table 2: Sample of the rate of reaction set of data for Robb and Harriot (1974) datapoints.

Reaction rate (kmol/m ³ .h)			Process conditions – partial pressures (atm)						
r ₅	r ₁₀	r _{CO}	MeOH	O ₂	H ₂ O	HCHO	CO ₂	H ₂	CO
4.83E+02	9.45E+01	2.85E-05	2.24E-02	3.94E-02	3.51E-03	5.24E-03	7.55E-04	3.76E-03	1.18E-10
3.84E+02	9.16E+01	4.27E-05	2.03E-02	3.86E-02	4.55E-03	6.87E-03	1.21E-03	5.25E-03	2.91E-10
2.86E+02	1.09E+02	5.80E-05	1.73E-02	3.71E-02	5.99E-03	8.42E-03	2.54E-03	8.03E-03	6.99E-10
8.25E+02	9.42E+01	7.18E-06	2.62E-02	4.07E-02	1.64E-03	2.09E-03	1.73E-04	1.31E-03	6.99E-12
2.26E+02	1.07E+02	7.02E-05	1.50E-02	3.59E-02	7.13E-03	9.57E-03	3.68E-03	1.03E-02	1.25E-09
2.51E+02	8.44E+01	7.33E-05	1.60E-02	3.68E-02	6.62E-03	9.85E-03	2.39E-03	8.50E-03	1.08E-09
1.08E+02	8.44E+01	9.89E-05	8.59E-03	3.22E-02	1.02E-02	1.20E-02	7.46E-03	1.72E-02	4.75E-09
5.83E+02	9.60E+01	1.90E-05	2.40E-02	4.00E-02	2.75E-03	4.00E-03	4.80E-04	2.72E-03	4.91E-11
1.16E+02	8.63E+01	9.75E-05	9.07E-03	3.25E-02	1.00E-02	1.19E-02	7.10E-03	1.66E-02	4.34E-09
4.23E+02	9.29E+01	3.63E-05	2.12E-02	3.89E-02	4.09E-03	6.17E-03	9.97E-04	4.58E-03	2.01E-10

Rates for “r₅”, “r₁₀” and “r_{CO}” calculated by the trained neural network were compared to the experimental rates, showed on Figures 4, 5 and 6. High correlation coefficients (> 0.99) were obtained and calculated points were along x = y line, as shown on the graphs, indicating that the neural network could successfully fit the experimental data simultaneously for the three rates, based on the input data. The good fit was confirmed through the “F” test, expressed in equation 27, where SQM is the sum of the squares of the model and SQR is the sum of squares of the residual (Box and Hunter, 1978).

$$F_{CALC} = \frac{SQM}{SQR} \quad (27)$$

The training statistics are:

Training time:	16 min (Pentium-4, 2.66 GHz, 480MB RAM).
Iterations:	955,166
Sum of squares of the model:	89.97
Sum of squares of residue:	0.02301
F-calc:	3909 (overwhelmingly significant)

Figure 7 shows Robb and Harriot’s (1974) experimental data points, as well as simulations performed by Andreassen et al. (2004) and the simulations performed in this work, using the trained ANN with the reactor simulator. The curves for the formaldehyde and carbon dioxide yields fit very well the experimental points, with improved accuracy when compared to Andreassen’s (2004) simulations, validating the effectiveness of the procedure and the training of the ANN.

The number of neurons at hidden layer was studied, observing the correlation between the calculated rates and experimental rates (correlation coefficient, r²), as shown on Table 3. On the range 6 to 8 neuron at hidden layer, it is clear that better fit is obtained with 7 neurons. With 9 neurons at hidden layer, the correlation

coefficient is better, but in this case the net loses its generalization characteristic, once there are too much adjustable variables (110 weights) to the number of data (144 points). The optimum number was then set at 7.

Table 3: Study on the number of neurons on hidden layer.

# neurons Hidden	$r^2 - r_5$	$r^2 - r_{10}$	$r^2 - r_{CO}$
6	0.99936	0.97987	0.99978
7	0.99959	0.99271	0.99984
8	0.99942	0.99232	0.99980
9	0.99988	0.99323	0.99997

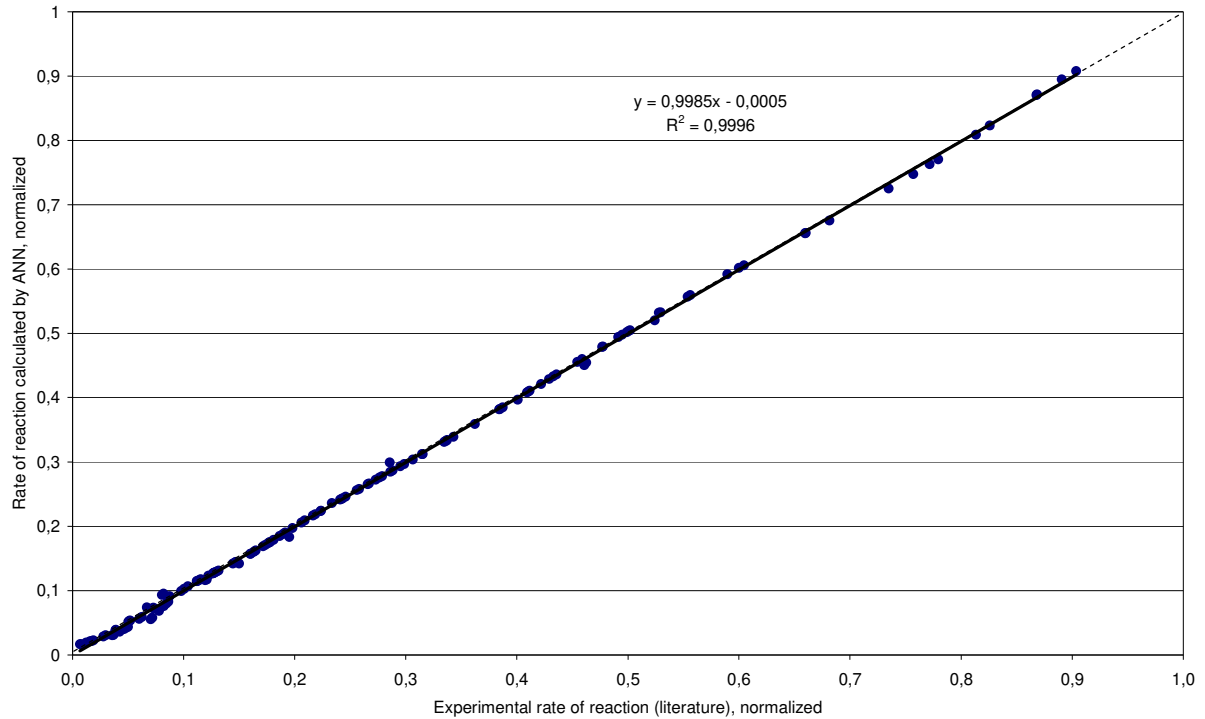


Figure 4: Correlation between experimental rate of reaction extracted from process data of Robb and Harriot (x-axis) and rates calculated by the ANN (y-axis) for the formaldehyde formation reaction (r_5).

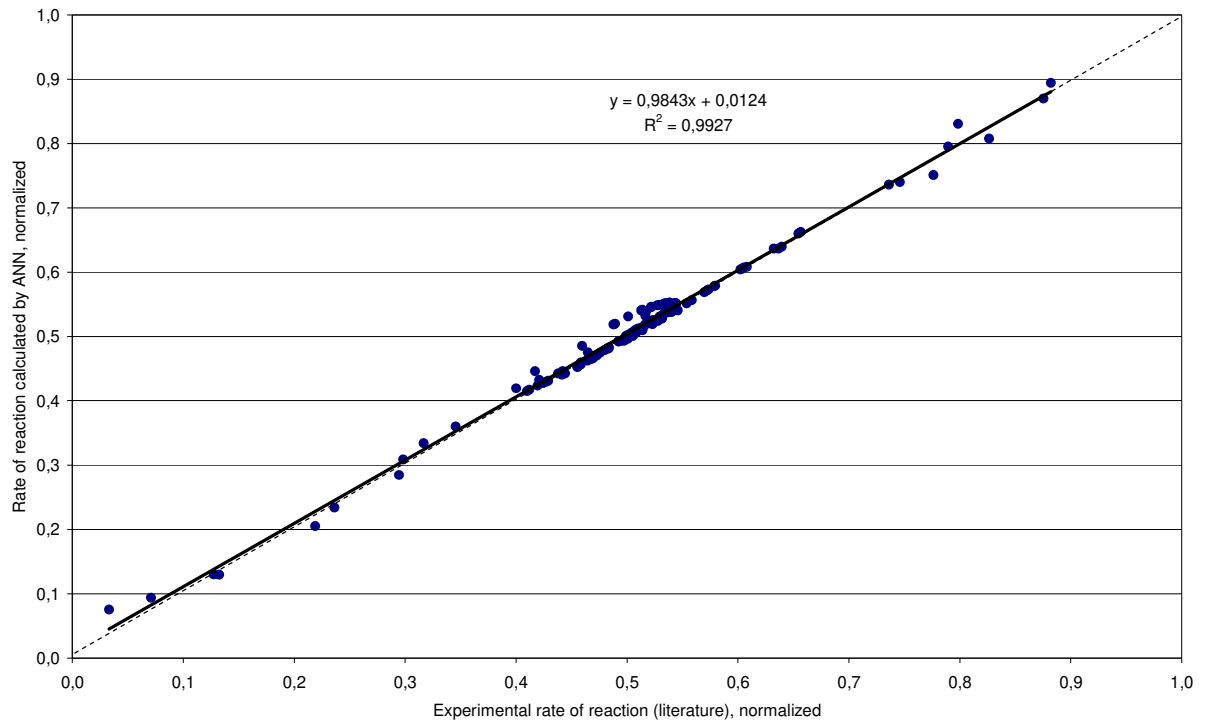


Figure 5: Correlation between experimental rate of reaction extracted from process data of Robb and Harriot (x-axis) and rates calculated by the ANN (y-axis) for the formaldehyde combustion reaction (r_{10}).

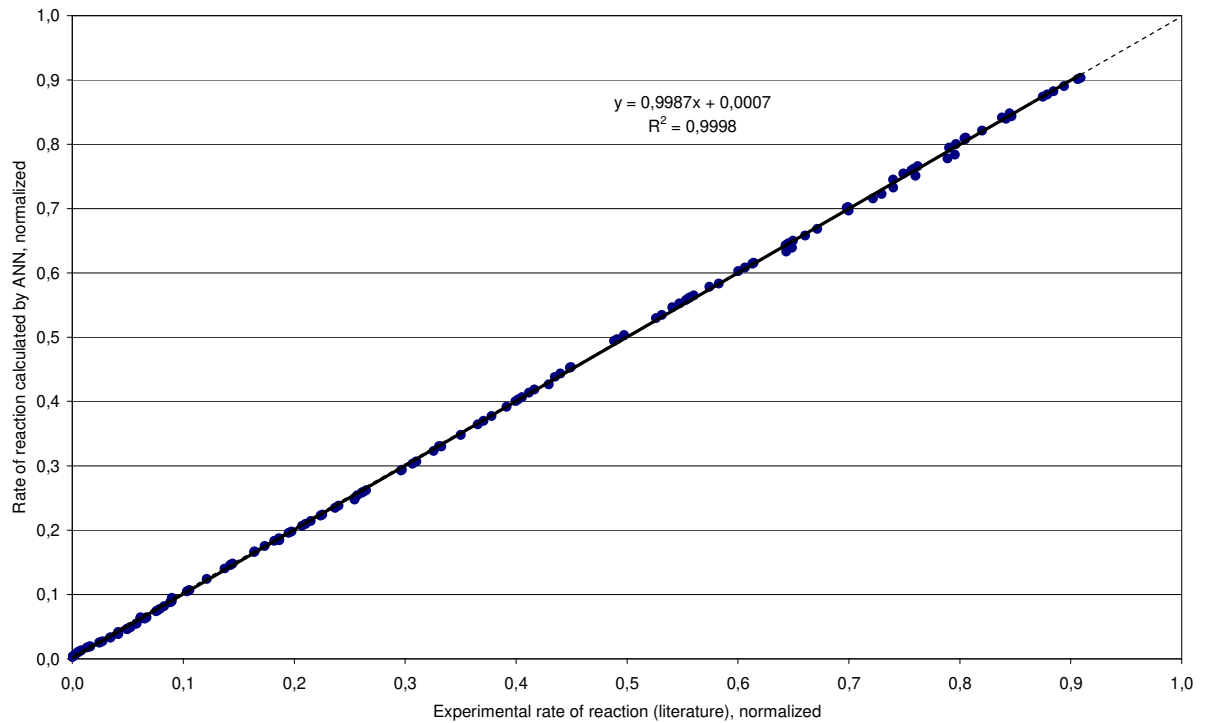


Figure 6: Correlation between experimental rate of reaction extracted from process data of Robb and Harriot (x-axis) and rates calculated by the ANN (y-axis) for the formaldehyde decomposition reaction (r_{CO}).

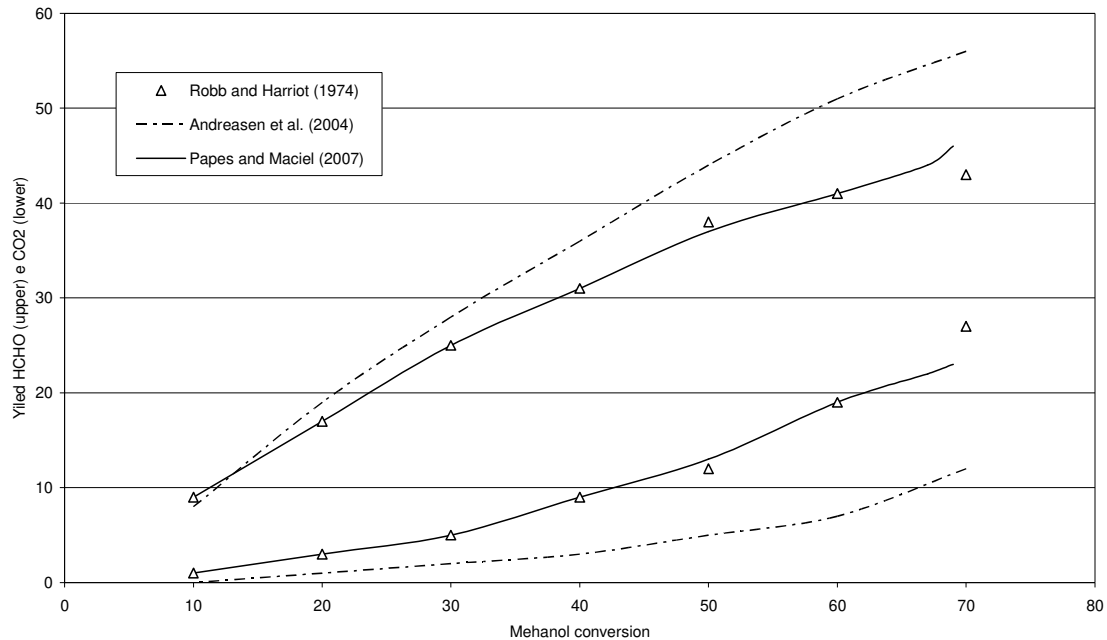


Figure 7: Simulation of experiments from Robb and Harriot, at 422 °C and 1.12 atm. Points are experimental measurements from Robb and Harriot (1974). Dashed lines are the simulations from Andreasen et al. (2004). Solid lines are the simulations with ANN. Upper curves are for formaldehyde yield and bottom curves for carbon dioxide yield.

The carbon monoxide formation was considered on Waterhouse et al. (2004) experimental work, studying the effect of temperature on the selectivity towards formaldehyde, carbon dioxide and carbon monoxide, using water at feed (water ballast process). They ran experiments with molar feed composition $\text{CH}_3\text{OH}/\text{O}_2/\text{H}_2\text{O}/\text{He}$ of 2.25/1.00/1.70/20.00 and space velocity of $1.25 \cdot 10^5 \text{ h}^{-1}$, varying the bed temperature.

Nine data points taken from Waterhouse's study were fit by the simulator, as described above, using the modified kinetic equations, generating 189 data points that correlate rate of reaction with local temperature and partial pressures of the reactants.

The rates for “ r_5 ”, “ r_{10} ” and “ r_{CO} ” calculated by the trained neural network were compared to the experimental rates, showed on Figures 8, 9 and 10. High correlation coefficients (> 0.99) were again obtained and calculated points concentrated along $x = y$ line, as showed on the graphs, indicating that equally the neural network could successfully fit the experimental data, generally speaking. However, some relevant deviations were seen for the three reactions.

Figure 11 shows the results of the reactor simulations using the trained ANN, together with Waterhouse's experimental points. The simulation curves show consistency to the experimental data for the selectivity towards formaldehyde, carbon dioxide and carbon monoxide. Besides differences are seen in some particular cases (5 percentage points on carbon dioxide selectivity at 450 °C), the simulator is able to represent very well the trends of experimental points, validating the procedure. Methanol conversion was not included on the figure for clarity reasons, but the fit was equally successful.

Relevant deviations of simulated formaldehyde selectivity and carbon monoxide selectivity close to 700 °C (Figure 11) are believed to be due to ANN training performance. Good correlation coefficients were obtained between calculated and experimental rates of reaction, but the deviations of some points from the 45° line on Figures 8, 9 and 10 may indicate that better ANN fit is required in this particular case.

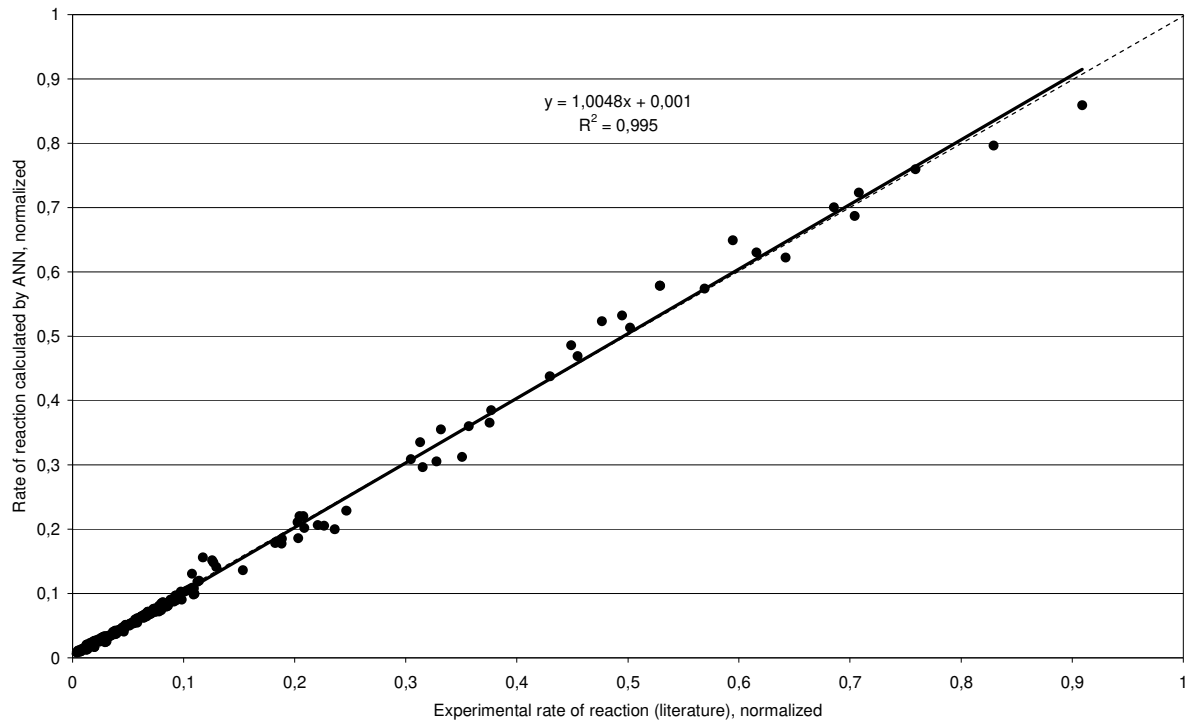


Figure 8: Correlation between experimental rate of reaction extracted from process data of Waterhouse et al. (x-axis) and rates calculated by the ANN (y-axis) for the formaldehyde formation reaction (r_5).

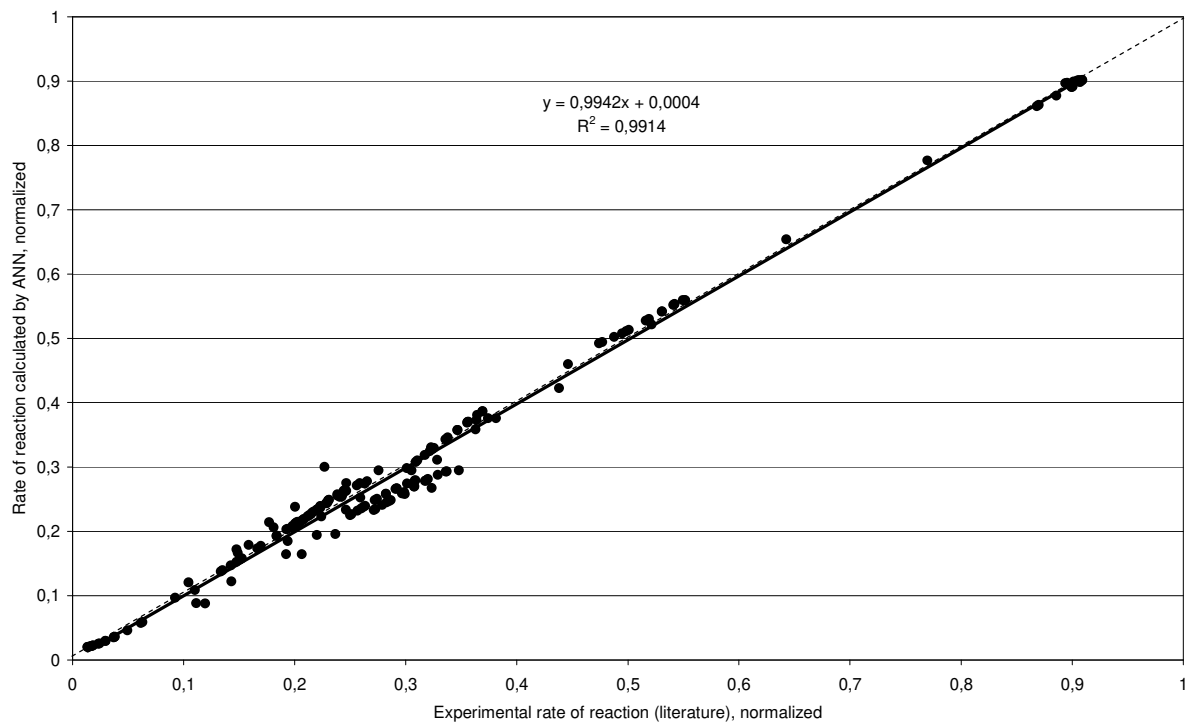


Figure 9: Correlation between experimental rate of reaction extracted from process data of Waterhouse et al. (x-axis) and rates calculated by the ANN (y-axis) for the formaldehyde combustion reaction (r_{10}).

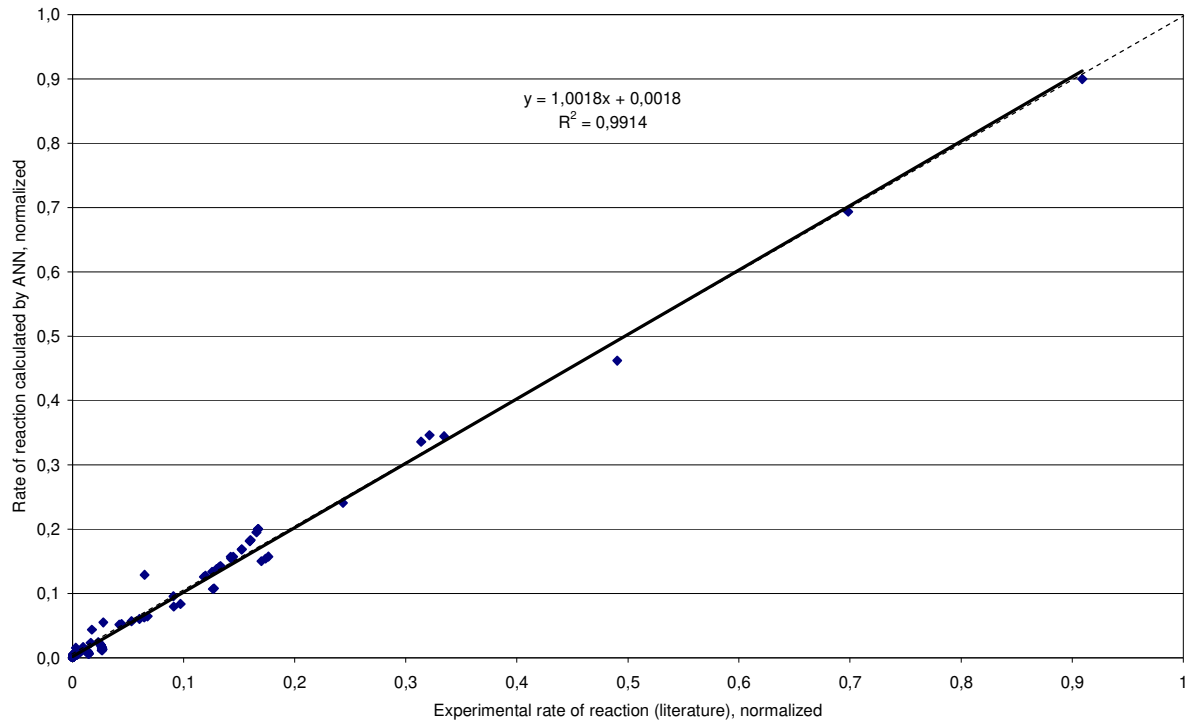


Figure 10: Correlation between experimental rate of reaction extracted from process data of Waterhouse et al. (x-axis) and rates calculated by the ANN (y-axis) for the formaldehyde decomposition reaction (r_{CO}).

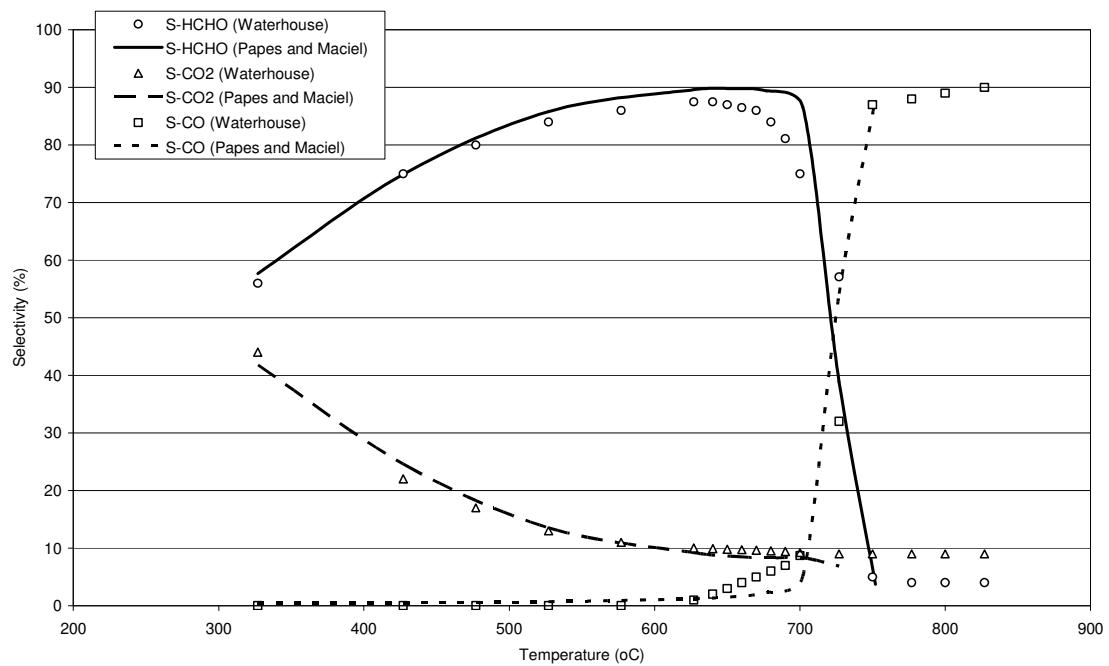


Figure 11: Simulation of experiments from Waterhouse et al. (2004), varying bed temperature. Points are experimental measurements for the selectivity towards formaldehyde (circles), carbon dioxide (triangles) and carbon monoxide (squares). Lines are the simulations with ANN. Methanol conversion was subtracted for clarity of the picture.

The authors are studying improvements on the ANN training in order to obtain better fit and simulation performance, accordingly (Papes Filho, 2007). This work justifies by the fact of 1 percentage point on formaldehyde selectivity represents a great deal of money on methanol consumption. Despite the trends for selectivity reported here are good, more accurate values are essential for process optimization.

Temperatures below 327 °C are too far from industrial conditions and were not considered here. Negligible amounts of formic acid were formed under the conditions of the experiments, agreeing with the results from the reaction mechanism from Wachs and Maddix (1978), used by Andreasen et al. (2003). Methanol conversion and selectivity towards formaldehyde increase with bed temperature up to 650 °C, and above 700 °C, the selectivity to formaldehyde decreases dramatically due to the gas phase decomposition of formaldehyde to carbon monoxide. Selectivity towards carbon dioxide decreases consistently with increasing temperature. In the other hand, the higher the temperature, the higher the carbon monoxide selectivity. Methanol conversion increases constantly with temperature, approaching to 100% at 727 °C.

Waterhouse's (2004) experiments were run at near industrial conditions, where many laboratory studies had failed, which they attributed to differences in catalyst, bed construction, reactor design and testing conditions. In accordance with industrial practices, Waterhouse et al. identified the importance of water presence at feed for achieving high formaldehyde yields.

The effect of the oxygen to methanol molar ratio was also studied by Waterhouse at 650 °C, with constant space velocity ($1.25 \cdot 10^5 \text{ h}^{-1}$). Figure 12 shows Waterhouse's experiments and simulations made with ANN, showing good agreement.

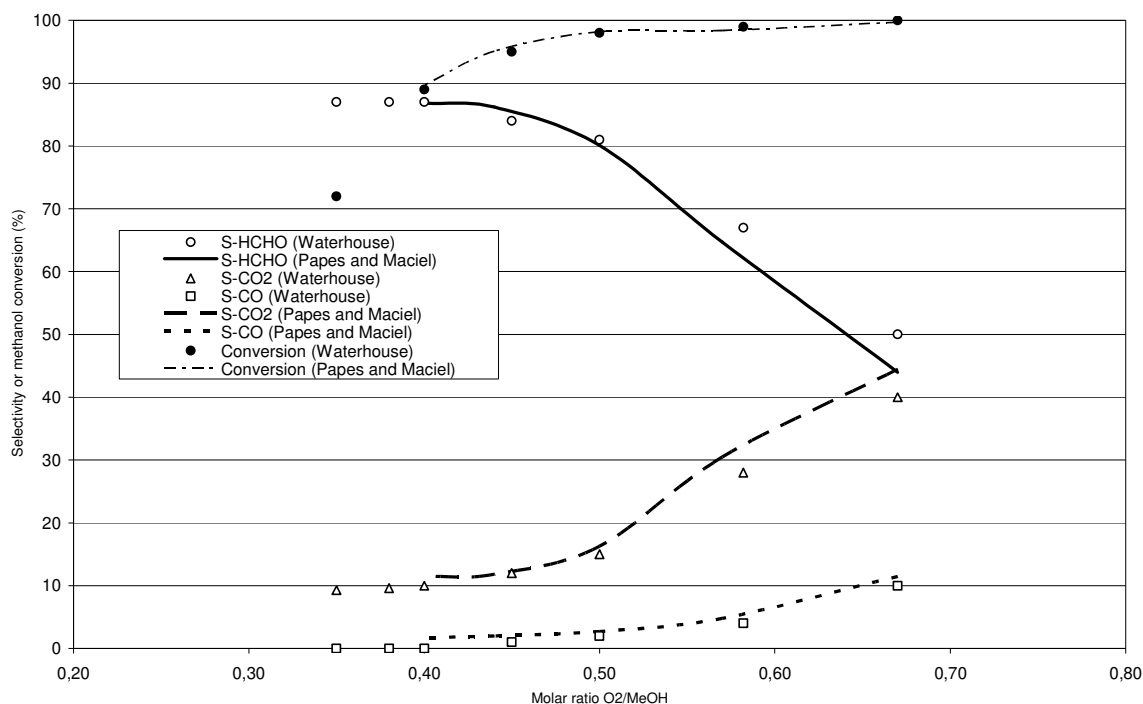


Figure 12: Simulation of experiments from Waterhouse et al. (2004), varying oxygen/methanol molar ratio. Points are experimental measurements for the methanol conversion (black circles), selectivity towards formaldehyde (open circles), carbon dioxide (open triangles) and carbon monoxide (open squares). Lines are the simulations with ANN.

The higher the oxygen/methanol ratio, the higher the methanol conversion, but the selectivity towards formaldehyde decreases. The same trend reported by Robb and Harriot – higher conversion, lower formaldehyde selectivity – is seen in this case. Waterhouse reported that there is a maximum on formaldehyde selectivity at an O_2/MeOH ratio of 0.44, and below this value there is a very small decrease on the selectivity, practically constant.

The selectivity to CO also increased with oxygen concentration, what is not expected once it is formed by homogeneous decomposition of formaldehyde. At higher oxygen concentrations, the exothermic oxidation reactions may cause localised hot spots on catalyst surface, favouring the decomposition of formaldehyde. Higher oxygen concentrations also increase methanol conversion and more formaldehyde yields mean more formaldehyde available for decomposition (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007)

To the best of our knowledge, this is the first time that this approach is used to obtain rate of reaction data from process information for training an ANN. It is worthwhile mentioning that this proposed approach allows dealing with data set even when the regime is not kinetic but rather mass transfer controlled which may occur in some industrial operating conditions. Thus, the real process reaction rate may be extracted from the operational data and measured reactor temperature profiles.

4. Conclusion

Rate of reaction data was extracted from process conditions using a novel approach presented in this paper. The best kinetic model in literature was employed as a base reference to develop a modified model, used together with a reactor simulator in order to fit experimental data. For every data point, the parameters of the modified model were adjusted, until the conversion and selectivity matched the experimental values for a given process condition.

The rate of reaction set of data obtained was used for training an Artificial Neural Network (ANN), with a standard back-propagation algorithm. Once trained, the weights of the ANN were stored in a data file. The ANN was implemented in a reactor simulator software, where it was able to calculate the rate of reaction, using the saved weights, for any process condition. The simulator equipped with the ANN could then estimate conversions and selectivity for new operation conditions.

The approach was tested with experimental work from two authors: Robb and Harriot (1974), who performed studies correlating methanol conversion to formaldehyde and carbon dioxide yields; and Waterhouse et al. (2004a), who studied the influence of temperature and oxygen/methanol molar ratio on reactor performance.

Reasonable correlation was achieved between the rates calculated by ANN and the extracted ones. The procedure was successfully validated by simulating the results presented by Robb and Harriot, Andreassen et al. and Waterhouse et al. with the reactor simulator containing ANN, developed in this work. The selectivity trends obtained with the proposed procedure are very consistent with literature but an improvement on ANN training is required to achieve excellence level on simulation performance.

References

- ABRAF (Brazilian Association of Formaldehyde Manufacturers) report; "Panorama of productive chain", www.abraf.com.br, 2004.
- Andreassen, A.; Lynggaard, H.; Stegelmann, C. and Stoltze, P.; "A microkinetic model of the methanol oxidation over silver", *Surface Science*, 544, pp.5-23, 2003.
- Andreassen, A.; Lynggaard, H.; Stegelmann, C. and Stoltze, P.; "Simplified kinetic models of methanol oxidation on silver", *Applied Catalysis A: General*, 289, pp.267-273, 2005.
- Barteau, M and Madix, R.J.; *Surf. Sci*, 40, p.108, 1984.
- Bazilio, C.A.; Thomas, W.J.; Ullah, U. and Hayes, K.E.; "The catalytic oxidation of methanol", *Proc. R. Soc. Lond. A*, 399, pp.181-194, 1985.
- Berne, R. M. and Levy, M. N.; "Fisiologia", Editora Guanabara, 2nd ed., 1990.
- Bhagat, P.; "An Introduction to Neural Nets", *Chemical Engineering Progress*, August, p.55, 1990.
- Bhattacharyya, S.K.; Nag, N.K. and Ganguly, N.D.; "Kinetics of vapor-phase oxidation of methanol on reduced silver catalyst", *J. of Catalysis*, v.23, i.2, pp.158-167, 1971.
- Box, G.E.P and Hunter, J.S.; "Statistics for experimenters", Wiley and Sons, 1st ed., New York, 1978.
- Cancho, J.C.; Sanchez, A.M.E.; Tena, A.F. and Moreno, M.C.M.; *Chem. Biochem.*, Q3, n. 1-2, p.51, 1989.
- Cao, E. and Gavriilidis, A.; "Oxidative dehydrogenation of methanol in a microstructured reactor"; *Catalysis Today*, 110, pp.154-163, 2005.
- Carrol, D.L.; "Chemical laser modeling with genetic algorithm", *AIAA Journal*, v.34, no 2, pp.338-346, 1996.

Crank, J. and Nicholson, P.; *Proc. Phil. Soc.*, v.43, p.50, 1947.

Davis, L.; "Handbook of Genetic Algorithms", International Thomson Computer Press, Boston, 1991.

Fogler, H.S.; "Elements of chemical reaction engineering", Prentice-Hall International, 2nd ed., New Jersey, p.71, 1992.

Goldberg, D.E.; "Genetic Algorithms in Search, Optimization, and Machine Learning", Ed. Addison-Wesley Publishing Company, Inc; New York, 1989.

Irdam, E.A.; Kiefer, J.H.; Harding, L.B. and Wagner, A.F.; "The formaldehyde decomposition chain mechanism", *International Journal of Chemical Kinetics*, v.25, pp.285-303, 1993.

Lefferts, L.; Ommen, J.G. and Ross, J.R.H.; "The oxidative dehydrogenation of methanol to formaldehyde over silver catalysts in relation to the oxygen-silver interaction", *Appl. Catal.*, 23, 1986, p.385.

Lennox, B.; Montague, G.A.; Frith, A.M.; Gent, C. and Bevan, V.; "Industrial application of neural networks – an investigation", *Journal of Process Control*, v.11, pp.497-507, 2001.

Lynggaard, H.; Andreasen, A.; Stegelmann, C. and Stoltze, P.; "Analysis of simple kinetic models in heterogeneous catalysis", *Progress in Surface Science*, 77, pp.71-137, 2004.

Mao, C.F and Vanice, M.A.; "Formaldehyde oxidation over Ag catalysts", *Journal of Catalysis*, 154, pp.230-244 (1995).

Nagy, A.; Mestl, G.; Ruhle, T.; Weinberg, G. and Schlogl, R.; "The dynamic restructuring of electrolytic silver during the formaldehyde synthesis reaction", *J. of Catalysis*, 179, pp.548-559, 1998.

Nagy, A. and Mestl, G.; "High temperature partial oxidation reactions over silver catalysts", *Applied Catalysis A: General*, 188, pp.337-353, 1999.

Papes Filho, A.C.; "Simulation and optimization of a silver formaldehyde reactor, using artificial intelligence techniques", PhD thesis (in English), UNICAMP – University of Campinas, Brazil, 2007.

Papes Filho A.C. and Maciel Filho R.; "Concurrent Engineering Reactor Design", *Computer Aided Chemical Engineering*, v.20 A, Edited by Luis Puijagner and Antonio Espuña, Elsevier B.V., ISSN 1570-7946, pp.559-564, 2005.

Papes Filho, A.C. and Maciel Filho, R.; "Hybrid simulation of a fixed-bed formaldehyde silver-catalyzed reactor using artificial neural networks", to be published, 2007.

Pham, D.T. and Pham, P.T.; "Artificial intelligence in engineering", *International Journal of Machine Tools & Manufacture*, v.39, pp. 937-949, 1999.

Piccoli, R.L.; "Kinetic study of methanol selective oxidation to formaldehyde on iron molybdate catalyst", Master dissertation, Rijksuniversiteit Gent, Belgium, 1992.

Press, W.H., Flannery, B.P., Teukolsky, S.A., Vetterling, W.T.; "Numerical Recipes", Press Syndicate of the University of Cambridge, 1st ed., 1992.

Psichogios, D.C. and Ungar, L.H.; "A hybrid neural network-first principles approach to process modeling", *AIChE Journal*, 38, 10, pp. 1499-1511, 1992.

Qian, M.; Liauw, M.A. and Emig, G.; "Formaldehyde synthesis from methanol over silver catalysts", *Applied Catalysis A: General*, 238, pp.211-222, 2003.

Reid, R.C; Prausnitz, J.M and Poling, B.E.; "The properties of gases and liquids", McGraw-Hill Book Company, New York, 4th ed., 1987.

Robb, D.A. and Harriot, P; "The kinetics of methanol oxidation on a supported silver catalyst", *J. of Catalysis*, 35, pp.176-183, 1974.

Rumelhart, D.E; Hinton, G.E. and Williams, R.J.; "Learning internal representations by error propagation" in *Parallel distributed processing*, v.1, pp.318-362, 1986.

Santacesaria, E. and Morbidelli, M.; "Kinetics of the catalytic oxidation of methanol to formaldehyde", *Chem. Engng. Sci.*, v.36, pp.909-918, 1981.

Schubert, H; Tegtmeier, U. and Schlogl, R.; "On the mechanism of the selective oxidation of methanol over elemental silver", *Catalysis Letters*, 28, pp.383-395, 1994.

SRI International; "Formaldehyde", Report n° 23A, Menlo Park, 1978.

Su, S; Zaza, P. and Renken, A.; "Catalytic dehydrogenation of methanol to water-free formaldehyde", *Chem. Eng. Technol.*, 17, pp.34-40, 1994.

Treybal, R.E.; "Mass-transfer operations", McGraw-Hill International Editions, 3rd ed., Singapore, 1981

Ullmann's Encyclopedia of Industrial Chemistry, v.A11, VHC Publishers, 5th ed., New York, 1988.

Van Veen, A.C, Hinrichsen, O. and Muhler, M.; "Mechanistic studies on the oxidative dehydrogenation of methanol over polycrystalline silver using the temporal-analysis-of-products approach", *J. of Catalysis*, 210, pp. 53-56. 2002.

Wachs, I.E. and Madix, R.; "The oxidation of methanol on a silver (110) catalyst", *Surface Science*, 76, pp. 531-558, 1978.

Walker, J.F; "Formaldehyde", Robert E. Krieger Publishing Company, 3rd ed, New York, 1975.

- Wasserman, P.D.; "Neural Computing: Theory and Practice", Van Nostrand Reinhold, 1^a ed., New York, 1989
- Waterhouse, G., Bowmaker, G. and Metson, J.; "Mechanism and active sites for the partial oxidation of methanol to formaldehyde over an electrolytic silver catalyst", Applied Catalysis A, 265, pp.85-101; 2004 (a).
- Waterhouse, G., Bowmaker, G. and Metson, J.; "Influence of catalyst morphology on performance of electrolytic silver catalysts for the partial oxidation of methanol to formaldehyde", Applied Catalysis A, 266, pp.257-273, 2004 (b).
- Welty, J.R.; Wicks, C.E. and Wilson, R.E.; "Fundamentals of momentum, heat and mass transfer", John Wiley & Sons editor, 3rd ed., New York, 1984.

3.3. Conclusões

Nesse capítulo, apresentou-se uma nova abordagem para extrair dados cinéticos (taxas de reação) a partir de dados macro de processo (conversão e seletividades). Um simulador de reator de leito fixo equipado com equações da taxa determinísticas modificadas foi usado para ajustar dados experimentais: para cada ponto, individualmente, os parâmetros do modelo modificado foram ajustados de modo que a conversão e seletividades preditas pelo simulador pudessem aproximar-se dos valores experimentais para uma dada condição de processo. Quando cada ponto experimental foi ajustado, o perfil de taxas de reação ao longo do reator foi arquivado. Após ajustar todos os pontos individualmente, os vários conjuntos de taxas de reação (perfis) foram agrupados em um único arquivo.

Realizou-se uma revisão da literatura para identificar o modelo cinético determinístico mais completo para a oxidação do metanol a formaldeído em leito de prata. O modelo micro-cinético reportado por ANDREASEN ET AL. (2003) foi selecionado como a referência para o desenvolvimento do modelo modificado descrito nesse capítulo, adicionando-se uma equação para descrever a decomposição do formaldeído na fase gasosa.

O conjunto agrupado de taxas de reação foi usado para treinar uma Rede Neural Artificial (RNA), com o algoritmo retro-propagação clássico. Uma vez treinada, os pesos da RNA foram salvos e a rede foi então implementada como uma sub-rotina em um segundo simulador, responsável por calcular a taxa de reação usando os pesos previamente salvos, para novas condições de processo.

Foram desenvolvidos dois simuladores nessa etapa: um simulador equipado com equações da taxa simplificadas para extração de dados cinéticos dos dados de processo e o outro equipado com a RNA para predição.

O simulador com as equações cinéticas modificadas não é capaz de prever corretamente a conversão e seletividade para diferentes condições de processo, usando os mesmo parâmetros ajustados. Essa abordagem é somente viável para obter dados de taxa de reação, mas não para simular novas condições. O simulador equipado com a RNA, diferentemente, é capaz de simular corretamente o desempenho do reator para condições de processo variadas usando o mesmo conjunto de pesos treinado.

Essa abordagem foi testada com dados experimentais publicados por ROBB E HARRIOT (1974) e WATERHOUSE ET AL. (2004b). Os dados de Robb e Harriot correlacionam conversão e seletividade para formaldeído e dióxido de carbono. Essas condições foram também simuladas por Andreasen et al para testar seu modelo microcinético proposto. Waterhouse et al. estudaram as influências da temperatura e razão molar oxigênio/metanol na conversão e seletividades para formaldeído, dióxido de carbono e monóxido de carbono sob condições operacionais próximas às industriais.

As taxas de reação foram extraídas dos dados de processo de acordo com o procedimento exposto nesse capítulo, para os dois casos reportados na literatura. A RNA foi treinada com esses dados, individualmente, para os dois casos. As taxas calculadas pela RNA foram comparadas com as taxas extraídas, com boa correlação.

O procedimento foi validado com sucesso simulando-se as condições de processo apresentadas por Robb e Harriot e Andreasen et al., com o simulador contendo a RNA, desenvolvido nesse trabalho. Para os dados de Waterhouse et al., foram detectados alguns pontos que se desviaram dos valores experimentais, próximo a 700 °C (ainda dentro da faixa de operação industrial), identificando-se uma deficiência no treinamento da RNA. Apesar de as tendências da conversão e das seletividades estarem muito coerentes com a literatura, há discrepâncias significativas em valores individuais, o que motivou o aprimoramento do algoritmo de treinamento, explorado no próximo Capítulo.

CAPÍTULO 4

MÉTODO HÍBRIDO DE TREINAMENTO DA RNA USANDO ALGORITMO GENÉTICO PARA ESTIMATIVA DE TAXAS DE REAÇÃO: APLICAÇÃO À OXIDAÇÃO INDUSTRIAL DO METANOL A FORMALDEÍDO SOBRE CATALISADOR DE PRATA

4.1. Introdução

Nesse capítulo, os mesmos dados de taxa de reação obtidos pelo método descrito no capítulo anterior foram usados para o treinamento da rede neural, porém, usando uma abordagem híbrida para o ajuste da RNA através de uma associação de algoritmo genético (AG) e retro-propagação (RP).

A RNA foi treinada isoladamente (diferentemente da abordagem que será apresentada no capítulo seguinte), apresentando-se à rede um conjunto de dados correlacionando temperaturas e pressões parciais com as taxas das três reações de interesse.

O método tradicional de treinamento é a RP, um método de busca que ajusta os pesos (parâmetros internos) da RNA de modo a minimizar o erro da rede, ou seja, a diferença entre as taxas de reação calculadas e as taxas experimentais. A RP é um método baseado nos gradientes, que parte de uma estimativa inicial aleatória (conjunto de pesos aleatório, inicialmente), ajustando os pesos a cada iteração.

Como o método de ajuste dos pesos (RP) foi desenvolvido particularmente para as equações envolvidas nos cálculos dos neurônios virtuais, as fórmulas são bem definidas, não necessitando utilizar derivadas numéricas e não correndo o risco de impossibilidade no cálculo dessas. Entretanto, o método ainda baseia-se em uma estimativa inicial aleatória, que pode levar a um mínimo local: dependendo do conjunto de pesos escolhido aleatoriamente no início do treinamento, a RP pode evoluir até um conjunto de pesos que confira à rede um erro que pode não ser o mínimo erro possível. Isso é possível em um modelo como a RNA, bastante complexo e com muitos parâmetros onde a probabilidade de existência de múltiplos mínimos é alta. Na impossibilidade de visualizar a existência desses múltiplos mínimos em um gráfico, por se tratar de um problema de várias dimensões, a solução apresentada pela RP é geralmente vista como o mínimo global, o que pode não ser verdadeiro.

Para casos como esse, métodos estocásticos aleatórios têm sido utilizados para aumentar a probabilidade de encontrar o mínimo global. O algoritmo genético (GA) é um

exemplo desse tipo de método que usa escolhas aleatórias para guiar uma busca altamente exploratória sobre todo o domínio dos parâmetros a serem otimizados.

O AG, publicado pela primeira vez na monografia de HOLLAND (1975), é um método matemático de solucionar problemas baseado na seleção natural das espécies e na genética, combinando as definições de “sobrevivência do mais adaptado” com operadores genéticos copiados da natureza (HOLLAND, 1976; WANG, 1997). Suas vantagens são (GOLDBERG, 1989; GARRARD AND FRAGA, 1998):

- Realização de uma busca global com menor probabilidade de convergir para um mínimo local;
- Busca a partir de uma população de estimativas e não de uma única estimativa inicial;
- Não há necessidade de calcular gradientes;
- A função-objetivo pode ser uma caixa-preta, sem necessidade de derivadas;
- Cada iteração produz uma melhor aproximação da solução final e múltiplas soluções podem ser encontradas;
- É um algoritmo comprovadamente robusto para sistemas complexos, do ponto de vista teórico e empírico.

O método simula o processo evolutivo e demonstra capacidade de solucionar problemas que outros métodos numéricos clássicos não conseguiram lidar (GOLDBERG, 1989; PHAM AND PHAM, 1999; PAPES FILHO, 2005).

A desvantagem do AG é o grande tempo computacional para convergir para uma solução, com a precisão requerida, e nesse ponto reside a grande vantagem da RP.

A melhor abordagem, proposta nesse trabalho, foi associar os dois métodos: o AG inicia o treinamento, partindo de uma população de conjuntos aleatórios de pesos e trabalha até encontrar uma melhor estimativa, supostamente próxima do mínimo global, mas que ainda não convergiu. Esse conjunto de pesos é usado como estimativa inicial para a RP, que converge rapidamente para a solução com a precisão necessária.

Com a associação dos dois métodos, pretende-se obter os seguintes benefícios em relação ao uso individual de cada um:

- Maior probabilidade de atingir o erro mínimo global da rede, obtendo realmente o melhor conjunto de pesos;

- Maior precisão na solução, chegando mais próximo do erro mínimo absoluto da rede e, conseqüentemente, no melhor conjunto de pesos;
- Menor tempo computacional.

Usando o método híbrido, a RNA foi treinada com dados de taxa de reação extraídos de dois casos: dados experimentais publicados por WATERHOUSE ET AL. (2004b) e dados industriais.

Para o treinamento realizado com os dados de WATERHOUSE ET AL., monitorou-se o erro da rede ao longo das iterações com o AG e RP, mostrado na Figura 4 do artigo anexado, onde se observa a estagnação do erro após algumas gerações do AG. Esse algoritmo consegue rapidamente evoluir de uma população inicial (alto erro da rede) até uma boa estimativa, porém, tem dificuldade de refiná-la. Quando a RP assume o treinamento, o erro cai rapidamente nas primeiras iterações, mostrando que o AG ainda encontrava-se longe da resposta precisa e que a RP consegue rapidamente convergir para o resultado. A associação traz o benefício de aumentar a probabilidade de a solução final ser a melhor possível.

Obteve-se boa correlação entre as taxas de reação calculadas e as taxas experimentais para os dois casos estudados (as taxas experimentais foram extraídas de dados de processo experimentais, utilizando-se o procedimento descrito no capítulo anterior). O número de neurônios na camada oculta foi otimizado para obter maior eficiência da RNA.

O simulador do reator, equipado com a RNA treinada, foi executado para estimar as condições experimentais de WATERHOUSE ET AL., como realizado no Capítulo 3, de modo a comparar o método híbrido com o método clássico.

Condições industriais também foram simuladas, comparando-se com dados de conversão e seletividades obtidos da planta em operação. Novamente, obteve-se boa correlação, mostrando a eficiência do algoritmo de treinamento apresentado.

4.2. Desenvolvimento.

O desenvolvimento desse capítulo é descrito no artigo intitulado “Hybrid Training Method for Artificial Neural Networks using Genetic Algorithms: Application to Industrial Methanol Oxidation to Formaldehyde over Silver Catalyst”, apresentado a seguir, a ser submetido para publicação em periódico indexado internacional.

Hybrid Training Method for Artificial Neural Networks using Genetic Algorithms for Rate of Reaction Estimation: Application to Industrial Methanol Oxidation to Formaldehyde over Silver Catalyst

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Abstract

Genetic algorithms were used in this work as a training method for artificial neural networks, in order to calculate rate of reaction of methanol oxidation to formaldehyde over silver catalyst. The trained artificial neural network was implemented in a simulator for the formaldehyde fixed bed catalytic reactor in substitution to the rate equations. The back-propagation method for neural net training was used together with the genetic algorithms to produce refined solutions. Standard training methods, as back-propagation rely on random initial estimations and these approaches are prone to reach local minima and not the global minimum net error. Associating genetic algorithms to these standard methods, they can first perform a wide search for good solutions in the studied range of variables and provide a solution much closer to the global optimum. Standard methods, as back-propagation, can start from this point to refine the solution to the desired precision. The Neural Network was successfully trained with this hybrid approach, and simulated data confirmed this results when compared to experimental data. With the proposed procedure for obtaining the kinetic rate, more realistic predictions can be made especially near industrial operating conditions. For instance, the gas-phase decomposition of formaldehyde to carbon monoxide becomes important above 650 °C and in this region, the standard approaches failed in predicting good estimates, while the hybrid method was able to calculate correctly the selectivity in the range 600 – 700 °C.

Key words: formaldehyde, silver, artificial neural networks, genetic algorithms, artificial intelligence, methanol oxidation, kinetic modeling.

1. Introduction

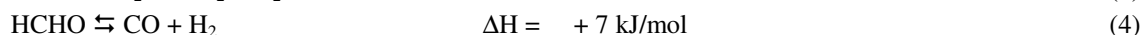
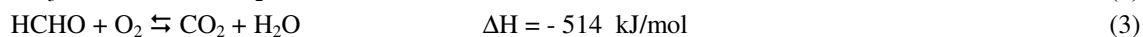
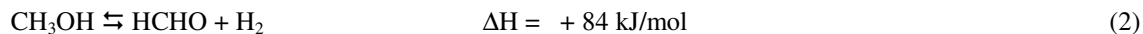
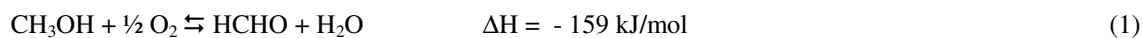
The oxidation of methanol to formaldehyde over silver catalyst is an important industrial process due to the versatility of the simplest aldehyde as an intermediate for the production of a wide variety of substances mainly for the construction and automotive sectors (Walker, 1975). Production in 2004 was estimated to be about 32 million metric tones of formalin 37% solution basis per year (ABRAF, 2004).

Two processes are commonly employed for formaldehyde manufacture, namely: the Silver process and the Formox process (Santacesaria and Morbidelli, 1981; Piccoli, 1992). In the former, methanol-rich methanol-air-stream mixture is passed through a simple silver catalyst fixed-bed at 600 – 700 °C. The Formox process differs in the nature of the catalyst (iron-molybdenum oxides), methanol concentration (oxygen-rich), bed temperature (300 – 400 °C) and bed configuration (multitubular reactor). In both processes, aqueous solutions are obtained and commercialized as final products. The silver catalyzed route accounts for approximately 30 - 50% of the current world's capacity (Van Veen et al, 2002; Qian et al., 2003; Waterhouse et al., 2004a). Its advantages are low investment cost, high yield and stable process.

The silver process is carried out on atmospheric pressure and the feed consists of a fuel-rich mixture of methanol and air. The process of formaldehyde formation consists basically in two parallel reactions: methanol oxidation (Eq.1) and methanol dehydrogenation (Eq.2), both taking place over the silver surface. The first reaction (oxidation) accounts for approximately 50-60% of the formaldehyde produced. Besides a dehydrogenation step exists, formaldehyde is only formed in the presence of oxygen, once it activates the

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catalyst. The reaction is extremely exothermic and it is carried out under adiabatic conditions. Formaldehyde may also react with oxygen over the silver catalyst, forming carbon dioxide (Eq.3) and at high temperatures, the rate of gas phase decomposition of formaldehyde (Eq.4) is significant. Reactions 3 and 4 reduce the selectivity towards the desired product.



The oxygen interaction with silver catalyst plays an important role on the mechanism of the reaction. It is supposed to be responsible for keeping the catalyst active (Bhattacharyya et al., 1971). Water plays an important role in increasing the selectivity towards the desired product. Due to the high heat capacity, water vapor removes a great deal of reaction heat, preventing detrimental overheating as well sintering of catalyst. It also cleans the catalyst surface, blocks specific surface sites and displaces the reaction mechanism reducing the formation of undesirable by products (Barteanu and Madix, 1984; Qian et al, 2003; Andreasen et al., 2003).

The silver-catalyzed process has two major variations used industrially: *Methanol Ballast Process*, where only air and pure methanol are fed to the silver bed, featuring incomplete methanol conversion and requiring a distillation recovery of the raw material; and *Water Ballast Process, or BASF Process*, where extra water is fed with the reactant mixture, and higher conversion of methanol can be achieved (98-100%) with economical selectivity towards formaldehyde (85 – 90%).

After more than a century since formaldehyde synthesis was developed, there is no full mechanistic and kinetics understanding of methanol oxidation on silver surfaces under industrial conditions (Gravilin and Popov, 1965; Bazilio et al., 1985; Ullman, 1988; Van Veen et al., 2002; Andreasen et al., 2003; Waterhouse et al., 2004b; Cao and Gavriilidis, 2005). In only a few reported studies in literature, attention has been paid to the way that by-products are formed. No single study covers the influence of temperature, methanol and oxygen concentrations and residence time under near industrial conditions (temperature: 600 – 700 °C; methanol/oxygen molar ratio: 2.3 – 3.0 and water/methanol molar ratio: 0.15 – 0.75). Because of differences in the catalysts and operational conditions used in the various studies, it is not clear how the process takes place (Lefferts et al., 1986; Andreasen et al., 2003). Lack of good quality kinetic experiments is also caused by difficulties in avoiding mass transfer limitations, hot-spots, deactivation and aging of silver catalyst in conventional reactors (Cao and Gavriilidis, 2005).

Considering the potential market demand for formaldehyde and strong competition, economic incentives do exist to improve the selectivity of the process (Van Veen et al., 2002): methanol cost represents more than 80% of the production cost of formaldehyde and an improvement of 1 percentage point on the selectivity in an average size plant means saving about 200,000 US\$ per year on methanol purchasing. This is certainly one of the reasons that quite some research work is devoted to this system (Qian et al., 2003; Andreasen et al., 2005), including experimental work and development of reactor simulators. Environmental pressure is also a driver to optimize this process, once the carbon emissions generated by formaldehyde plants (carbon dioxide and carbon monoxide) will have to be reduced soon in order to comply with world's efforts against global warming.

Many articles explore kinetic models for this process but they are not complete and fail in simulating some actual industrial conditions. The development of new models is costly, time consuming and they are not the focus of industrial personnel. Any attempt to obtain kinetic models applied to industrial conditions in a timely fashion would be a powerful tool for understanding and optimizing this process. In these cases, novel approaches like neural networks are efficient for predicting the rate of reaction, based on available data.

Artificial Neural Networks (ANNs) are widely used for simulation of situations where deterministic models are not available or fail in fitting the data (Psychogios and Ungar, 1992). ANN were initially developed as models for organic brain and they have been successfully used as a complex mathematical model to solve problems in different study areas (Papes Filho, 2001). The ANN model is easily implemented in computing codes, with powerful capacity to manage problems with multiple outputs and multiple inputs (MIMO system). The model is known to be generic and can be used for a variety of problems with minor adaptations (Lennox et al., 2001). A regression model is not necessary, once the ANN itself is the model, which uses less parameters than polynomial regression and tolerates hardware failures or data noise.

The ANN learn the data pattern using an algorithm known as “training”, where many data rows [input/output] are presented to the net until it fits the data. Mathematically, it “learns” from data set, adjusting its internal parameters until the error between predicted output and experimental output is minimized. The net is able to learn the data pattern and store the knowledge into its internal parameters (known as “weights”), as a memory. This is the reason why ANN is considered part of the Artificial Intelligence field (Wasserman, 1989; Davis, 1991; Pham and Pham, 1999; Papes Filho and Maciel Filho, 2005).

The back-propagation (BP) is the most used method for training an ANN in chemical engineering applications. It uses the error of the output neurons (between calculated and experimental outputs) to calculate the adjustment of the weights on the previous network layer. The error is then back-propagated to the preceding layers until all weights are adjusted. The process is repeated until the net error is minimized. For the first iteration, the set of weights is chosen randomly.

Normally a huge number of weights is involved in an ANN and it is not practical to study the curve of the net error as a function of the weights to analyze if the achieved minimum error is indeed the optimum point (global minimum) or if the algorithm was trapped into a local minima. Once the BP is a gradient-driven type of algorithm, the quality of the solution will heavily depend on the initial estimate, but as it is random, there is no guarantee that it will be a good one.

The Genetic Algorithms (GA) have been successfully used to solve optimization problems involving multiple parameters, where many local optima may exist and there is a need to perform a wide search throughout the variables range in order to achieve the global optimum.

Genetic algorithm, firstly published in Holland’s (1975) monograph, is a mathematical method to solve problems, based on the mechanics of natural selection and natural genetics, combining an artificial survival of the fittest with genetic operators abstracted from nature (Holland, 1976; Wang, 1997). Its advantages are (Goldberg, 1989; Garrard and Fraga, 1998):

- They perform a global search and are less likely to converge to a local optima;
- They search from a population of points and not from a single point;
- No need to calculate derivatives;
- The objective function may be a black box and no derivative information is required;
- Every iteration presents a better estimative of the solution and multiple solutions may be found;
- They are theoretically and empirically proven to provide a robust search in complex spaces.

GA simulates the evolutionary process and has demonstrated ability to solve complex problems that other classical numerical methods were not able to handle (Goldberg, 1989; Pham and Pham, 1999). This is an iterative methodology, where the starting point is a set of random solutions (initial population or first generation). All of the solutions are evaluated and ranked according to specified criteria (objective or target function). The best solutions will be kept for reproduction and the worse solutions will be deleted (extinction).

In this work, a GA was used together with BP algorithm on ANN training. The training session starts with GA, which performs a global search on the net weights range, refining an initial random set of weights to obtain a better estimative, more probable to be close to the global optimum. The BP algorithm then assumes the training, refining the solution provided by GA to reach the optimum solution. GA can do the entire task

alone, but as it is time consuming, the best benefit may be obtained by using both algorithms associated. The training process is seen as an optimization problem, where the net error is minimized.

The ANN was trained using rate of reaction data for the methanol oxidation to formaldehyde with silver catalyst. The kinetic data were not available for the ANN training and they had to be extracted from process data according to the procedure described by Papes Filho (2007): a simplified kinetic model was implemented into the reactor simulator and, for each process point, the model parameters were adjusted until the conversion and selectivity calculated by the simulator matched the experimental ones. Once the individual point was fit, the rate of reaction profile through the catalytic bed was saved with the associated local operational conditions. The adjustment on the simplified kinetic model was only valid for a single data point, but after repeating the procedure for all available experimental points, a huge set of rate of reaction data may be obtained (Papes Filho and Maciel Filho, 2007a). Once trained with extracted rate of reaction data, the ANN weights were stored in a data file.

The trained ANN was included in a reactor simulator to calculate the rate of reaction. The hybrid model (simulator + ANN) was used to simulate many cases with successful results, proven to be an effective tool for the simulation of this process. Results obtained with a standard ANN training (only BP) were compared to the new approach (GA + BP), showing the advantages of the last one.

2. Methods

2.1. Formaldehyde reactor simulator

A hybrid simulator was developed by the authors to model the formaldehyde silver reactor, using deterministic equations for the fixed-bed and ANN to calculate the rate of reaction. The simulator was used in this work to validate the ANN training with experimental process data.

The formaldehyde fixed-bed reactor was simulated based on mass balance (Eq 5), derived from the equation of continuity (Welty, 1984) for the bidimensional flow on cylindrical coordinates, considering plug-flow tubular model, molecular diffusion and steady-state operation (Treybal, 1981; Fogler, 1992). Calculations and industrial observations indicated that, for practical ends, the reactor (fixed-bed) operates isothermally and adiabatically (Nagy et al., 1998; Nagy and Mestl, 1999; Papes Filho, 2007; Papes Filho and Maciel, 2007b). Figure 1 shows a scheme of a typical silver reactor.

$$D_L \cdot \frac{\partial^2 C}{\partial z^2} + D_R \cdot \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial C}{\partial r} \right) - V_z \cdot \frac{\partial C}{\partial z} + \nu_A \cdot R_V = 0 \quad (5)$$

where: “C” is the substance concentration (kg/m³); “r” is the distance from the reactor central line – radius on cylindrical coordinates (m); “z” is the distance from the reactor inlet – axial distance on cylindrical coordinates (m); “D_L” is the axial diffusion coefficient (m²/s); “D_R” is the radial diffusion coefficient (m²/s); “V_z” is the axial velocity (m/s); “ν_A” is the stoichiometric coefficient for the studied substance (dimensionless) and “R_V” is the rate of the reaction per reaction volume (kg/m³.s).

The mass balance differential equation was solved numerically using the Crank-Nicholson algorithm, described in literature (Crank and Nicholson, 1947; Press et al., 1992), a semi-implicit method known to be intrinsically stable. The physical properties of pure substances and mixtures were calculated (Reid et al., 1987) at each step of Crank-Nicholson method, according to the actual local conditions, as a function of temperature and pressure.

The simulator contains a sub-routine with the ANN algorithm to calculate the rate for the three reactions of interest in this process: formaldehyde formation (Eqs 1 and 2), oxidation (Eq 3) and gas-phase decomposition (Eq. 4), using the trained weights stored in a data file. For every step of the numerical method, the simulator provides to the ANN the local conditions (temperature and partial pressures) and it calculates the rates for the three reactions, which return to the simulator in order to predict the conditions for the next step.

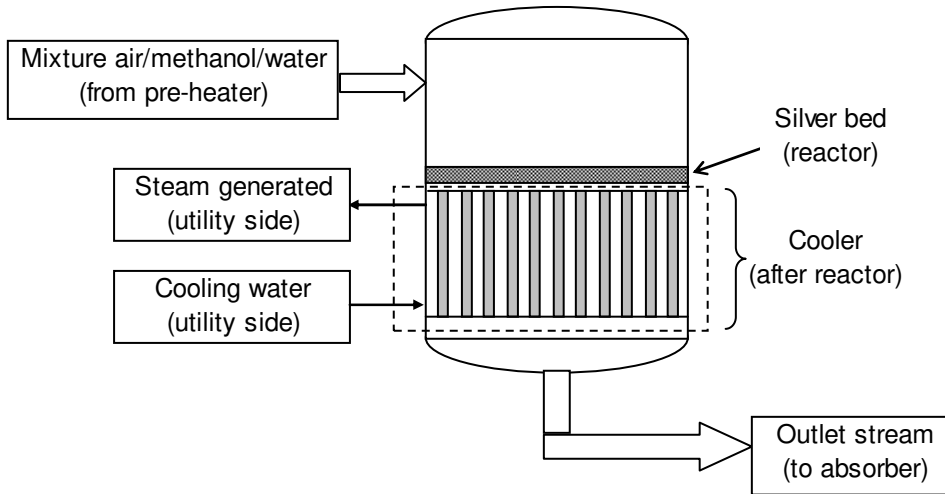


Figure 1: Scheme of a typical silver reactor, showing the fixed-bed, where reaction takes place, and the downstream cooler.

2.2. Artificial Neural Networks

An ANN calculates simultaneously the rate for the three reactions of interest, implemented as a sub-routine inside the reactor simulator. A neural network with three layers and bias neurons was used in this work, as described in Figure 2.

The inputs to the network are bed temperature (K); total pressure (atm); partial pressures of methanol, oxygen, water, hydrogen, formaldehyde, carbon dioxide and carbon monoxide, as well as the bias neuron (input = 1). The number of neurons at hidden layer was varied to obtain the optimum configuration. A bias neuron connected to “1” was included to this layer.

Three neurons compose the output layer, calculating the rate of the 3 reactions of interest simultaneously:

- The rate of methanol oxidation (r_{HCHO}), $\text{kmol/m}^3\cdot\text{h}$

$$2 \text{CH}_3\text{OH} + \frac{1}{2} \text{O}_2 \rightleftharpoons 2 \text{HCHO} + \text{H}_2 + \text{H}_2\text{O} \quad (6)$$

- The rate of formaldehyde oxidation (r_{CO_2}), $\text{kmol/m}^3\cdot\text{h}$

$$\text{HCHO} + \text{O}_2 \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} \quad (7)$$

- The rate of gas phase decomposition of formaldehyde (r_{CO}), $\text{kmol/m}^3\cdot\text{h}$

$$\text{HCHO} \rightleftharpoons \text{H}_2 + \text{CO} \quad (8)$$

Each virtual neuron of the ANN performs a calculation using the values provided by the neurons connected upstream, producing an output value transmitted to the neurons downstream. Equation 9 shows the calculation, where “ x_j^s ” is the value from the neuron “j” at layer “s”, “ w_{ji}^s ” is the weight associated to link between the neuron “j” at layer “s” and the neuron “i” at layer “s-1” and “ x_i^{s-1} ” is the value from the neuron “i” at layer “s-1”

$$x_j^s = f\left(\sum_i (w_{ji}^s \cdot x_i^{s-1})\right) = f(I_j) \quad (9)$$

The neuron output value is not simply an averaged sum of the input values, once the function “f” transforms the result. It is known as transfer function, typically a sigmoid, as in Eq.10.

$$f(I_j) = \frac{1}{1 + \exp(-I_j)} \quad (10)$$

The ANN training was performed using an association of genetic algorithms with classical back-propagation.

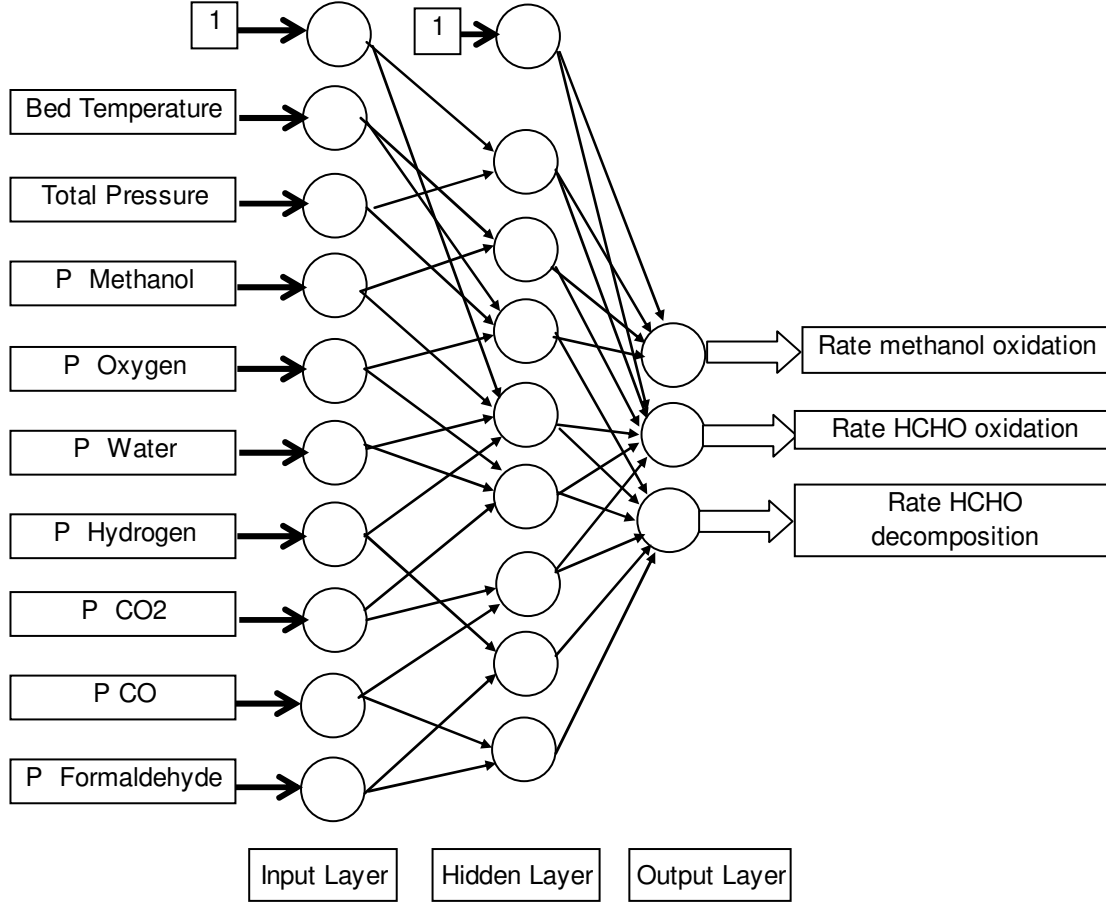


Figure 2: Schematic of the ANN used (not all arrows were drawn, in order to make the picture clear)

Back-propagation algorithm is the most used training method for engineering problems. It calculates the adjustment to be done for each weight, based on the difference between the experimental output (d_m) and the calculated output (o_m), according to the global error function E_n associated to the neuron “n” of the output layer (Eq.11).

$$E_n = 0.5 \cdot \sum_{m=1}^N ((d_m - o_m)^2) \quad (11)$$

The local error of each neuron at output layer is calculated by Eq.12 and the error is back-propagated to the previous layers by Eq.13.

$$e_n^{out} = (d_m - o_m) \cdot o_m \cdot (1 - o_m) \quad (12)$$

$$e_j^s = x_j^s \cdot (1 - x_j^s) \cdot \sum_k (e_k^{s+1} \cdot w_{kj}^{s+1}) \quad (13)$$

Where, “ e_n^{out} ” is the local error of neuron “n” of the output layer and “ e_j^s ” is the local error of neuron “j” of layer “s”. The weights are adjusted based on the local error, according to Eq.14.

$$w_{ji}^{new} = w_{ji}^{old} + \alpha \cdot e_j^s \cdot x_i^{s-1} \quad (14)$$

Where α is the learning coefficient, usually ranging between 0.01 and 1.0, typically set as 0.5.

The total error of the ANN, for comparison reasons, may be calculated by Eq.15, considering the studied ANN with 3 output neurons, trained with a set of “N” data-pairs.

$$E_{\text{TOT}} = \frac{1}{N} \cdot \sum_{k=1}^3 \left(\sum_{m=1}^N \left((d_{m,k} - o_{m,k})^2 \right) \right) \quad (15)$$

Details about the neural network algorithm calculations and training process may be found in Rumelhart et al. (1986), Wasserman (1989) and Bhagat (1990).

2.3. Genetic Algorithms

Genetic Algorithm (GA) is a search method based on natural evolution. The solutions are not calculated, but the best ones are encouraged to survive generation after generation, while new solutions are created by a mixture of the best solutions of previous generation. The method is repeated for a certain number of cycles or until a certain precision is achieved.

GA deals with a population of possible solutions (or individuals), that are evaluated every generation. Normally population size is constant throughout generations, differently than nature. There is no particular reason to keep the population size constant, just simplicity. It must be optimized, keeping the balance between precision and computing time at an optimum level. In large populations, the probability of finding a better individual in small number of generations is higher, but computing time will be larger. Some authors report methodologies for population size calculations, but in practice it is set as large as computing time allows (Goldberg et al., 1992; Carrol, 1996a; Carrol, 1996b).

The possible solutions (individuals of the population) are represented by chromosomes. They are mathematically a vector with the parameters of the studied model. As an example, if a 4th order polynomial is used as a model; the chromosomes would contain 5 genes, as the model has 5 parameters. In the case of an ANN, the chromosome will contain the weights. Each weight is named a gene and a single chromosome will have as much genes as the weights of the studied ANN.

When the model has small number of parameters (less than 3, arbitrarily), the operations with the chromosomes loses its meaning, as will be explained below. In these cases, each gene should not be represented by the value of the parameter, but as a binary representation (Goldberg, 1989; Davis, 1991). Depending on the precision of the study, a single parameter may be written as a sequence of “0” and “1”, the way that the chromosome has many more genes than the number of parameters. With this approach, the crossover operations are much more meaningful.

As the ANN generally contains much more parameters than 3, there is no need to use the binary representation, and each gene of the chromosomes is the real value of the parameters or weights (real code).

Each iteration of the GA is called a generation. The initial generation is normally formed by a set of a defined number of chromosomes whose values are chosen randomly. This initial set of random solutions is evaluated, using a model according to the studied problem. The evaluation of the individuals (solutions) is an important operation of the GA, once it is necessary to rank the solutions to identify the fittest individuals, which will survive and procreate.

When GA is used for data fit, a model has to be chosen to represent a defined set of input-output experimental values. In this work, the ANN was used as a model, and the set of input-output experimental data comprises the ANN input-output variables, as stated on the preceding section. The best chromosomes will contain the best ANN weights that allow obtaining rate of reaction values closer to experimental measurements, for a specific process condition. In this sense, the objective function of the GA will be the net error (E), the sum of

the squares of the differences between the rates calculated by the ANN (o_m) and the experimental rates (d_m) for the three reactions and all “N” data points of the available set.

$$E = \frac{1}{N} \cdot \sum_{i=1}^N \left(\sum_{m=1}^3 ((d_m - o_m)^2) \right) \quad (16)$$

After evaluating the individuals of the first generation (lower E), the best solutions (parents) are mixed to generate the new individuals (children). The next generation of individuals is composed by children of the individuals from the previous generation. The parents (best solution of a generation) may or may not be maintained in the new generation. Usually, they are maintained in order to prevent losing this good solution in case of the children are less able than the parents (elitism). There are two ways to select the parents:

- *Selection of best individuals*

In this case, the best individuals of a generation are selected to be the parents of the new generation. The best individuals are the ones with better objective-function value. The number of parents in each generation may be fixed by user (generally the number of parents is adjusted to obtain better GA performance) or a limit may be defined (the selected parents are the ones with objective value better than certain limit). The selected individuals are grouped in pairs to generate children. The pairing method may vary: priority to the best individuals or random pairing.

- *Tournament*

Two pairs are randomly chosen. The best individual of each pair is selected and the two selected individuals generate a child. Two new pairs are chosen and the process is repeated until the new generation is completed.

Children are created from the mixture of the parents’ chromosomes. Initially the pair of parents is selected and then the child chromosome is created by the following procedures:

- *Single-point crossover*

The chromosome from one of the parents is copied to the child (e.g.: “abcde”). If the chromosome of the second parent is “ABCDE”, a random point of it is selected as cross-over point, as an example, between genes “C” and “D”. Then, part of the second parent’s chromosome is copied over the chromosome of the child and the result is “abcDE”.

- *Uniform crossover (Syswerda, 1989)*

A combination of any order with the parents’ chromosomes, as: “aBcDe” or “AbcdE” or “abCDe”.

- *Single or Uniform crossover?*

Researchers give probabilities for each case (uniform or single), distributing children formation through the two methods. Carrol (1996a) defined equal probabilities for the two methods.

The number of children per pair is a relatively new question on GA community. Generally, researchers use one child per parents’ pair. Some papers (Carrol, 1996a) point out better results with 2 children per pair. One important feature of single crossover is that it can produce children that are radically different from its parents. Another important feature is that it will not introduce differences for a gene in a position where both parents have the same value for the gene.

Crossover is an extremely important component of a genetic algorithm. Many researchers believe that if we exclude the crossover operator from a GA the result is no longer a GA and performance is degraded on a variety of problems. This claim has not been made for mutation operators (Davis, 1991). As in nature, a mutation on a gene of some children may occur. It is simulated in two ways:

- *Creep Mutation*

One gene (parameter) of an individual “just-born” may be slightly changed. In other words, a child with a chromosome “abCdE” may mutate to a chromosome “abCdF”, where “F” is not a gene from any of the two parents, but is similar.

- *Jump mutation*

The same case, but mutation is bigger. An individual with a chromosome “abCdE” may mutate to “abCdP”, where “P” is a gene very different from the parents’. A few new individuals may be completely random, simulating a big mutation on all genes.

- *Jump or Creep mutation?*

The probability for each type of mutation is defined by user. Usually, the probability for Creep mutation is “1/p” and the probability for Jump mutation is “2/p”, where “p” is population size (Carrol, 1996a).

Mutation may occur in one or more genes of the individual. The probability of mutation for each gene is the same.

Using the crossover and mutation operators, the new generation of individuals is composed by children, whose chromosomes were formed by the mating of the parents’ chromosomes. Part of the individuals of the new generation may be formed randomly. All individuals are evaluated again and a ranked, in order to select the fittest to pair for the next generation.

The main goal of the GA operators (crossover and mutation) is to keep the variability of the population, preventing the algorithm to converge to one solution. If all individuals of the population are much similar one to another, the algorithm will lose its power to find a better solution. GA algorithm may be run for a defined number of generations or until a certain error “E” is achieved. The best solution from GA, in this case, is the best set of weights that allows the ANN to fit better the experimental data. The GA used in this work was written in Fortran code, developed by the authors.

2.4. Training

GA is very useful for performing a global search throughout the full range of the parameters, increasing the probability of reaching a global minimum error (E) and not local minima. On the other hand, the method is time consuming and refining the solution for the desired precision may not be practical. In this sense, GA may be combined to back-propagation, running the GA for a reasonable number of generations and using the best solution provided by GA as the initial estimative for the BP.

After some GA generations (iterations), the ANN error, as in Eq.5, decreases slowly and when BP assumes the training, the error is quickly reduced to smaller levels. When BP converges to a minimum error, within desired precision, the optimum set of weights is stored in a data file and the ANN is then able to predict new outputs. Running with the reactor simulator, the local conditions at every step of the simulation are calculated and fed to the ANN, which generates the rate of the three reactions, using the trained weights stored in the data file. The rates return to the simulator, which calculates the advancement of the reactions and the new conditions at the next simulation step. Figure 3 shows a flow diagram with the complete procedure.

3. Results and Discussion

The procedure for training the ANN based on an association of GA and BP was used on experimental data extracted from process information obtained on literature (Waterhouse et al., 2004b) and industry. The hybrid simulator, with deterministic model for the catalytic fixed-bed and ANN for calculating the rate of reactions, was used to estimate conversion and selectivity for desired conditions, comparing simulated values to the experimental ones, for validation purposes.

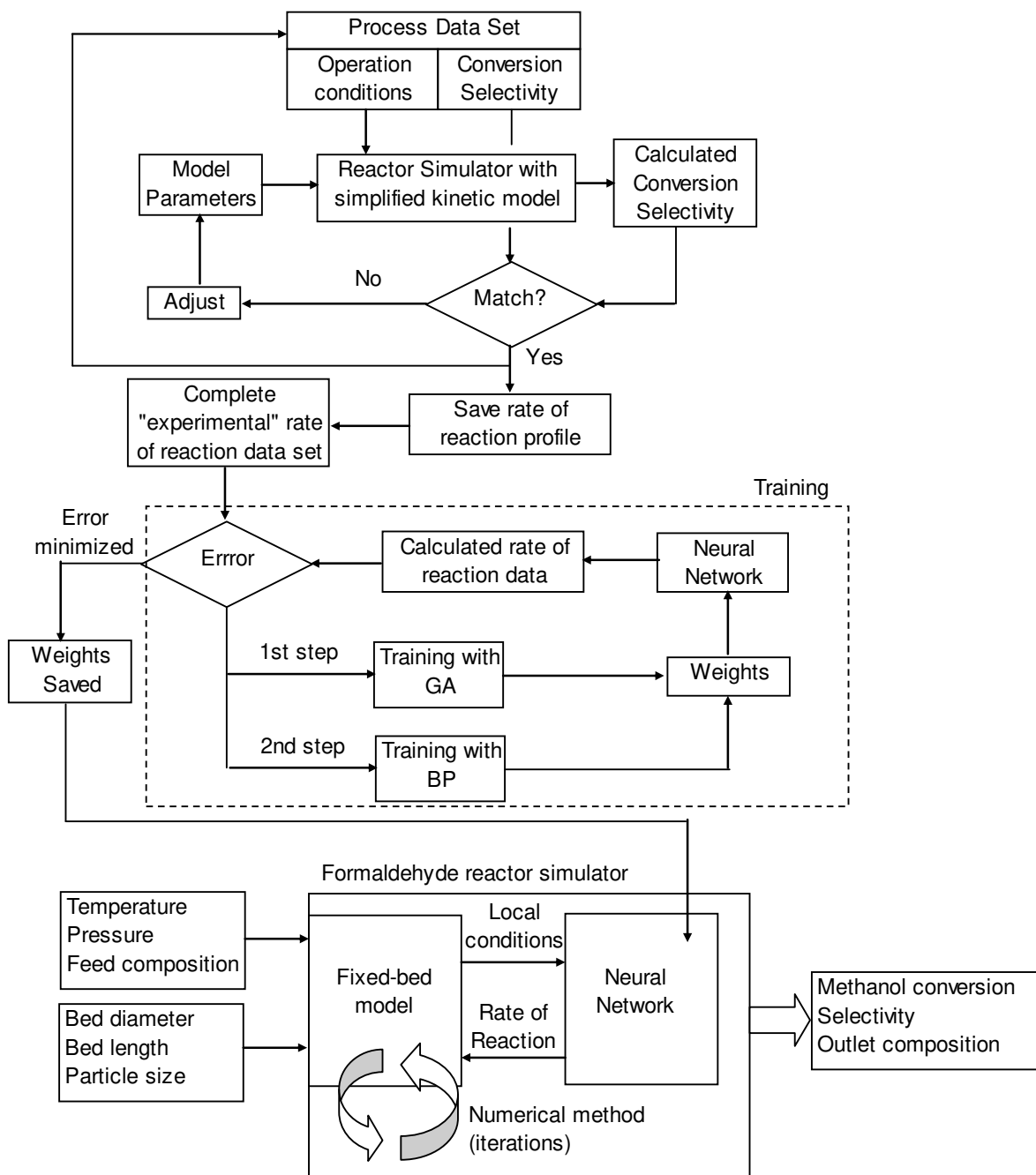


Figure 3: Flow diagram with the complete procedure

3.1. ANN training with literature data

Waterhouse and al. (2004b) performed experimental work with a fixed-bed microreactor, filled with silver catalyst, using water at feed (Water Ballast Process). They ran experiments with molar feed composition $\text{CH}_3\text{OH}/\text{O}_2/\text{H}_2\text{O}/\text{He}$ of 2.25/1.00/1.70/20.00, total pressure of 1.1 atm and space velocity of $1.25 \cdot 10^5 \text{ h}^{-1}$, varying the bed temperature.

A set of 670 data points that correlate rate of reaction with local temperature and partial pressures of the reactants were extracted from Waterhouse's study and used for the ANN training. Table 1 brings a sample of the data used on ANN training.

The training session begins with GA as the algorithm to adjust the ANN weights. It develops as follows:

- Initial population is chosen randomly: each individual of the first generation is characterized by a random set of ANN weights;
- Every individual of the population was evaluated: the ANN was run for all “N” experimental inputs, calculating the outputs, using the weights associated to each individual. The calculated outputs were compared to the experimental rates, according to Eq. 5.
- The individuals of the population were ranked according to the lower “E” (error) values.
- The lowest “E” value of the population (best individual) was copied to the next generation (elitism).
- The best parents were chosen to generate the children, using the crossover operators described above.
- If necessary, the next generation is completed with entire random individuals.
- The same procedure is repeated for the second generation and the algorithm is run for a defined number of cycles. The final set of weights (chromosome of the best individual of the last generation) is saved in a data file.

Table 1: Sample of the rate of reaction set of data

Rate of reaction (kmol/m ³ .h)			Process conditions – partial pressures (atm)						
R _{HCHO}	R _{CO₂}	r _{CO}	MeOH	O ₂	H ₂ O	HCHO	CO ₂	H ₂	CO
5.9715E+02	4.2389E+01	4.8627E+02	4.09E-02	2.44E-02	7.87E-02	2.47E-02	1.90E-03	3.27E-02	1.17E-02
4.6233E+02	1.6475E+01	2.1465E-01	6.36E-02	3.13E-02	7.00E-02	1.73E-02	3.79E-04	9.22E-03	2.88E-06
1.5812E+02	1.9595E+01	1.0479E+00	2.66E-02	2.04E-02	8.59E-02	4.98E-02	2.83E-03	2.93E-02	8.85E-05
5.9728E+01	1.7348E+01	1.4351E+00	1.12E-02	1.50E-02	9.25E-02	6.14E-02	5.50E-03	3.94E-02	2.73E-04
6.6853E+01	1.4969E+01	1.3753E+01	8.90E-03	1.52E-02	9.33E-02	6.33E-02	3.82E-03	4.06E-02	2.16E-03
5.7087E+01	1.7234E+01	1.4452E+00	1.07E-02	1.48E-02	9.26E-02	6.17E-02	5.63E-03	3.97E-02	2.83E-04
2.3453E+02	1.7311E+01	9.5235E+00	2.76E-02	2.12E-02	8.55E-02	4.95E-02	1.66E-03	2.81E-02	5.38E-04
2.3148E+01	1.1270E+01	7.4406E+01	2.61E-03	1.27E-02	9.43E-02	4.76E-02	5.10E-03	6.31E-02	2.11E-02
8.6629E+01	2.1837E+01	4.7030E-02	2.09E-02	1.74E-02	8.83E-02	5.21E-02	5.85E-03	3.49E-02	7.30E-06
2.6341E+02	2.4674E+01	5.3329E-05	7.27E-02	3.35E-02	6.60E-02	8.60E-03	5.53E-04	5.13E-03	6.96E-10

The GA features used in this work were:

- Population size: 50 to 150 (typical: 100)
- Parents selection: best 20 individuals
- Number of cycles: 1,000 to 5,000 (typical: 3,000)
- Chromosome code: real
- Single-point crossover probability: 50%
- Uniform crossover probability: 50%
- Creep mutation probability: 6.6 %
- Severity of creep mutation: ± 10 % of gene value
- Jump mutation probability: 3.4 %
- Severity of jump mutation: ± 80 % of gene value

Population size and the number of cycles were studied to find the best combination in order to favour the appearance of new solutions throughout the generations, with comfortable computing times. The best population size in the cases studied here was found to be 100, considering 3,000 generations.

The best 20 individuals of a generation were selected to be the parents for the new generation. If this number is small and the best individuals of a generation are much similar one to the other, the crossover operator will be less likely to improve the solution and the algorithm will count on the chance of a successful mutation to occur in order to produce a better solution. In this case, it may be increased to include in the parents set other individuals that are not so good, but add variability to enhance the crossover operator. In our studies, the parents set was started with 20% of the population size, arbitrarily, and it was increased only if necessary. In the study presented here, the algorithm developed accordingly with 20 individuals on the parents set.

The single-point crossover probability was set equal to the uniform crossover probability, according to the studies of Carrol (1996a). The jump mutation probability was set as half of the creep mutation probability (Carrol, 1996a), starting with an approximate probability of “1/n” (“n” is the population size) and increasing

this value if the algorithm takes too many generations to produce a better individual. In this study, the jump mutation probability was increased to 3.4% to achieve a good algorithm performance.

In the case of a mutation, the gene values were changed by the percentages stated above ($\pm 10\%$ and $\pm 80\%$). These values were defined as default after several GA studies performed by the authors with different applications.

After finishing the GA training (training time of 1 hour, Pentium-4, 2.66 GHz, 480MB RAM), the BP algorithm starts from the solution of GA stored in the data file. The BP continues according to the classical method, reducing the error “E” until it lies below a certain limit established by the user. When the training is finished, the final set of weights is stored in a data file and the ANN is used to calculate the rate values for a new set of data (validation).

Figure 4 shows the error of the ANN throughout the generations for GA and BP training, expressed as the ratio error/tolerance. The error drops dramatically through the first four generations, starting from a completely random set of solutions to an estimate approximately four times more precise. Until iteration 900, the error continues to decrease fast, and from iteration 900 to 3,000, it decreases slowly. Figure 5 brings a zoom on GA training error graph, from iteration 100 to iteration 3,000, where it is possible to see that sometimes the error does not decrease for generations (generation 900 to 1250, for example), once there is no better solution than the best individual of last generation (parent is more able than the children). When BP assumes, the error drops dramatically again for 1,000 iterations and in a fast fashion for more 5,000 iterations (as shown on Figure 4), then it goes down slowly through the further iterations (Figure 4 show only the error after 37,000 BP iterations).

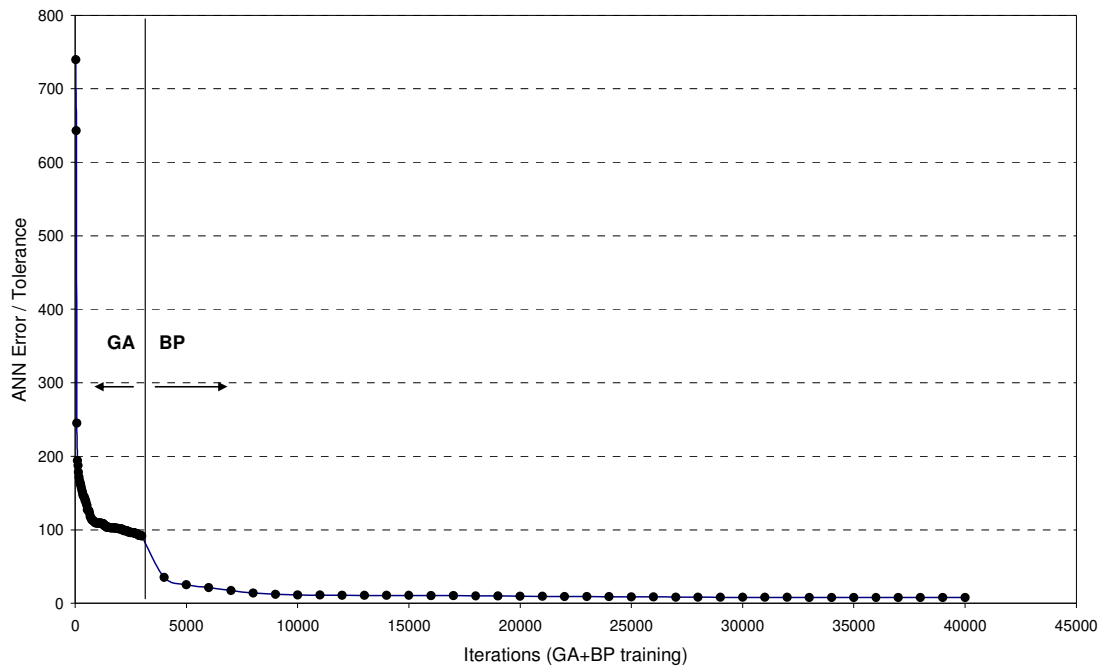


Figure 4: Error of the ANN through the training with genetic algorithm and back-propagation

As the generations of GA advance, it takes more and more iterations to find out a solution that is better than the best from last generation. The differences between best-of-generation individuals become smaller and the algorithm takes more generations to find out a new best individual: the crossover operator exhausts the possibilities to improve the solution and the algorithm depends on the luck of mutation operator to find the correct gene change to result in a better solution. When BP assumes, it starts from a point much closer to the optimum (lowest error) than a random initial estimate, but there is still room to improve the convergence of the solution: using high derivatives, the BP advances faster towards the minimum error in the first iterations. While the error approaches the minimum, the advancement of BP slows down and it takes more and more iterations to reduce the net error (in this case, more than 1,500,000 iterations to achieve a desired ANN error).

The BP training step exposed here was run for more iterations than necessary for didactic purposes. In practice, after iteration 20,000 very small reduction of net error is seen and the training could have been stopped. When using BP, the user must pay attention to the evolution of net error, in order to avoid unnecessary training iterations.

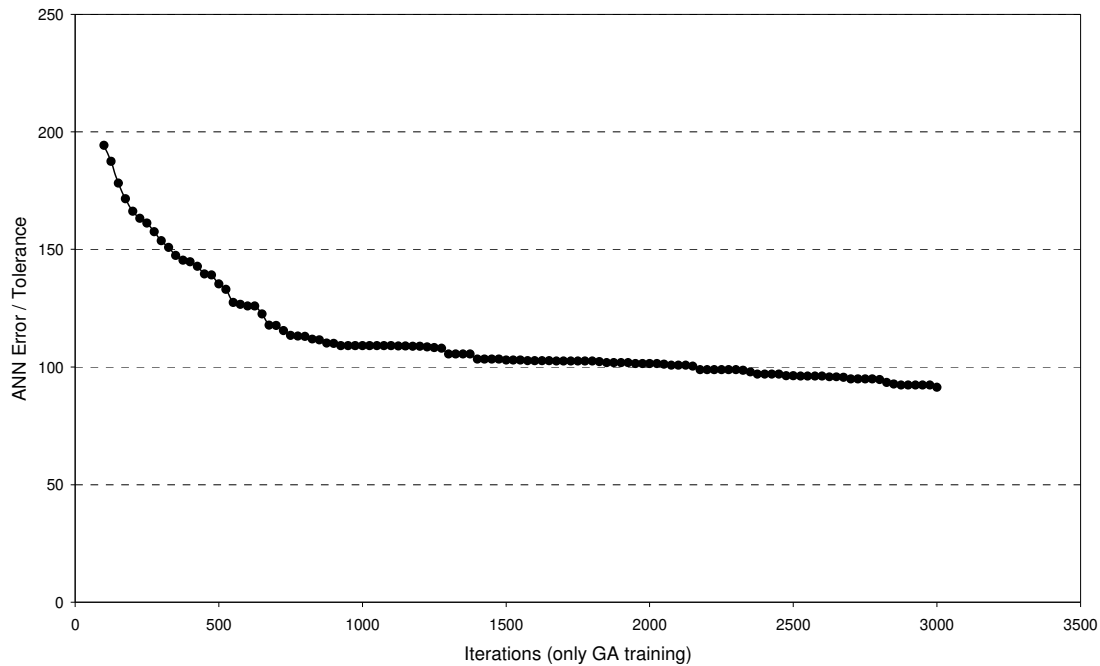


Figure 5: Error of the ANN through the generations of the genetic algorithm

After training the ANN, it was used to calculate new rates for “ r_{HCHO} ”, “ r_{CO_2} ” and “ r_{CO} ”, as a validation step. The calculated rates were compared to the experimental ones (formation, oxidation and gas-phase decomposition of formaldehyde, respectively). The results were shown on Figures 6, 7 and 8, where the rate of reaction calculated by the ANN was plotted against the experimental values extracted from Waterhouse et al. (2004b), both normalized between 0 and 1, for the three reactions stated above. High correlation coefficients (> 0.99) were obtained and calculated points concentrated along $x = y$ line, as shown on the graphs, indicating that the neural network could successfully fit the experimental data simultaneously for the three rates, based on the input data. The good fit was confirmed through the “F” test, expressed in Eq.17, where SQM is the sum of the squares of the model and SQR is the sum of squares of the residual (Box and Hunter, 1978).

$$F_{\text{CALC}} = \frac{SQM}{SQR} \quad (17)$$

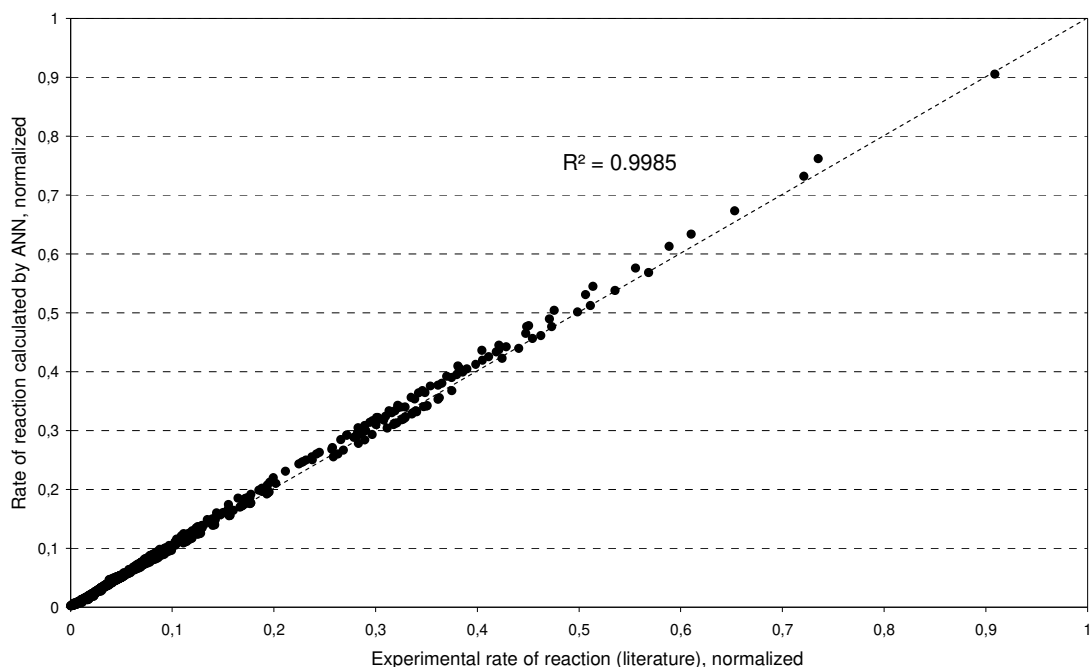


Figure 6: Correlation between experimental rate of reaction extracted from process data of Waterhouse et al. (x-axis) and rates calculated by the ANN (y-axis) for the formaldehyde formation reaction (Eq.1 + Eq.2).

The number of neurons at hidden layer was studied, observing the correlation between the calculated rates and experimental rates (correlation coefficient, r^2), as shown on Table 2. On the range 10 to 13 neurons at hidden layer, it is clear that better fit is obtained with 12 neurons. With 13 neurons at hidden layer, we observed that the net loses its generalization ability and the ANN could not properly calculate the selectivity for all studied range.

The training statistics for 12 neurons at hidden layer are:

Training time:	5 hours (Pentium-4, 2.66 GHz, 480MB RAM).
Iterations:	1,677,943
Sum of squares of the model:	127.0
Sum of squares of residue:	0.26
F-value:	489

The F-test demonstrates how well the model could fit the experimental data. The calculated number 489 is overwhelmingly significant when compared to the F-distribution (Box and Hunter, 1978), demonstrating the success of the ANN model to fit the experimental rates.

The process conditions reported by Waterhouse et al. were then estimated using the reactor simulator equipped with the trained ANN. Figures 9, 10 and 11 show Waterhouse's (2004b) experimental points, the results of simulations with the ANN trained by GA+BP, together with the results of previous simulations where the ANN was trained only by BP (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007a).

Simulations with ANN trained by the hybrid approach produced excellent results when compared to the traditional training algorithm (back-propagation), with simulations closer to the experimental points. Figure 9 shows the experimental points for selectivity towards formaldehyde (Waterhouse et al., 2004b) together with the simulations using the ANN trained with GA+BP and classical BP training. It is clear that the hybrid algorithm could produce simulations much closer to the experimental points principally on the range of 600 – 700 °C, where most industrial plants are operated. This improvement on selectivity estimate precision with the hybrid approach allows proper optimization of the plant, once it shows the selectivity decrease above 625 °C, while the standard approach makes the simulator foresee incorrect good selectivity up to 670 °C.

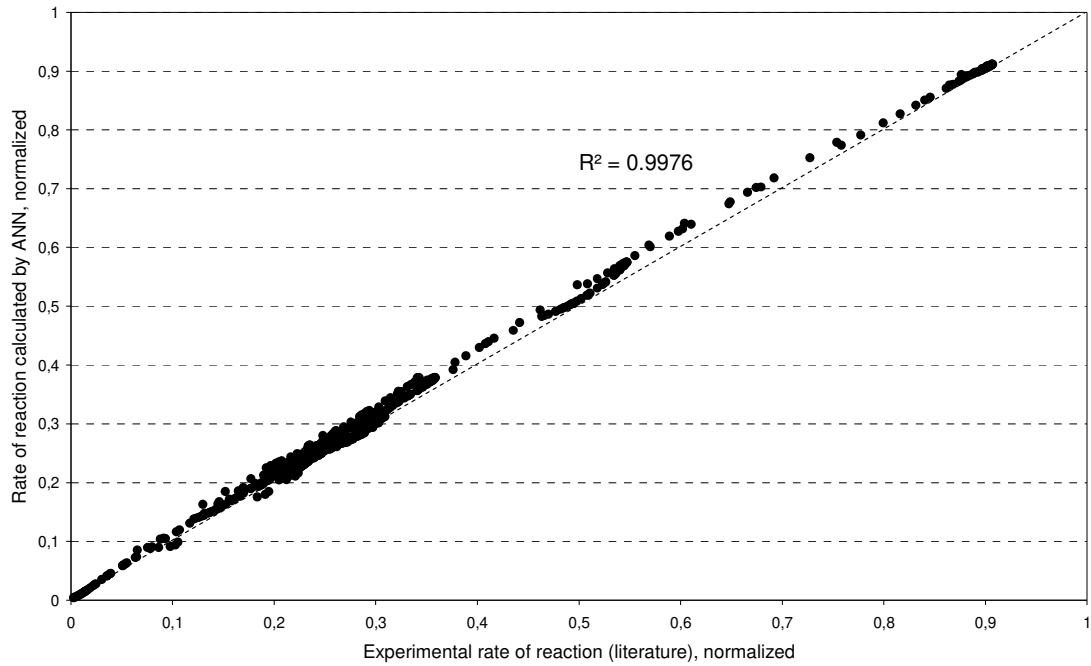


Figure 7: Correlation between experimental rate of reaction extracted from process data of Waterhouse et al. (x-axis) for the formaldehyde oxidation reaction (Eq.3).

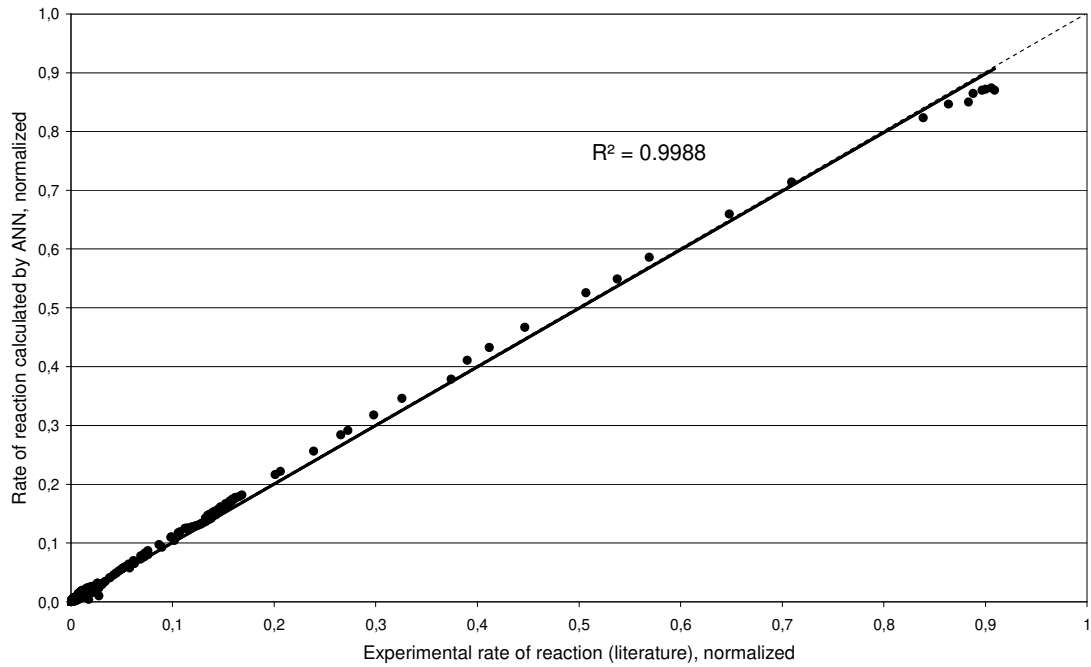


Figure 8: Correlation between experimental rate of reaction extracted from process data of Waterhouse et al. (x-axis) for the formaldehyde gas phase decomposition reaction (Eq.4).

Some deviation from experimental points for formaldehyde selectivity is still observed with the hybrid approach in the range 700 – 730 °C, above industrial operation range, with small impact on practical use of the simulator.

Table 2: Study of the number of neurons on hidden layer.

# neurons Hidden	$r^2 - r_{HCHO}$	$r^2 - r_{CO2}$	$r^2 - r_{CO}$
10	0.9977	0.9831	0.9978
11	0.9985	0.9962	0.9989
12	0.9985	0.9976	0.9988
13	0.9987	0.9965	0.9988

Figure 10 brings the experimental points for the selectivity towards carbon dioxide together with the simulations. The hybrid approach could produce estimates in the range 400 – 500 °C closer to the experimental points, when compared to the classical BP approach. Principally, it was able to predict estimates equal to experimental points in the industrial operational range (600 – 700 °C), while the standard approach shows deviations towards lower selectivity. This behaviour reflects the better estimate for the formaldehyde selectivity in the same range.

The same behaviour is seen on Figure 11, where the experimental points for the selectivity towards carbon monoxide were plotted against the predicted by simulations. The gas-phase decomposition of formaldehyde to carbon monoxide becomes important above 650 °C and in this region, the standard BP approach failed in predicting good estimates, while the hybrid method was able to calculate correctly the selectivity in the range 600 – 700 °C.

Selectivity towards formaldehyde increases with bed temperature up to 650 °C and then starts to decrease, with a dramatic drop above 700 °C, due to the gas phase decomposition of formaldehyde to carbon monoxide. Selectivity towards carbon dioxide decreases consistently with increasing temperature. On the other hand, the higher the temperature, the higher the carbon monoxide selectivity, showing a quick increase above 700 °C. These trends are very important to understand and optimize the Silver process, and the hybrid approach has proven to allow the ANN to capture correctly the relationships with less deviation than the standard BP training.

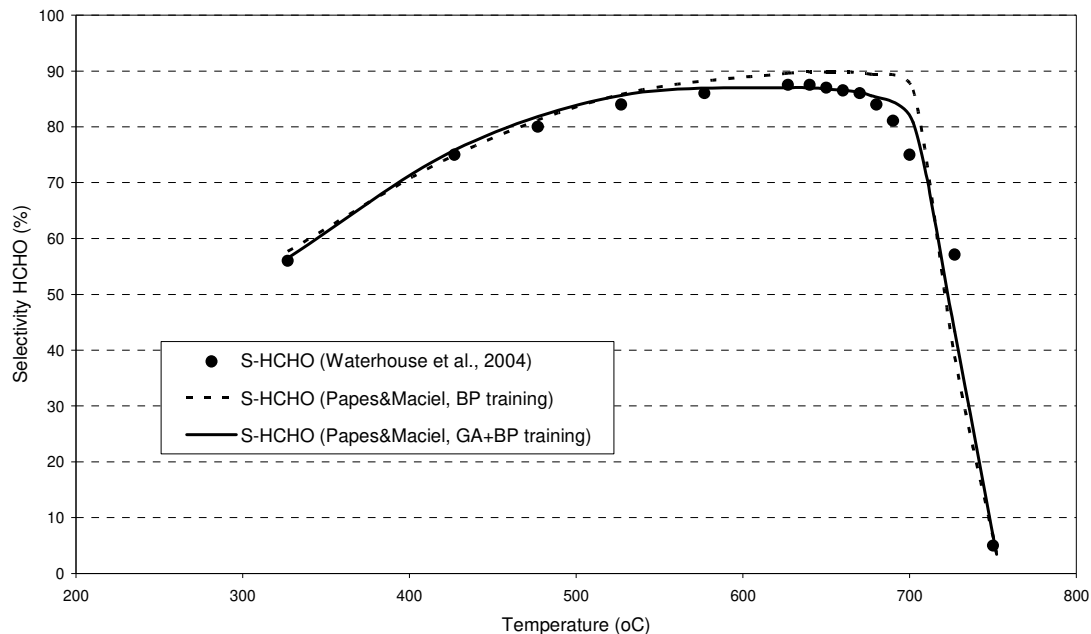


Figure 9: Simulation of experiments from Waterhouse et al. (2004b), varying bed temperature. Points are experimental measurements for the selectivity towards formaldehyde (circles), solid line refers to the simulations with ANN trained by the hybrid algorithm (GA+BP), and dashed line refers to the simulations with classical training algorithm (BP).

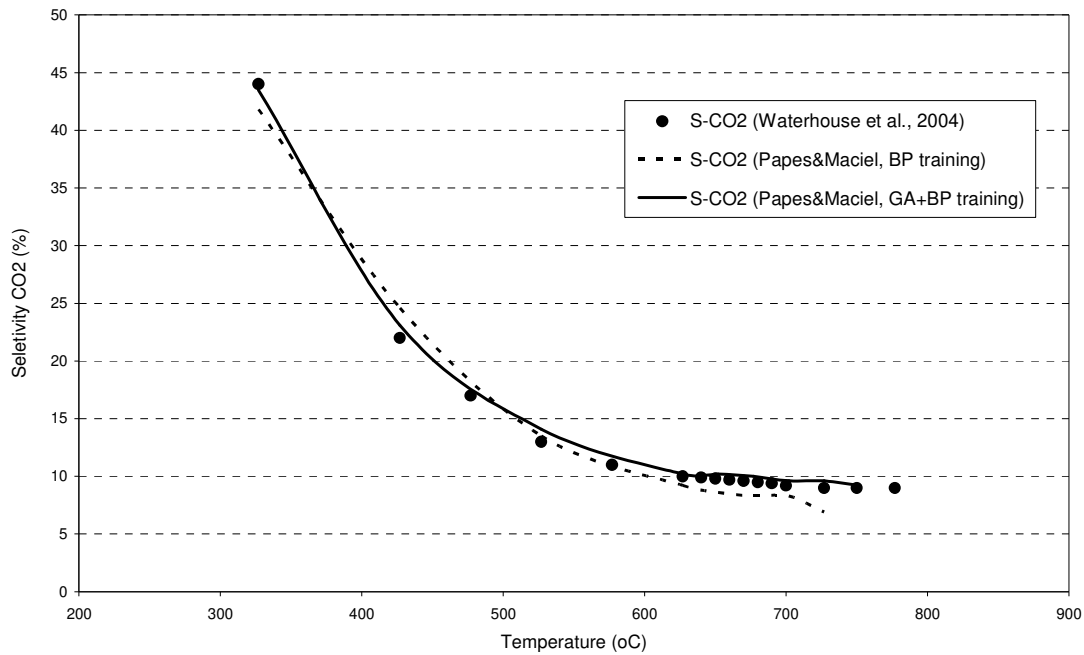


Figure 10: Simulation of experiments from Waterhouse et al. (2004b), varying bed temperature. Points are experimental measurements for the selectivity towards carbon dioxide (circles), solid line refers to the simulations with ANN trained by the hybrid algorithm (GA+BP), and dashed line refers to the simulations with classical training algorithm (BP).

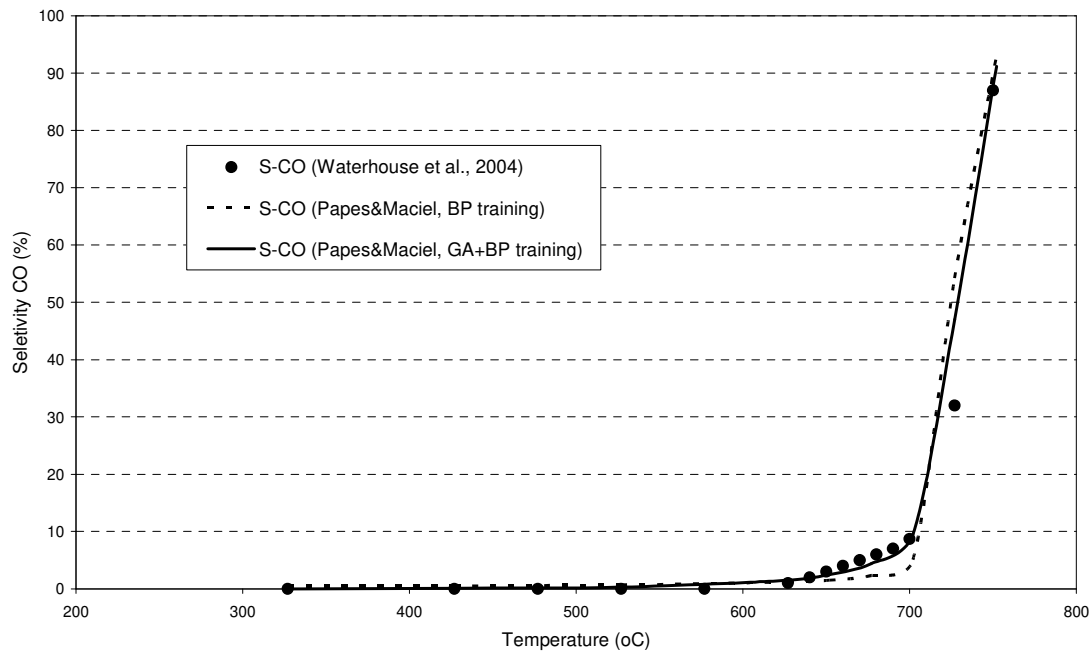


Figure 11: Simulation of experiments from Waterhouse et al. (2004b), varying bed temperature. Points are experimental measurements for the selectivity towards carbon monoxide (circles), solid line refers to the simulations with ANN trained by the hybrid algorithm (GA+BP), and dashed line refers to the simulations with classical training algorithm (BP).

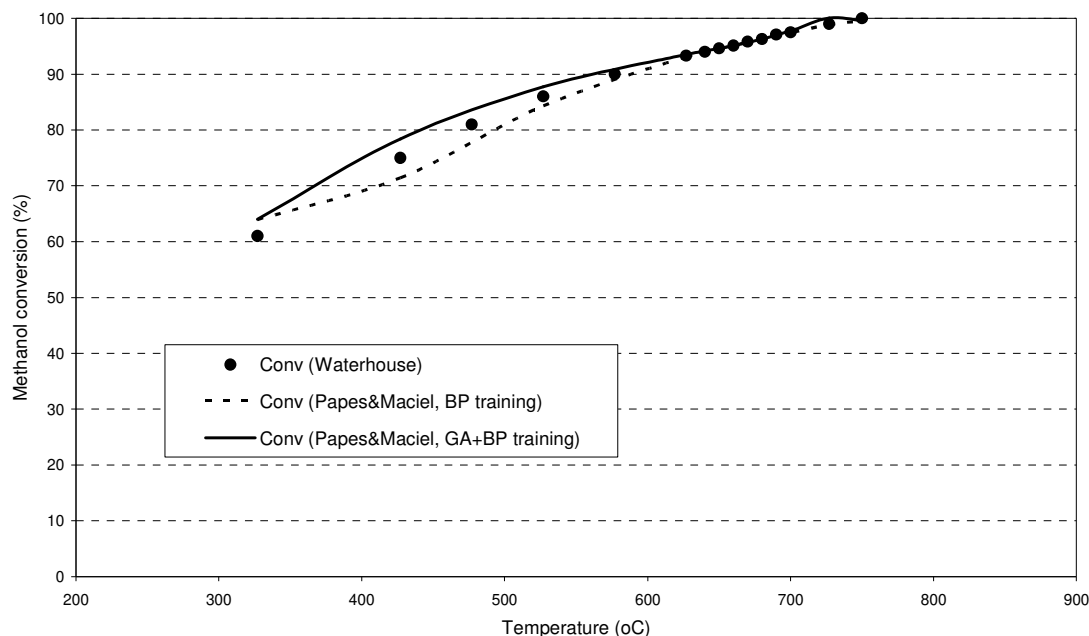


Figure 12: Simulation of experiments from Waterhouse et al. (2004b), varying bed temperature. Points are experimental measurements for the methanol conversion (circles), solid line refers to the simulations with ANN trained by the hybrid algorithm (GA+BP), and dashed line refers to the simulations with classical training algorithm (BP).

Both algorithms could calculate good methanol conversion estimates in the range 600 – 700 °C, identical to the experimental points, as shown on Figure 12. For lower temperatures, both methods produced small deviations from the experimental points, but the hybrid approach predicted a smoother curve, following the experimental trend.

Waterhouse’s (2004b) experiments were run at near industrial conditions, where many laboratory studies had failed, which they attributed to differences in catalyst, bed construction, reactor design and testing conditions. In accordance with industrial practices, Waterhouse et al. identified the importance of water presence at feed for achieving high formaldehyde yields.

3.2. ANN training with industrial data

Industrial data from an operating Silver plant were studied according to the same procedure. Real process information was extracted from the plant, based on Water Ballast Process, with basic molar feed composition $\text{CH}_3\text{OH}/\text{O}_2/\text{H}_2\text{O}/\text{N}_2$ of 2.60/1.00/0.46/3.76 (air is the carrier gas), total pressure of 1.2 atm, space velocity of $6.1 \times 10^6 \text{ h}^{-1}$, and temperature set-point of 625 °C.

A set of 4050 data points which correlate rate of reaction with local temperature and partial pressures of the reactants were extracted from plant process data and used for the ANN training, performed in the same fashion as explained above, starting with GA and then refining the solution by BP. The optimum number of neurons at hidden layer was also found to be 12 in this case.

The trained ANN was used to calculate new rates for “ r_{HCHO} ”, “ r_{CO_2} ” and “ r_{CO} ”, compared to the experimental rates (formation, oxidation and decomposition of formaldehyde, respectively). The results were shown on Figures 13, 14 and 15, where the rate of reaction calculated by the ANN was plotted against the experimental values extracted from industrial Silver plant, both normalized between 0 and 1, for the three reactions stated above. High correlation coefficients (> 0.99) were obtained and calculated points concentrated along $x = y$ line, as shown on the graphs, indicating that the neural network could successfully fit the actual experimental data from the plant simultaneously for the three rates, even containing noise from a normal plant in operation (instrument errors, unregistered deviations, record errors, measurement lags and normal oscillations from set-

points). For higher rate values, the ANN calculated lower rates compared to experimental ones, but these deviations seemed to show no negative influence on the simulation results.

Table 3 shows a comparison between the correlation coefficients found with the hybrid approach and the ones with the standard approach (ANN trained only by BP). For the rate of formaldehyde formation and the rate of formaldehyde oxidation, the hybrid approach produced estimates similar to the standard approach (same correlation coefficient), but for the gas-phase decomposition of formaldehyde, the GA+BP approach produced significant better estimates, compared to the BP approach. Once again, the hybrid approach has proven to be more effective in training the ANN compared to the standard BP algorithm.

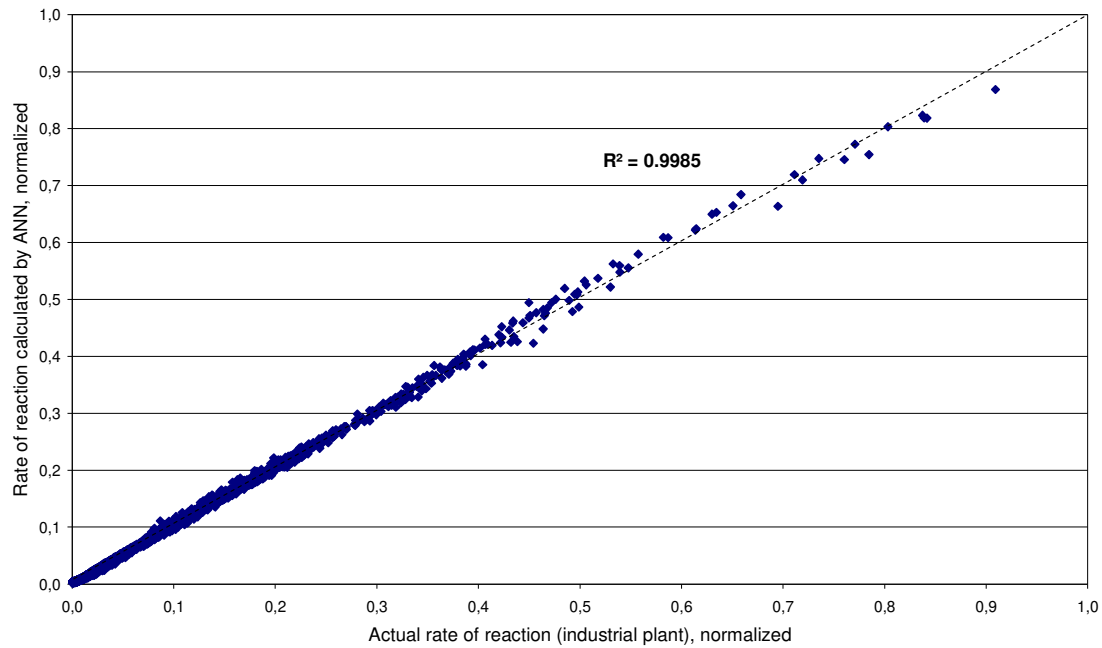


Figure 13: Correlation between rate of reaction extracted from industrial process data (x-axis) and rates calculated by the ANN (y-axis) for the formaldehyde formation reaction (Eq.1 + Eq.2).

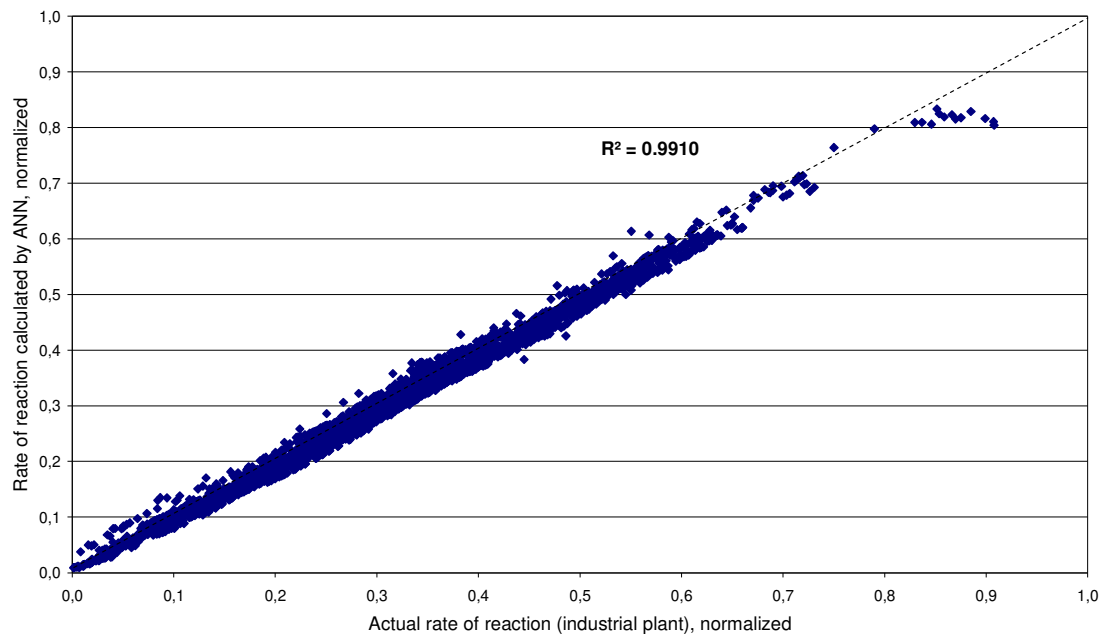


Figure 14: Correlation between rate of reaction extracted from industrial process data (x-axis) and rates calculated by the ANN (y-axis) for the formaldehyde oxidation reaction (Eq.3).

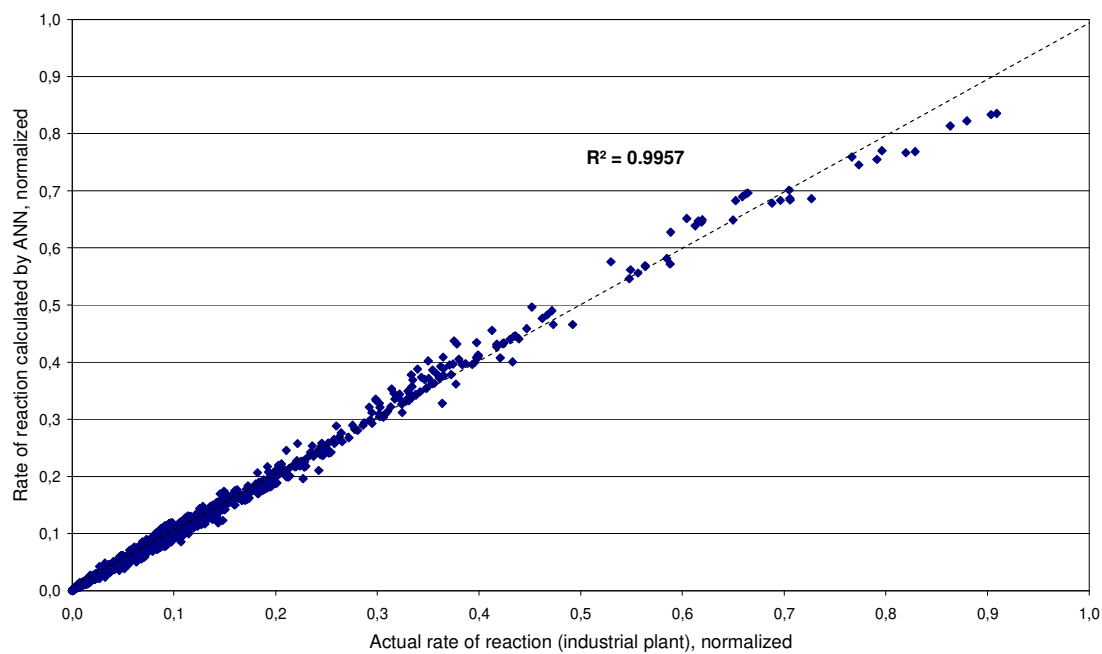


Figure 15: Correlation between rate of reaction extracted from industrial process data (x-axis) and rates calculated by the ANN (y-axis) for the formaldehyde gas phase decomposition reaction (Eq.4).

Table 3: Comparison of correlation coefficient from two different training approaches

<i>Training Approach for ANN</i>	$r^2 - r_{HCHO}$	$r^2 - r_{CO_2}$	$r^2 - r_{CO}$
Hybrid: GA + BP	0.9985	0.9910	0.9957
Standard: BP	0.9985	0.9910	0.9924

Process simulations for industrial conditions with the ANN trained by the hybrid approach have demonstrated the ability of the neural net in estimating methanol conversion and selectivity towards formaldehyde, carbon dioxide and carbon monoxide close to industrial measurements. Figure 16 shows some of the comparison results, where simulations were performed with different operating temperatures. The available industrial process data were plotted together with simulated data and literature data from Waterhouse's (2004b) study, for reference (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007b).

Another important feature of ANN is the incorporation of experimental deviations into its model. Even if the system is not on kinetic regimen, the ANN is still able to learn the kinetic data pattern. There is no need to care about adsorption mechanisms, reaction limiting step or eventual non-homogeneous activity throughout the catalyst surface: the ANN can capture the data pattern, provided that it is correctly measured.

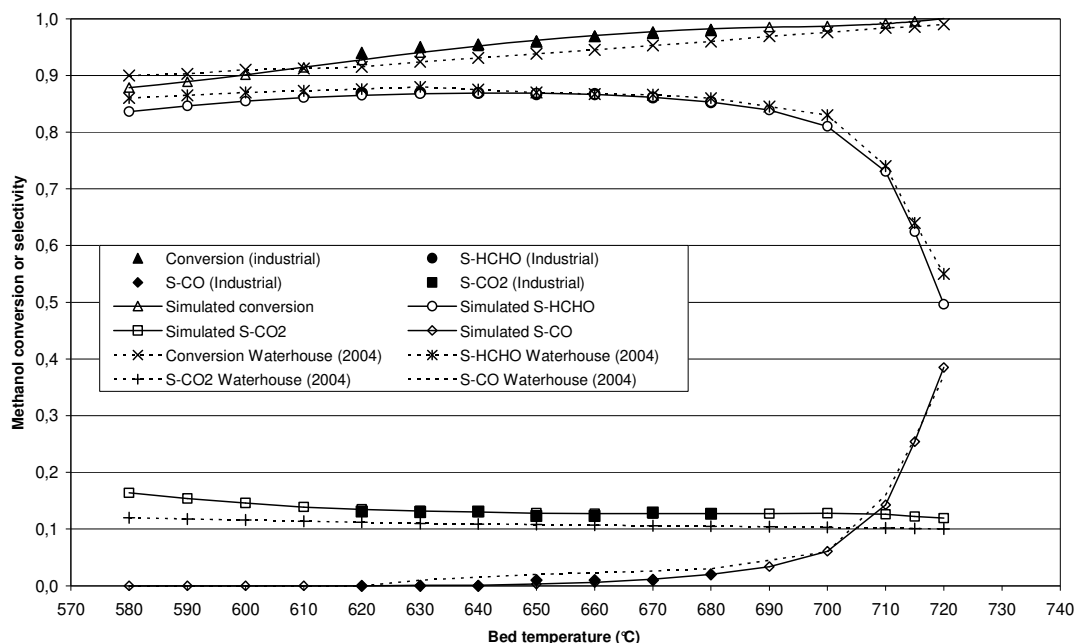


Figure 16: Effect of temperature on methanol conversion, selectivity towards formaldehyde (S-HCHO), carbon dioxide (S-CO₂) and carbon monoxide (S-CO). Simulations performed according to the base industrial operational conditions, varying the bed temperature, compared to some industrial and literature data (Waterhouse et al, 2004b).

The hybrid simulator and the ANN training approach presented in this work proved to be effective in simulating the Silver process with existing available data. In this sense, it represents an effective tool to understand this process, aiding operators and engineers in foreseeing abnormal situations and allowing anticipation of corrective actions. The system may also be used for process optimization, helping process engineers to define best operational policies to reduce costs, improve throughput and minimize carbon emissions (Papes Filho, 2007; Papes and Maciel Filho, 2007c).

4. Conclusions

A hybrid approach for Artificial Neural Network (ANN) training was presented in this work for fitting experimental rate of reaction data for the oxidation of methanol to formaldehyde over silver catalyst. A Genetic Algorithm (GA) was used in the first part of the training session, starting from a random population of solutions (in this case, the ANN internal parameters, or weights) and achieving a solution believed to be close to the optimum one, after a certain number of iterations (generations). In the second part of the training session, the classical back-propagation (BP) is used to refine the weights, but using the GA solution as the starting point and not a random initial estimate, as commonly employed.

The objective function in the studied case is the ANN error or the difference between the rates of reaction estimated by the ANN and the experimental ones, for the three reactions involved on the formaldehyde process: formaldehyde formation, oxidation and gas-phase decomposition.

The use of GA for ANN training increases the probability of reaching the global minimum error, as this algorithm performs a wide search on the variables range, but it is time consuming and takes too long to refine the solution to the desired precision. Classical BP, on the other hand, starts from a random estimate and goes towards a minimum from that point, following the derivatives. It may converge to a local minimum error, but with less computing time. The best benefit for ANN training is proposed to be the hybrid approach, where GA delivers to the BP an initial estimate believed to be close to the global minima and BP can effectively converge to the solution. The final solution after BP session is the best set of weights that allows the ANN to properly fit the experimental data. The optimum weights are stored in a data file and then the ANN is able to predict new rates for desired process conditions. A hybrid reactor simulator, constructed with deterministic fixed-bed model and a trained ANN, proved the ability to correctly predict conversion and selectivity for desired formaldehyde process conditions.

The methods presented here were tested with two case-examples: experimental work from Waterhouse et al. (2004b) and actual industrial data. The later one comprised a set of 4050 data rows, containing noisy and imprecise plant measured data.

In a first step, the rate of reaction calculated by the ANN was compared to the experimental values, for the three involved reactions, using the hybrid training algorithm (GA+BP).

In a second step, the simulator containing the ANN was used to estimate process data for methanol conversion, selectivity towards formaldehyde, carbon dioxide and carbon monoxide. The experimental process data were compared to the simulated values using two different trained set of weights: one produced from the hybrid training (GA+BP) and the other produced by classical back-propagation training. Good results were achieved in the two studied cases with the hybrid approach, providing estimates much closer to the experimental values for conversion and selectivity than with the classical approach.

The hybrid approach for ANN training has proven to provide an advantage over the classical BP training algorithm, generating more reliable results, with higher probability to achieve the best solution (global minimum net error). The simulator for the formaldehyde fixed-bed silver reactor, equipped with the trained ANN, demonstrated ability to calculate methanol conversion and selectivity for the three reactions simultaneously, close to the experimental values. The system is a powerful tool for operators and engineers in foreseeing abnormal situations, anticipating corrective actions, defining best operational policies to reduce costs, improve throughput and minimizing carbon emissions.

The reactor simulator, the ANN subroutine for rate of reaction calculation and the training program based on GA were all written by the authors in Fortran code. To the best of our knowledge, this is the first time GA was used to train an ANN with formaldehyde-silver kinetics.

References

- ABRAF (Brazilian Association of Formaldehyde Manufacturers) report; "Panorama of productive chain", www.abraf.com.br, 2004
- Andreasen, A.; Lynggaard, H.; Stegelmann, C. and Stoltze, P.; "A microkinetic model of the methanol oxidation over silver", *Surface Science*, 544, pp.5-23, 2003.
- Andreasen, A.; Lynggaard, H.; Stegelmann, C. and Stoltze, P.; "Simplified kinetic models of methanol oxidation on silver", *Applied Catalysis A: General*, 289, pp.267-273, 2005.
- Barteau, M and Madix, R.J.; *Surf. Sci*, 40, p.108, 1984.
- Bazilio, C.A.; Thomas, W.J.; Ullah, U. and Hayes, K.E.; "The catalytic oxidation of methanol", *Proc. R. Soc. Lond. A*, 399, pp.181-194, 1985.
- Bhagat, P.; "An Introduction to Neural Nets"; *Chemical Engineering Progress*, August, p.55, 1990.
- Bhattacharyya, S.K.; Nag, N.K. and Ganguly, N.D.; "Kinetics of vapor-phase oxidation of methanol on reduced silver catalyst", *J. of Catalysis*, v.23, i.2, pp.158-167, 1971.
- Box, G.E.P and Hunter, J.S.; "Statistics for experimenters", Wiley and Sons, 1st ed., New York, 1978.
- Cao, E. and Gavriilidis, A.; "Oxidative dehydrogenation of methanol in a microstructured reactor", *Catalysis Today*, 110, pp.154-163, 2005.
- Carrol, D.; "Genetic Algorithms and Optimizing Chemical Oxygen-Iodine Lasers", *Developments in Theoretical and Applied Mechanics*, v.XVIII, pp.411-424, 1996a.
- Carrol, D.L., "Chemical laser modeling with genetic algorithm", *AIAA Journal*, v.34, no 2, pp.338-346, 1996b.
- Crank, J. and Nicholson, P.; *Proc. Phil. Soc.*, v.43, p.50, 1947.
- Davis, L.; "Handbook of Genetic Algorithms", International Thomson Computer Press, Boston, 1991.
- Fogler, H.S.; "Elements of chemical reaction engineering", Prentice-Hall International, 2nd ed., New Jersey, p.71, 1992.
- Garrard, A. and Fraga, E.S.; "Mass exchange network synthesis using genetic algorithms", *Computers Chem. Engng.*, v.22, n.12, pp.1837-1850, (1998).
- Goldberg, D.E.; "Genetic Algorithms in Search, Optimization, and Machine Learning"; Ed. Addison-Wesley Publishing Company, Inc; New York, 1989.
- Goldberg, D.E; Deb, K. and Clark, J.H.; "Genetic Algorithms, Noise and the Sizing of Populations", *Complex Systems*, 6, pp. 333-362, 1992.
- Gravilin, V.N. and Popov, B.I; *Kinet. Catal.*, 6, p.799, 1965.
- Holland, J.H.; "Adaptation in natural and artificial systems", Ann Arbor: The University of Michigan Press, 1975.
- Holland, J.H.; "Adaptation", *Progress in theoretical biology*, 4, pp.263-293, 1976.
- Lefferts, L.; Ommen, J.G. and Ross, J.R.H.; "The oxidative dehydrogenation of methanol to formaldehyde over silver catalysts in relation to the oxygen-silver interaction", *Appl. Catal.*, 23, p.385, 1986.
- Lennox, B.; Montague, G.A.; Frith, A.M.; Gent, C. and Bevan, V.; "Industrial application of neural networks – an investigation", *Journal of Process Control*, v.11, pp.497-507, 2001.
- Nagy, A.; Mestl, G.; Ruhle, T.; Weinberg, G. and Schlogl, R.; "The dynamic restructuring of electrolytic silver during the formaldehyde synthesis reaction", *J. of Catalysis*, 179, pp.548-559, 1998.
- Nagy, A. and Mestl, G.; "High temperature partial oxidation reactions over silver catalysts", *Applied Catalysis A: General*, 188, pp.337-353, 1999.
- Papes Filho, A.C.; "Prediction of paper internal bond using neural networks", *O Papel*, 2001.
- Papes Filho, A.C.; "Simulation and optimization of a silver formaldehyde reactor, using artificial intelligence techniques", PhD thesis (in English) , UNICAMP – University of Campinas, Brazil, 2007.
- Papes Filho A.C. and Maciel Filho R.; "Concurrent Engineering Reactor Design", *Computer Aided Chemical Engineering*, v.20 A, Edited by Luis Puijgner and Antonio Espuña, Elsevier B.V., ISSN 1570-7946, pp.559-564, 2005.
- Papes Filho, A.C. and Maciel Filho, R.; "Novel approach for acquiring rate of reaction data from process information for neural network training: application to an industrial reactor for methanol oxidation to formaldehyde over silver catalyst process", to be published, 2007a.
- Papes Filho, A.C. and Maciel Filho, R.; "Hybrid simulation of a fixed-bed formaldehyde silver-catalyzed reactor using artificial neural networks", to be published, 2007b.
- Pham, D.T. and Pham, P.T.; "Artificial intelligence in engineering", *International Journal of Machine Tools & Manufacture*, v.39, pp. 937-949, 1999.
- Piccoli, R.L.; "Kinetic study of methanol selective oxidation to formaldehyde on iron molybdate catalyst", Master dissertation, Rijksuniversiteit Gent, Belgium, 1992.

- Press, W.H., Flannery, B.P., Teukolsky, S.A. and Vetterling, W.T.; "Numerical Recipes", Press Syndicate of the University of Cambridge, 1st ed., 1992.
- Psichogios, D.C. and Ungar, L.H.; "A hybrid neural network-first principles approach to process modeling", *AIChE Journal*, 38, 10, pp. 1499-1511, 1992.
- Qian, M.; Liauw, M.A. and Emig, G.; "Formaldehyde synthesis from methanol over silver catalysts", *Applied Catalysis A: General*, 238, pp.211-222, 2003.
- Reid, R.C; Prausnitz, J.M and Poling, B.E.; "The properties of gases and liquids", McGraw-Hill Book Company, New York, 4th ed., 1987.
- Rumelhart, D.E; Hinton, G.E. and Williams, R.J.; "Learning internal representations by error propagation" in *Parallel distributed processing*, v.1, pp.318-362, 1986.
- Santacesaria, E. and Morbidelli, M.; "Kinetics of the catalytic oxidation of methanol to formaldehyde", *Chem. Engng. Sci.*, v.36, pp.909-918, 1981.
- Syswerda, G.; "Uniform crossover in genetic algorithms", *Proceedings of the third international conference on genetic algorithms*. San Mateo, California, Morgan Kaufmann publishers, 1989.
- Treybal, R.E.; "Mass-transfer operations", McGraw-Hill International Editions, 3rd ed., Singapore, 1981.
- Ullmann's Encyclopedia of Industrial Chemistry, v.A11, VHC Publishers, 5th ed., New York, 1988.
- Van Veen, A.C, Hinrichsen, O. and Muhler, M.; "Mechanistic studies on the oxidative dehydrogenation of methanol over polycrystalline silver using the temporal-analysis-of-products approach", *J. of Catalysis*, 210, pp. 53-56, 2002.
- Wachs, I.E. and Madix, R.; "The oxidation of methanol on a silver (110) catalyst", *Surface Science*, 76, pp. 531-558, 1978.
- Walker, J.F; "Formaldehyde"; Robert E. Krieger Publishing Company, 3rd ed., New York, 1975.
- Wang, Q.J.; "Using Genetic Algorithms to Optimise Model Parameters", *Environmental Modelling & Software*, v.12, n.1, pp 27-34, 1997.
- Wasserman, P.D.; "Neural Computing: Theory and Practice", Editora van Nostrand Reinhold, 1st ed., New York, 1989.
- Waterhouse, G., Bowmaker, G. and Metson, J.; "Mechanism and active sites for the partial oxidation of methanol to formaldehyde over an electrolytic silver catalyst", *Applied Catalysis A*, 265, pp.85-101; 2004 (a).
- Waterhouse, G., Bowmaker, G. and Metson, J.; "Influence of catalyst morphology on performance of electrolytic silver catalysts for the partial oxidation of methanol to formaldehyde", *Applied Catalysis A*, 266, pp.257-273, 2004 (b).
- Welty, J.R.; Wicks, C.E. and Wilson, R.E.; "Fundamentals of momentum, heat and mass transfer", John Wiley & Sons editor, 3rd ed., New York, 1984.

4.3. Conclusões

Um método híbrido de treinamento de RNA foi usado nesse trabalho para ajustar dados de taxa de reação para a oxidação do metanol a formaldeído, em catalisador de prata. O AG foi usado na primeira parte da sessão de treinamento, partindo de uma população aleatória de soluções (nesse caso, o conjunto de parâmetros internos da RNA ou pesos), atingindo uma solução que provavelmente estivesse próxima da solução ótima, após certo número de iterações (gerações). Na segunda parte do treinamento, a RP clássica é usada para refinar o conjunto de pesos, mas partindo da solução dada pelo AG ao invés de uma estimativa inicial aleatória.

A função objetivo para o AG no caso estudado é o erro da RNA, calculado com base na diferença entre as taxas de reação calculadas pela rede e as taxas experimentais, para cada uma das três reações envolvidas no processo: formação, oxidação e decomposição na fase gasosa do formaldeído.

O uso do AG para treinamento da RNA aumenta a probabilidade de atingir o mínimo erro global da rede, uma vez que o AG realiza uma ampla busca em todo o domínio das variáveis (pesos). Porém, o método consome grande tempo computacional para refinar a solução na precisão desejada.

A RP clássica, por outro lado, parte de uma estimativa aleatória inicial e evolui até um mínimo, seguindo os gradientes. Ela pode convergir para um mínimo local, mas consumindo menos tempo computacional para atingir a precisão desejada.

A melhor abordagem, proposta nesse trabalho, é um método híbrido onde o AG entrega à RP uma iniciativa inicial, que se acredita estar próxima do erro mínimo global da rede. Dessa forma, a RP pode eficientemente refinar a solução, fornecendo um conjunto de pesos ótimo, que permite à RNA ajustar adequadamente os dados experimentais.

O conjunto ótimo de pesos é salvo em um arquivo de dados e a RNA é capaz de prever novas taxas de reação para outras condições de processo, usando tais pesos.

Um simulador híbrido para o reator, construído com um modelo determinístico para o leito fixo e uma RNA treinada, mostrou sua capacidade para prever corretamente a conversão e seletividades para determinadas condições de processo da planta de formaldeído.

Os métodos apresentados nesse capítulo foram testados com dois casos-exemplo separadamente: trabalhos experimentais de WATERHOUSE ET AL. (2004b) e dados industriais reais. Esse último consiste em um conjunto de 4050 dados, com ruído e medidas de planta com imprecisões.

Em um primeiro passo, as taxas de reação calculadas pela RNA foram comparadas com as taxas experimentais para as três reações de interesse, usando o método de treinamento híbrido (AG + RP).

Em um segundo passo, o simulador contendo a RNA foi usado para estimar dados de processo para conversão do metanol e seletividades para formaldeído, dióxido de carbono e monóxido de carbono. Os dados de processo experimentais foram comparados com valores simulados usando dois conjuntos de pesos diferentes: um deles obtido através do treinamento híbrido (AG + RP) e o outro obtido pelo método de treinamento clássico (RP). Bons resultados foram obtidos nos dois casos estudados com o método híbrido, fornecendo estimativas mais próximas dos valores experimentais de conversão e seletividade que com o método tradicional.

O treinamento híbrido para a RNA mostrou grande vantagem sobre o método RP clássico, gerando resultados mais confiáveis com maior probabilidade de fornecer a solução ótima (mínimo erro global da rede). O simulador para o reator de formaldeído, equipado com a RNA, demonstrou capacidade de calcular a conversão de metanol e as seletividades para as três reações simultaneamente, com resultados próximos dos valores experimentais. O sistema é uma ferramenta poderosa para operadores e engenheiros para prever situações anormais e antecipar ações corretivas, bem como definir as melhores políticas operacionais para reduzir custos, aumentar a capacidade da planta e minimizar as emissões de carbono na atmosfera.

O simulador do reator, a sub-rotina com RNA para cálculo das taxas de reação e o “software” de treinamento baseado em AG foram desenvolvidos pelos autores em código Fortran. A aplicação de AG para treinar a RNA com dados cinéticos do reator de formaldeído por processo prata é inédito.

CAPÍTULO 5

MÉTODO DE TREINAMENTO ACOPLADO PARA MODELO CINÉTICO UNIVERSAL BASEADO EM REDES NEURAIS E ALGORITMO GENÉTICO: APLICAÇÃO À OXIDAÇÃO INDUSTRIAL DO METANOL A FORMALDEÍDO SOBRE CATALISADOR DE PRATA

5.1. Introdução

Nos capítulos anteriores, a rede neural foi treinada usando dois algoritmos diferentes, porém sempre empregando dados de taxa de reação para o ajuste dos pesos. A RNA foi primeiramente treinada em uma sessão isolada e somente com os pesos definidos e salvos em um arquivo de dados, ela foi executada em conjunto com o simulador para calcular as taxas de reação.

Uma vez que os dados de taxa de reação não se encontram disponíveis para o processo formaldeído-prata e há grande dificuldade em obtê-los experimentalmente com qualidade necessária para o treinamento da RNA, é preciso realizar a operação de extração das taxas a partir de dados de processo, usando equações cinéticas aproximadas, conforme descrito no Capítulo 3. Os dados de processo nesse caso são conversão de metanol, consumo específico de metanol, composição da corrente de saída, seletividades para formaldeído, dióxido de carbono e monóxido de carbono. No entanto, essa operação não é simples e representa uma dificuldade a mais no processo de treinamento da rede e, conseqüentemente, na simulação do processo.

No presente capítulo, uma nova abordagem de treinamento é apresentada, onde a RNA já se encontra implementada como uma sub-rotina dentro do simulador do reator, para o cálculo das taxas de reação, porém inicialmente, o conjunto de pesos não está definido.

Utilizando AG, os pesos da rede são ajustados, de modo que o simulador consiga prever os dados de processo (conversão e seletividades), sendo que a RNA é vista como uma caixa-preta nesse processo. Os dados de saída da RNA não são analisados e para o usuário eles permanecem desconhecidos, pois não é feita qualquer comparação das taxas calculadas.

Através do mesmo processo descrito no capítulo anterior, o AG inicia-se com uma população de conjuntos de pesos aleatórios, que vão sendo refinados geração após geração. A função objetivo nesse caso não é o erro da RNA, mas sim o erro do simulador para um conjunto de dados de processo, definido por:

$$E = \sum_{i=1}^N \left(0.25 * (\chi_C - \chi_E)^2 + 0.25 * (S_C - S_E)_{HCHO}^2 + 0.25 * (S_C - S_E)_{CO_2}^2 + 0.25 * (S_C - S_E)_{CO}^2 \right)$$

onde: “E” é o erro do simulador; “N” é o número de dados de processo experimentais; “ χ ” é a conversão de metanol; “S” é a seletividade; “C” representa valores calculados; “E” representa valores experimentais; “HCHO” refere-se a formaldeído; “CO₂” refere-se ao dióxido de carbono e “CO” refere-se ao monóxido de carbono.

A seleção do melhor conjunto de pesos pelo AG não é realizada pelo cálculo do erro sobre um dado experimental, mas sim sobre um conjunto de “N” pontos, o que torna o algoritmo bastante complexo e lento.

Se o erro cai abaixo de certo valor desejado, o simulador está automaticamente apto a estimar os dados de processo, utilizando o conjunto ótimo de pesos fornecido pelo treinamento com AG.

O treinamento foi exemplificado em dois casos: dados experimentais da literatura, publicados por WATERHOUSE ET AL. (2004b) e dados industriais.

No primeiro caso, obteve-se excelente correlação entre os 17 pontos experimentais extraídos do trabalho de WATERHOUSE ET AL. e os dados calculados pelo simulador, após treinamento da RNA pelo método exposto acima, considerando conversão de metanol e seletividades para formaldeído, CO e CO₂.

As curvas de conversão e seletividades em função da temperatura foram apresentadas, comparando-se os dados simulados com novos dados experimentais (não utilizados na etapa de treinamento), encontrando excelente aproximação.

Vários gráficos apresentam as curvas de seletividade para formaldeído, CO₂, CO e conversão em função da temperatura. Nessas figuras, destaca-se a comparação entre os dados experimentais, valores simulados com a RNA treinada pelo modelo acoplado (capítulo presente) e valores simulados com a RNA treinada pelo modelo híbrido AG+RP (capítulo anterior).

No segundo caso estudado, obteve-se igualmente excelente correlação entre os 50 pontos coletados de um processo industrial e os dados simulados.

O treinamento da RNA com a abordagem acoplada foi bem sucedido, mostrando ser tão ou mais eficiente que a abordagem tradicional utilizando as taxas de reação. A grande vantagem é a facilidade do processo de treinamento, não necessitando obter previamente as taxas de reação e utilizando diretamente os dados de processo facilmente obtidos de uma planta em operação. A grande desvantagem é o tempo computacional: a abordagem acoplada consumiu aproximadamente 200 horas computacionais, enquanto a abordagem híbrida, usando as taxas de reação, consumiu aproximadamente 5 horas.

A RNA é um modelo perfeito para a abordagem acoplada, uma vez que ela captura a essência do conjunto de dados, sem a necessidade de formular hipóteses sobre limitações na transferência de massa entre o meio reacional e a superfície do catalisador (regime cinético), mecanismos de reação, etapas limitantes ou homogeneidade da atividade do catalisador. Essa característica não é encontrada nos modelos determinísticos que falham quando as hipóteses não são corretamente formuladas ou quando os dados experimentais são incorretamente obtidos.

Como a abordagem acoplada nada mais é que um processo de otimização, tentou-se usar o algoritmo determinístico clássico de otimização SQP (Programação Quadrática Sucessiva), através de uma rotina comercial. Essa abordagem mostrou-se impraticável, pois em nenhuma das tentativas o SQP foi capaz de concluir o treinamento por interromper a execução com um erro devido à impossibilidade de calcular o gradiente. O SQP mostrou não ser capaz de lidar com grande número de parâmetros a otimizar: da ordem de 150 pesos da RNA a serem ajustados. Dessa forma, demonstrou-se a vantagem do AG ao lidar com problemas complexos como esse, apresentando robustez na execução.

5.2. Desenvolvimento.

O desenvolvimento desse capítulo é descrito no artigo intitulado “A Built-in Training Method for Universal Kinetic Models Through Neural Networks and Genetic Algorithms: Application to Industrial Methanol Oxidation to Formaldehyde over Silver Catalyst”, apresentado a seguir, a ser submetido para publicação em revista indexada internacional.

A Built-in Training Method for Universal Kinetic Models Through Neural Networks and Genetic Algorithms: Application to Industrial Methanol Oxidation to Formaldehyde over Silver Catalyst

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Abstract

A built-in approach for Artificial Neural Networks training was used in this work, based on Genetic Algorithms. The Neural Network was implemented in a fixed bed reactor simulator for calculating the rate of reaction of methanol oxidation to formaldehyde with silver catalyst. The simulator, based on deterministic model, was constructed to predict the reactor conversion and the selectivity towards formaldehyde (desired product), carbon dioxide and carbon monoxide (main by-products), based on given process conditions, but rate of reaction data is necessary to perform this task, which is given by a trained neural network. There is not enough experimental data on literature, providing rate of reaction information correlated to process conditions. In most cases, only conversions and selectivity are reported, in such way this information cannot be directly used to train the neural net for rate calculation, once standard training methods, as back-propagation, use the difference between the rates calculated by the net and the experimental rates of reaction. Using a genetic algorithm approach, the neural network could be trained, with only experimental data of conversion and selectivity, and no information about rate of reaction, minimizing the error between calculated selectivity/conversion and experimental ones. The neural net is handled here as a black-box: the weights of the net are adjusted to provide the desired conversion and selectivity from the simulator (not from the net), with no attempt to manipulate reaction rate data. A classical search method – SQP – was tested in place of the genetic algorithm for this task with unsuccessful results.

The Neural Network was successfully trained with this approach, and simulated data confirmed this results when compared to experimental and industrial data.

Key words: formaldehyde, silver, artificial neural networks, genetic algorithms, artificial intelligence, methanol oxidation, kinetic modeling.

1. Introduction

Formaldehyde is ranked among 50 most important products of industrial organic chemistry and plays a key role as intermediate for a variety of engineering products used by the construction and automotive sectors, such as phenolic resins, urea-formaldehyde resins and butenediol (Walker, 1975). The consumption has increased fast and worldwide production is about 32 million metric tones of formalin, 37% solution basis, per year (ABRAF, 2004).

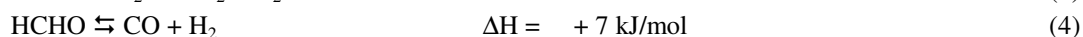
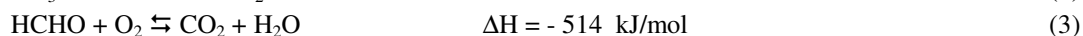
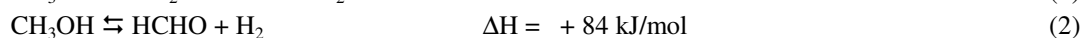
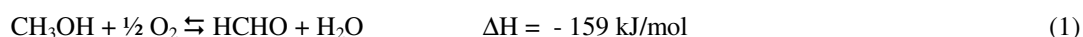
The industrial manufacture of formaldehyde can be performed by two commercially available routes: the Silver process and the Formox process (Santacesaria and Morbidelli, 1981; Piccoli, 1992). In the former, methanol-rich methanol-air-stream mixture is passed through a simple silver catalyst bed at 600 – 700 °C, at near atmospheric pressure. The Formox process differs in the nature of the catalyst (iron-molybdenum oxides), methanol concentration (oxygen-rich), bed temperature (300 – 400 °C) and bed configuration (multitubular reactor). Formalin, an aqueous solution of formaldehyde, is obtained and commercialized as final product by these two processes.

New plants are preferably built with Formox process, but approximately 30 - 50% of the current world's capacity rely on plants operated with Silver process (Van Veen et al, 2002; Qian et al., 2003; Waterhouse et al., 2004b). Even considered an outdated process, there are many Silver plants in operation with potential to

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improve raw-material costs, increasing the selectivity towards formaldehyde: methanol cost represents more than 80% of the production cost of formaldehyde and an improvement of 1 percentage point on the selectivity in an average size plant means saving about 200,000 US\$ per year on methanol purchasing. Environmental pressure is also a driver to optimize this process, once the carbon emissions generated by formaldehyde plants (carbon dioxide and carbon monoxide) will have to be reduced soon in order to comply with world's efforts against global warming.

The industrial process of formaldehyde production over silver catalyst is composed basically by four reactions. Two parallel reactions account for the formaldehyde formation from methanol: methanol oxidation (1) and methanol dehydrogenation (2). The formed formaldehyde reacts with oxygen over the silver catalyst, forming carbon dioxide (3) and it may also decompose on gas phase to carbon monoxide at high temperatures (4). Reactions 3 and 4 reduce the selectivity towards the desired product, so care has to be taken in the definition of operational conditions. The oxidation reactions are extremely exothermic and the reactor has a high heat generation.



Oxygen plays a key role on the reaction mechanism of the reaction, keeping the catalyst active (Bhattacharyya et al., 1971). Even the dehydrogenation reaction, which does not involve oxygen directly, does not happen in the absence of oxygen.

Water is also an important reactant in this reaction, increasing the selectivity towards the desired product. Due to the high heat capacity, water vapor removes a great deal of reaction heat, preventing overheating and sintering of catalyst. It also helps to keep the silver surface clean, blocks specific surface sites and displaces the reaction mechanism reducing the formation of undesirable by products (Barteau and Madix, 1984; Qian et al., 2003; Andreasen et al., 2003). Typical selectivity is found on 85 – 90% range, achieving 97-97% conversion when water is added to the feed, whereas without water the plant is run with lower conversions (77 – 87%) in order to keep the selectivity (Ullman, 1988).

There is no full mechanistic and kinetics understanding of methanol oxidation on silver surfaces under industrial conditions, even after decades of studies on the subject (Gravilin and Popov, 1965; Bazilio et al., 1985; Ullman, 1988; Van Veen et al., 2002; Andreasen et al., 2003; Waterhouse et al., 2004b; Cao and Gavriilidis, 2005). Most of the works focus on the formaldehyde formation, with no attempt to the formation of by-products, principally carbon monoxide.

Kinetic models for this process have been created, but they are not complete and fail in simulating some actual industrial conditions, for instance the water influence and the temperature influence above 650 °C, on the formaldehyde selectivity. The development of new improved models is costly, time consuming and they are not the focus of industrial personnel. Any attempt to obtain kinetic models readily applicable to industrial conditions in a timely fashion would be a powerful tool for understanding and optimizing this process, giving Silver plants a renewed breath to compete with brand new Formox facilities. In these cases, novel approaches like neural networks are efficient for modelling systems based on noisy actual data with no need to have a full understanding of reaction mechanism to derive classical rate equations.

Artificial Neural Networks (ANNs) have successfully been used to model problems where deterministic models were not available or failed in representing the data (Psichogios and Ungar, 1992; Papes Filho and Maciel Filho, 2005). They were firstly developed by biologists as models of living brains, but showed big potential for other science areas as complex models, having powerful capacity to calculate multiple outputs from multiple inputs (MIMO system).

It is a generic model that can be used for a variety of problems with minor adaptations. Different from a simple regression or data fit, they are able to learn the pattern of the data and a regression model is not necessary, once the ANN itself is the model (Lennox et al., 2001). They use less parameters than polynomial regression and tolerate hardware failures or data noise.

The ANN learns the data pattern using an algorithm known as “training”, where a set of known data rows [input/output] is presented to the net, which is adjusted until it properly fits the data: the net is able to capture the data pattern and store the knowledge into its internal parameters, as a memory. This is the reason why ANN is considered part of the Artificial Intelligence field (Wasserman, 1989; Davis, 1991; Pham and Pham, 1999).

Many training algorithms are available. The most used for engineering problems is the back-propagation (BP), that considers the error on the output neurons (difference between ANN output and experimental value) to calculate the adjustment of the weights on the previous network layer. The error is then back-propagated to the preceding layers until all weights are adjusted. The process is repeated until the net error is minimized. For the first iteration, the set of weights is chosen randomly and then the algorithm adjusts them by back-propagation (Wasserman, 1989; Davis, 1991). Once the BP is a gradient-driven type of algorithm, the quality of the solution will heavily depend on the initial estimate, but as it is random, there is no guarantee that it will be a good one.

Hybrid training methods may employ a Genetic Algorithm (GA) to perform an initial search for a good solution, more probable to be close to the global optimum. The solution from the GA training session is used as an initial estimate for BP algorithm that refines the solution in a timely fashion (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007b).

GA have been widely used to solve a variety of problems involving multiple parameters, where local optima may exist and there is a need to perform a wide search throughout the variables range in order to achieve the global optimum. Firstly published in Holland’s (1975) monograph, it is a mathematical method based on natural selection and natural genetics (Holland, 1976; Wang, 1997). They search from a population of points and not from a single point, so that they are more likely to converge to a global optimum, and not be trapped into local solutions. GA does not require the calculation of derivatives and the objective function may be a black box. They are theoretically and empirically proven to provide a robust search in complex spaces (Goldberg, 1989; Garrard and Fraga, 1998) for problems that classical numerical methods were not able to handle (Pham and Pham, 1999).

When ANN is implemented inside a reactor simulator for calculating the rate of reaction, the net needs to be trained with rate of reaction data. Normally, kinetic information is not available either in literature or from industrial processes, where macro-parameters as conversion, selectivity or raw-material specific consumption are commonly handled. Papes Filho and Maciel Filho (2007a) proposed a procedure for extracting the kinetic data from process conditions (Papes Filho, 2007), but this represents one additional step between the available data and the ANN training. For some plant personnel, this procedure may be complex enough to give up configuring the reactor simulator (or train the ANN).

The best training procedure would be using the process information straightforward to train the ANN, without looking into kinetic data (rate of reaction). This procedure is unlikely for a classical training method (BP or the hybrid GA+BP), once they are based on the difference between the rates of reaction calculated by the ANN and the experimental rates. Only after having the ANN trained, the simulator is able to estimate conversion and selectivity.

In this work, a different approach, based on GA, was used to train the ANN employing only process information and no kinetic data. The ANN will be seen as a black-box and it will be trained inside the simulator. The population of solutions evaluated by GA algorithm will contain the ANN weights (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007b), but the objective function, or evaluation function, will not

be the difference between calculated and experimental rates, but the difference between calculated conversion/selectivity and experimental ones. The training procedure is seen as an optimization problem, where the simulator error is minimized (and not the ANN error). The best solution will be the best set of weights that allows the simulator to foresee conversion and selectivity closer to experimental values, with no attempt to the output of the ANN (the rate of reactions remain inside the black-box).

The ANN was trained here using process data obtained from industrial plant and from literature, for the methanol oxidation to formaldehyde with silver catalyst. The algorithm is slow (it takes days for the training process to be completed), but it is a much easier way to model the process without manipulating the available data. The “trained” simulator was run for many cases with successful results, proven to be a useful tool for the simulation of this type of process.

2. Methods

2.1. Formaldehyde reactor simulator

In this paper, the ANN is trained as a built-in model inside the reactor simulator, which is run for every solution (individual) evaluated by GA. The output from the simulator (and not from the ANN) is compared to the experimental data (methanol conversion and selectivity). When the ANN is trained, the simulator is able to predict new conditions.

The formaldehyde reactor simulator was written using Fortran language and the fixed-bed reactor model was based on mass balance (equation 5), derived from the equation of continuity (Welty, 1984) for the bidimensional flow on cylindrical coordinates, considering plug-flow tubular model, molecular diffusion and steady-state operation (Treybal, 1981; Fogler, 1992). Heat transfer calculations on the silver bed and industrial observations on an operating reactor indicate that, for practical ends, the reactor (fixed-bed) runs isothermally and adiabatically (Bazilio et al., 1985; Nagy et al., 1998; Nagy and Mestl, 1999; Van Veen et al., 2002; Papes Filho, 2007; Papes Filho and Maciel Filho, 2007c). Figure 1 shows a scheme of a typical silver reactor.

$$D_L \cdot \frac{\partial^2 C}{\partial z^2} + D_R \cdot \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial C}{\partial r} \right) - V_z \cdot \frac{\partial C}{\partial z} + v_A \cdot R_V = 0 \quad (5)$$

In this equation “C” is the substance concentration (kg/m³); “r” is the distance from the reactor central line or the radius on cylindrical coordinates (m); “z” is the distance from the reactor inlet or the axial distance on cylindrical coordinates (m); “D_L” is the axial diffusion coefficient (m²/s); “D_R” is the radial diffusion coefficient (m²/s); “V_z” is the axial velocity (m/s); “v_A” is the stoichiometric coefficient for the studied substance (dimensionless); “R_V” is the rate of the reaction per reaction volume (kg/m³.s).

Three differential mass balance equations are solved simultaneously, one for each reaction considered for the Silver process (Andreasen et al, 2003; Papes Filho and Maciel Filho, 2007a), represented by formaldehyde formation (R_{HCHO}), carbon dioxide formation (R_{CO2}) and carbon monoxide formation (R_{CO}):



The differential equations were solved numerically using the Crank-Nicholson algorithm, a semi-implicit method known to be intrinsically stable (Crank and Nicholson, 1947; Press et al., 1992), very suitable for reactor simulators. The physical properties of pure substances and mixtures were calculated (Welty et al., 1984; Reid et al., 1987; Sandler, 1989) at each step of Crank-Nicholson method, according to the actual local conditions. Diffusion coefficients were calculated by the correlation of Papes Filho and Cremasco (1995). The concentration of all species was calculated at every iteration using the partial pressures and total pressure, considering the mole balance in the reactor:

For formaldehyde:	$n_1 = n_1^0 + \xi_{\text{HCHO}} - \xi_{\text{CO}_2} - \xi_{\text{CO}}$
For carbon dioxide	$n_2 = n_2^0 + \xi_{\text{CO}_2}$
For carbon monoxide	$n_3 = n_3^0 + \xi_{\text{CO}}$
For methanol	$n_4 = n_4^0 - \xi_{\text{HCHO}}$
For oxygen	$n_5 = n_5^0 - 0.25 \cdot \xi_{\text{HCHO}} - \xi_{\text{CO}_2}$
For water	$n_6 = n_6^0 + 0.5 \cdot \xi_{\text{HCHO}} + \xi_{\text{CO}_2}$
For hydrogen:	$n_7 = n_7^0 + 0.5 \cdot \xi_{\text{HCHO}} + \xi_{\text{CO}}$
For nitrogen:	$n_8 = n_8^0$

where “ n_i ” is the number of moles of the substance “ i ” at a particular numerical step; “ n_i^0 ” is the initial number of moles of the substance “ i ”; “ ξ_{HCHO} ” is the advancement of the reaction of formaldehyde formation; “ ξ_{CO_2} ” is the advancement of the reaction of formaldehyde combustion and “ ξ_{CO} ” is the advancement of the reaction of formaldehyde decomposition. Bed pressure and temperature are constant and given by the user.

The rate of reaction for the three involved reactions is calculated by the ANN by means of a Fortran subroutine, using the weights supplied by the GA (that is, the individuals of every generation). The final set of weights (final solution of GA) is used for running the simulator to predict new conditions.

The inputs to the simulator are: methanol flowrate (kg/h); air flowrate (kg/h); water flowrate (kg/h); bed temperature (°C) and bed pressure (atm). Other information, also provided by the user, but not changed for a studied case, is reactor geometry, bed geometry, silver particle size and oxygen concentration on air.

The outputs from the simulator are the final composition (moles or partial pressures) from the last “ z ”-step of Crank-Nicholson algorithm (bed outlet), that allows the calculation of the methanol conversion and selectivity towards formaldehyde, carbon dioxide and carbon monoxide (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007c).

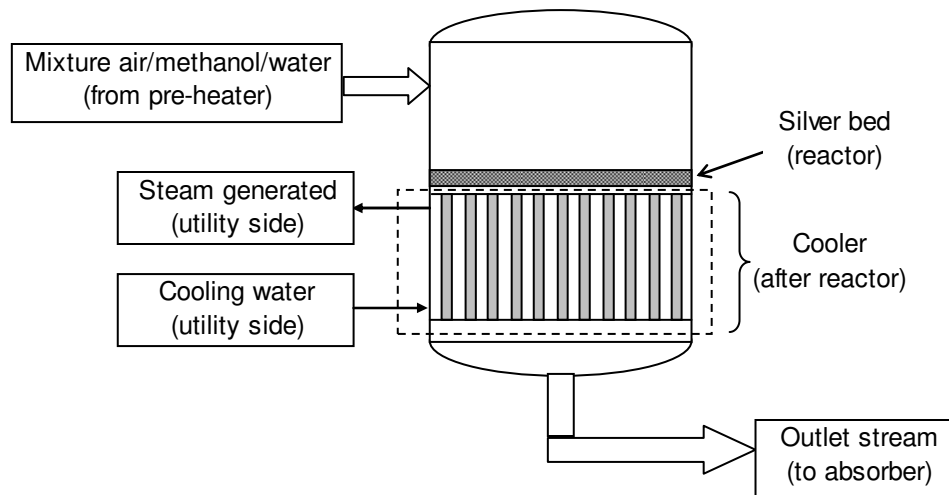


Figure 1: Scheme of a typical silver reactor, showing the fixed-bed, where reaction takes place, and the downstream cooler.

2.2. Artificial Neural Networks

A neural network with three layers and bias neurons was used in this work to calculate the rate of reaction, as exposed above. The schematic of the used ANN is shown on Figure 2.

The input layer contains 10 neurons for the input parameters to the ANN: bed temperature (K), total pressure (atm), methanol partial pressure, oxygen partial pressure, water partial pressure, hydrogen partial pressure,

formaldehyde partial pressure, carbon dioxide partial pressure, carbon monoxide partial pressure and bias neuron (input = 1).

The number of neurons at hidden layer is usually varied to obtain the optimum configuration. Small number of neurons at the hidden layer may cause the net to be too simple to properly fit the data, but, in the other hand, if the ANN has too many weights, it may become too specific to the training data and lose its generalization power. A bias neuron connected to “1” was included to this layer.

Three neurons compose the output layer, calculating the rate of the 3 reactions of interest: the rate of methanol oxidation (r_{HCHO}), the rate of formaldehyde oxidation (r_{CO_2}) and the rate of gas phase decomposition of formaldehyde (r_{CO}), all in $\text{kmol/m}^3\cdot\text{h}$.

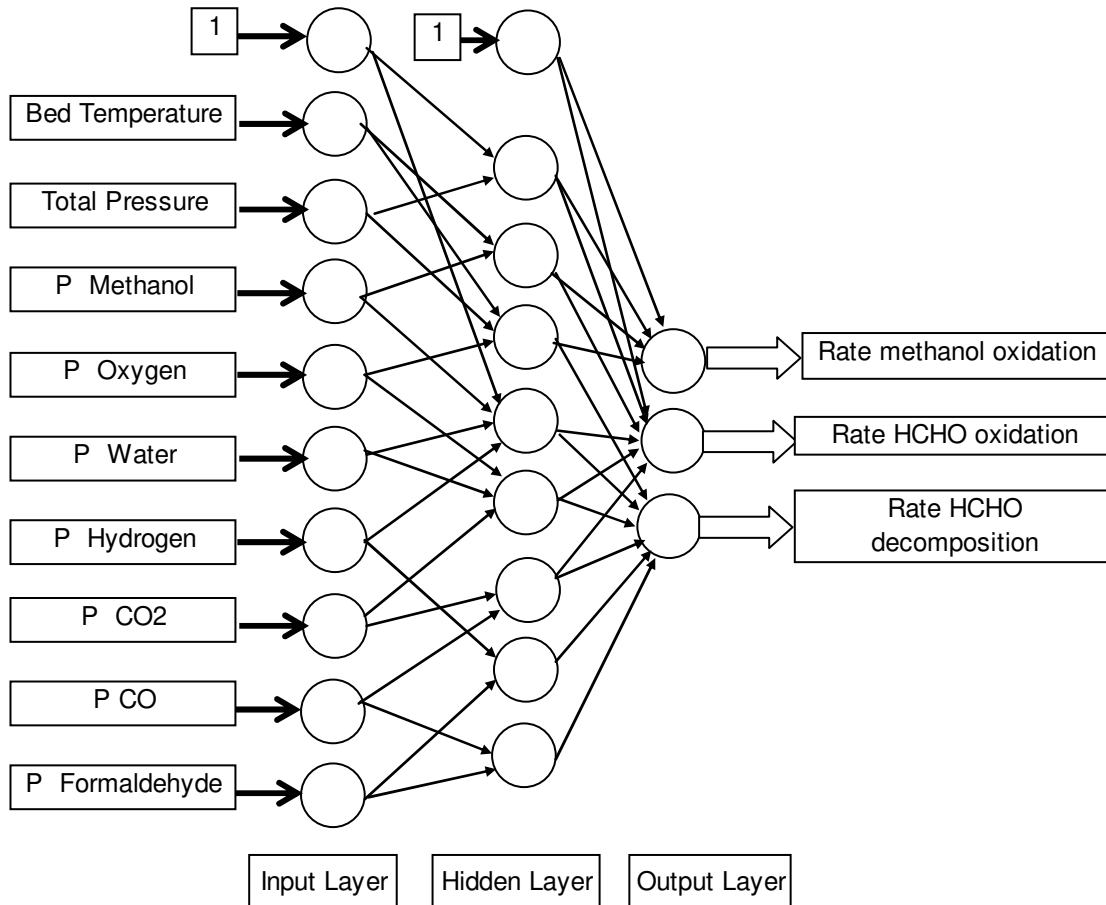


Figure 2: Schematic of the ANN used (not all arrows were drawn, in order to make the picture clear)

The perceptron, name given to the virtual neuron of the neural net, generates a signal (value), correspondent to the sum the inputs from neurons of the previous layer, after being multiplied by the weight associated to the two neurons involved (the one that sends the value and the one that receives). The input layer only receives the external inputs and passes them to the hidden layer. The neurons at the hidden layer receive the signals from the input layer, calculate the outputs and pass them to the output layer. The same procedure is done with the output layer, which generates the ANN outputs (Rumelhart et al., 1986; Wasserman, 1989 and Bhagat, 1990).

The value associated with each neuron (output signal) is calculated by equation 9.

$$x_j^s = f\left(\sum_i (w_{ji}^s \cdot x_i^{s-1})\right) = f(I_j) \quad (9)$$

where: “ x_j^s ” is the signal from the neuron “j” at layer “s”; “ w_{ji}^s ” is the weight associated to link between the neuron “j” at layer “s” and the neuron “i” at layer “s-1” and “ x_i^{s-1} ” is the signal from the neuron “i” at layer “s-1”.

The summation presented on equation 9 cannot be the output of the neuron, because the final ANN model would be simplified to a linear model (Wasserman, 1989). This value must be transformed by means of a transfer function, typically a sigmoid, as in equation 10.

$$f(I_j) = \frac{1}{1 + \exp(-I_j)} \quad (10)$$

Once input data is supplied to the ANN, as on Figure 2, the net calculates the output data, given that a particular set of weights is considered. The ANN is only able to calculate correct estimates if it is trained, in other words, if the weights are adjusted according to experimental known relationships input-output.

Details about the neural network algorithm calculations and training processes may be found in Rumelhart et al. (1986), Wasserman (1989) and Bhagat (1990).

2.3. Genetic Algorithms

Genetic Algorithm (GA), firstly published in Holland’s (1975) monograph, is a powerful search method based on natural evolution (Holland, 1976; Wang, 1997), considered part of the Artificial Intelligence field (Pham and Pham, 1999). The algorithm does not calculate solutions, but it encourages the best ones to survive generation after generation, while new solutions are created by a mixture of the best solutions of previous generation. Its advantages are: global search; less likely to converge to a local optima; searching from a population of points and not from a single point; the objective function may be a black box and no derivative information is required; every iteration presents a better estimative of the solution and multiple solutions may be found (Goldberg, 1989; Garrard and Fraga, 1998).

GA deals with a population of possible solutions (or individuals), that are evaluated at every generation. The individuals are created according to particular GA operators, always maintaining variability among the solutions. Normally population size is constant throughout generations and it must be optimized, keeping the balance between precision and computing time. In large populations, the probability of finding a better individual in small number of generations is higher, but computing time will be larger. Some authors report methodologies for population size calculations, but in practice it is set as large as computing time allows (Goldberg et al., 1992; Carrol, 1996a; Carrol, 1996b).

The possible solutions (individuals of the population) are represented by chromosomes. They are mathematically a vector with the parameters of the studied model. As an example, if a 4rd order polynomial is used as a model; the chromosomes would contain 5 genes, as the model has 5 parameters. In the case of an ANN, the chromosome will contain as much genes as the weights of the studied ANN. Each position of the chromosome is associated with a defined weight.

When the model has small number of parameters (less than 4, arbitrarily), the operations with the chromosomes lose its meaning and each gene should not be represented by the value of the parameter, but as a binary representation (Goldberg, 1989; Davis, 1991). Depending on the precision of the study, a single parameter may be written as a sequence of “0” and “1”, so that the chromosome has many more genes than the number of parameters. In this way, the crossover operations are much more meaningful. As the ANN generally contains much more parameters than 4, there is no need to use the binary representation, and each gene of the chromosomes is the real value of the weights (real code).

Each iteration of the GA is called a generation. The initial generation is normally formed by a population of chromosomes whose values are chosen randomly. This initial set of random solutions is evaluated, using a model according to the studied problem. The evaluation of the individuals (solutions) is an important operation of the GA, once it is necessary to rank the solutions to identify the fittest individuals, which will survive and procreate.

When GA is used for data fit, a model has to be chosen to represent the input-output relationship over experimental data. In this work, the reactor simulator is the model, which contains the ANN for calculating the rate of reaction. It is a hybrid model, composed by a deterministic part for fixed-bed reactor representation and by an ANN part for calculation of the rate of reaction. The parameters for the reactor model are well defined and given by the user, while the parameters for the ANN will be adjusted on the training session, using GA, allowing the simulator to fit experimental data.

The best chromosomes will contain the best ANN weights that make the simulator calculate conversion and selectivity values closer to experimental measurements, for a specific process condition. In this case, the ANN is assumed to calculate the correct rate of reaction, but once it acts as built-in model, no attempt is made to this comparison. The objective function of the GA for this case will be a composition of the differences between conversion and selectivity calculated by the simulator and the experimental values:

$$E = \sum_{i=1}^N \left(0.25 * (\chi_C - \chi_E)^2 + 0.25 * (S_C - S_E)_{HCHO}^2 + 0.25 * (S_C - S_E)_{CO_2}^2 + 0.25 * (S_C - S_E)_{CO}^2 \right) \quad (11)$$

where: “E” is the fitting error; “N” is the number of experimental data points; “ χ ” is the methanol conversion; “S” is the selectivity; “C” stands for calculated values; “E” stands for experimental values; “HCHO” term refers to the selectivity towards formaldehyde; “CO₂” term refers to the selectivity towards carbon dioxide and “CO” term refers to the selectivity towards carbon monoxide.

In this case, the selectivity and the conversion have the same importance on the “E” calculation, once all variables range from 0 to 1. In some cases, one of these factors may have higher importance to force the algorithm to improve the fitting efforts in a particular output.

After evaluating the individuals of the first generation, the best solutions (“lower E” parents) are mixed to generate the new individuals (children). The next generation of individuals is composed by children of the individuals from the previous generation. The parents (best solution of a generation) may or may not be maintained in the new generation. Usually, they are maintained in order to prevent losing this good solution in case of the children are less able than the parents (elitism). There are two ways to select the parents:

- *Selection of best individuals*

In this case, the best individuals of a generation are selected to be the parents of the new generation. The best individuals are the ones with better objective-function value. The number of parents in each generation may be fixed by user (generally the number of parents is adjusted to obtain better GA performance) or a limit may be defined by user (the selected parents are the ones with objective value better than certain limit). The selected individuals are grouped in pairs to generate children. The pairing method may vary: priority to the best individuals or random pairing.

- *Tournament*

Two pairs are randomly chosen. The best individual of each pair is selected and the two selected individuals generate a child. Two new pairs are chosen and the process is repeated until the new generation is completed.

Children are created from the mixture of the parents’ chromosomes. Initially the pair of parents is selected and then the child chromosome is created by the following ways:

- *Single-point crossover*

The chromosome from one of the parents is copied to the child (e.g.: “abcde”). If the chromosome of the second parent is “ABCDE”, a random point of it is selected as cross-over point, as an example, between genes “C” and “D”. Then, part of the second parent’s chromosome is copied over the chromosome of the child and the result is “abcDE”.

- *Uniform crossover* (Syswerda, 1989)

A combination of any order with the parents’ chromosomes, as: “aBcDe” or “AbcdE” or “abCDe”.

- *Single or Uniform crossover?*

Researchers give probabilities for each case (uniform or single), distributing children formation through the two methods. Carrol (1996a) defined equal probabilities for them.

The number of children per pair is a relatively new question on GA community. Generally, researchers use one child per parents’ pair. Some papers (Carrol, 1996a; Costa and Maciel Filho, 2005) point out better results with 2 children per pair. One important feature of single crossover is that it can produce children that are radically different from its parents. Another important feature is that it will not introduce differences for a gene in a position where both parents have the same value for the gene.

Crossover is an extremely important component of a genetic algorithm. Many researchers believe that if it is excluded, the result is no longer a GA and performance is degraded on a variety of problems. This claim has not been made for mutation operators (Davis, 1991).

As in nature, a mutation on a gene of some children may occur. It is simulated in two ways:

- *Creep Mutation*

One gene (parameter) of an individual “just-born” may be slightly changed. In other words, a child with a chromosome “abCdE” may mutate to a chromosome “abCdF”, where “F” is not a gene from any of the two parents, but is similar.

- *Jump mutation*

The same case of creep mutation, but mutation is larger. An individual with a chromosome “abCdE” may mutate to “abCdP”, where “P” is a gene very different from the parents’. A few new individuals may be completely random, simulating a big mutation on all genes.

- *Jump or Creep mutation?*

The probability for each type of mutation is defined by user. As a reference for starting the studies, the probability for Creep mutation may be set as “1/n” and the probability for Jump mutation as “2/n”, where “n” is population size (Carrol, 1996a).

Mutation may occur in one or more genes of the individual. The probability of mutation for each gene is the same.

Using the crossover and mutation operators, the new generation of individuals is composed by children, whose chromosomes were formed by mating the parents’ chromosomes. Part of the individuals of the new generation may be formed randomly. All individuals are evaluated again and a ranked, in order to select the fittest to pair for the next generation.

The main goal of the GA operators (crossover and mutation) is to keep the variability of the population, preventing the algorithm to converge to one solution. If all individuals of the population are much similar one to another, the algorithm will have no possibility to find out a better solution. GA algorithm may be run for a defined number of generations or until a certain error “E” is achieved. The best solution, in this case, is the

best set of weights that allows the ANN to fit better the experimental data. The final set of weights is then stored in a data file, for future use by the simulator.

2.4. Training

ANN training using this built-in approach is performed according to the following steps, based on a defined reactor and process data. Figure 3 exemplifies the built-in training system.

- A collection of “N” experimental points is taken: inputs and outputs for the simulator;
- The first generation of GA establishes a population “P” of random solutions (“solution” or “individual” here is a set of weights to the ANN);
- For each individual of the population “P”, the weights stored in the chromosome of the individual are copied to the ANN input file;
- The simulator is run for all “N” experimental conditions and the simulation error “E” is calculated, according to Eq. 11;
- The previous step is repeated for each one of the “P” individuals;
- The individuals of the population are ranked according to the lower “E” value;
- The lowest “E” individual is kept for the next generation (elitism);
- The better individuals (lower “E”) are selected to mate and generate children according to the operators described above;
- Once the new generation is populated with “P” new individuals, the procedure is repeated;
- After a defined number of generation or until the error “E” lies below a certain limit, given the desired precision for the estimates, the procedure is stopped. The best individual of the last generation contains the best set of weights that allows the hybrid simulator to predict the better values of conversion and selectivity, with no attempt to the rate of reaction data.

3. Results and Discussion

In this work, an ANN was trained using the built-in procedure based on GA, as part of a fixed-bed formaldehyde silver reactor simulator. In the first case, experimental data obtained from literature reported by Waterhouse et al. (2004a) was used to train the ANN. The second case was run using actual industrial data. Both cases are from silver process.

3.1. ANN training with experimental data from the literature

Consistent experimental work from Waterhouse and al. (2004a) was used as an example. They performed the experiments with a fixed-bed microreactor, filled with silver catalyst, using water at feed (water ballast process). Molar feed composition was $\text{CH}_3\text{OH}/\text{O}_2/\text{H}_2\text{O}/\text{He} = 2.25/1.00/1.70/20.00$ with molar ratio MeOH/O_2 of 2.25, molar ratio $\text{H}_2\text{O}/\text{MeOH}$ of 0.76 and space velocity of $1.25 \cdot 10^5 \text{ h}^{-1}$ (residence time of 29 msec, calculated using the ratio of reactor volume containing catalyst to gas volumetric flowrate at reaction temperature). Bed temperature was varied, covering the range 227 – 827 °C.

A set of 17 data points on the range 327 – 800 °C was considered from Waterhouse’s (2004a) study, correlating process conditions with conversion and selectivity.

The fitting procedure and ANN training were performed according to the steps stated above. GA features used in this work were

- Population size: 100
- Parents selection: best 50 individuals
- Chromosome code: real
- Number of children: 1 per pair of parents
- Single-point crossover probability: 50%
- Uniform crossover probability: 50%
- Creep mutation probability: 6.6 %
- Severity of creep mutation: $\pm 10 \%$ of gene value
- Jump mutation probability: 3.4 %
- Severity of jump mutation: $\pm 80 \%$ of gene value

Population size and the number of cycles were set as high as possible to reach the desired precision within a reasonable computing time. The higher the population size, the higher the probability of generating a better solution in the new generation. The best population size in the cases studied here was found to be 100, considering 3,000 generations. The ANN was configured with 12 neurons at hidden layer, based on previous study (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007b).

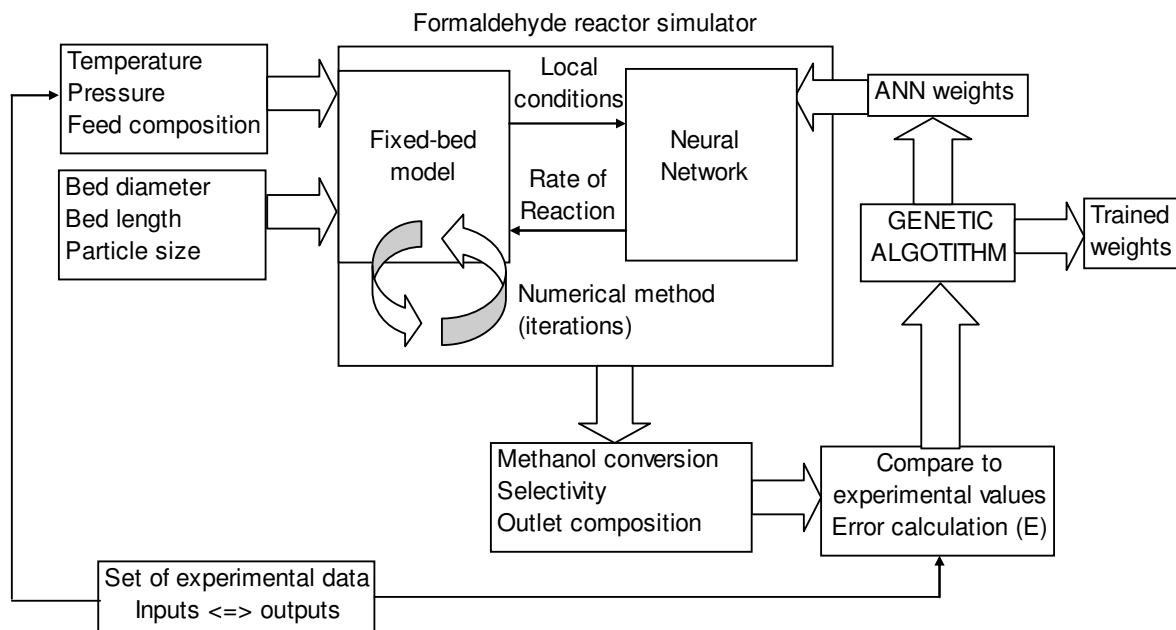


Figure 3: Built-in training system

The best 50 individuals of a generation were selected to be the parents for the new generation. If this number is small and the best individuals of a generation are much similar one to the other, the crossover operator will be less likely to improve the solution and the algorithm will count on the chance of a successful mutation to occur in order to produce a better solution. In this case, this number may be increased to include in the parents set other individuals that are not so good, but add variability to enhance the crossover operator. In our studies, the parents set was started with 20% of the population size, arbitrarily, and it was increased to 50% to improve GA performance.

The single-point crossover probability was set equal to the uniform crossover probability, according to the studies of Carrol (1996a). The jump mutation probability was set as half of the creep mutation probability (Carrol, 1996a), starting with an approximate probability of “1/n” (“n” is the population size) and increasing this value if the algorithm takes too many generations to produce a better individual. In this study, the jump mutation probability was increased to 3.4% to achieve a good algorithm performance.

In the case of a mutation, the gene values were changed by the percentages stated above ($\pm 10\%$ and $\pm 80\%$). These values were defined as default after several GA studies performed by the authors with different applications.

The training procedure was run for 3,000 GA generations, spending approximately 200 computing hours (Pentium-4, 2.66 GHz, 480MB RAM). Final model error (objective function “E”, as in Eq.11) divided by the number of data points was $2.27 \cdot 10^{-4}$.

Simulated results were plotted against the experimental ones on Figure 4, showing good agreement. Conversions values showed good correlation (0.985) and selectivity values presented excellent correlation (> 0.99). All values are concentrated along the 45° line.

The individual selected after the last GA generation contains the best set of weights from the training process. These weights were used to simulate new cases for a control data set in order to validate the training. Figure 5 shows the experimental conversion versus the simulated conversion; Figure 6 shows the experimental selectivity (towards HCHO, CO₂ and CO) versus the simulated selectivity, for the same process conditions. Excellent agreement was obtained in both cases, reinforcing the good training evaluation.

According to literature (Papes Filho and Maciel Filho, 2007c) methanol conversion increases monotonically with increasing temperature and this trend was also observed for the simulated results. For lower temperatures, simulated conversion was approximately 2 p.p. (percentage points) higher than experimental ones. For the temperature range of interest (600 – 700 °C), the simulated values were approximately 2 p.p. lower than experimental conversions. At 750 °C, the experimental conversion is 100%, while the simulator predicted 98.3% and only at 777 °C, the simulated conversion approached 100%. The 2 p.p. deviation on conversion may be high for some cases, but this difference can be easily managed on simulations, once it remains almost constant on the industrial working temperature range.

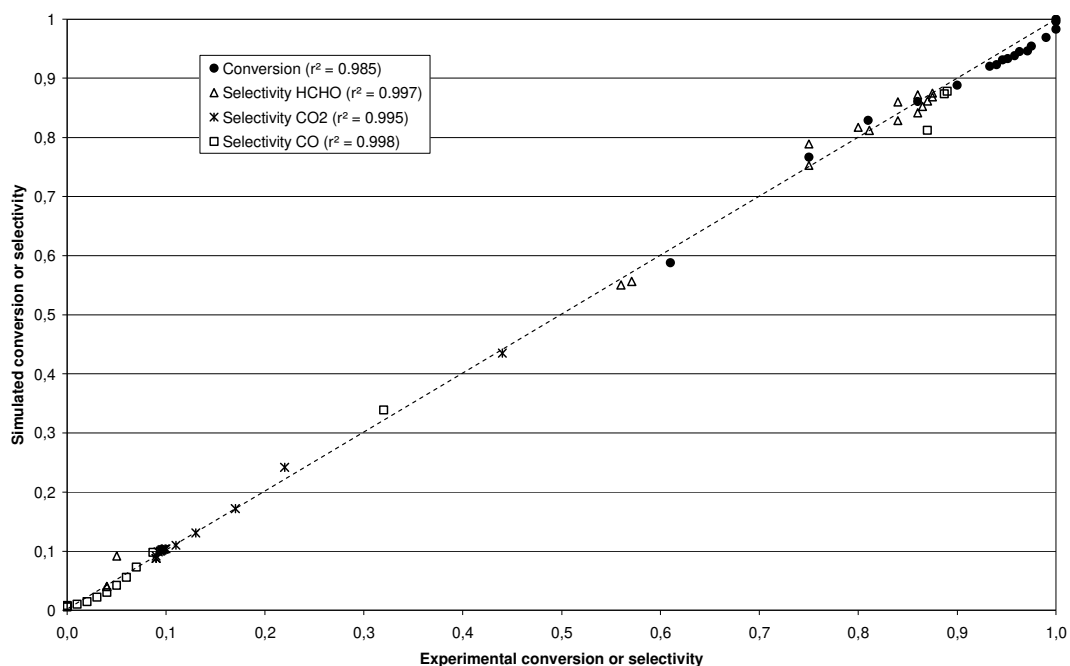


Figure 4: simulated results plotted against experimental measurements from Waterhouse et al. (2004a).

Simulated selectivity (Figure 6) expresses well the experimental data. Some deviation is seen on the formaldehyde and carbon dioxide selectivity below 600 °C, what is not critical once it is below the industrial operation range. The simulation can successfully represent the formaldehyde selectivity behaviour, showing a maximum close to 600 °C, almost constant close to this temperature (plateau). In direction of lower temperatures, the formaldehyde selectivity decreases consistently and, in the other direction, as temperature approaches 700 °C, there is a drop, with corresponding quick increase on carbon dioxide selectivity due to the gas phase decomposition of formaldehyde.

Best formaldehyde selectivity is reported to be in the range 620 – 650 °C (Papes Filho and Maciel Filho, 2007c). Simulated selectivity values indicate a maximum at about 625 °C, in agreement with Waterhouse's results.

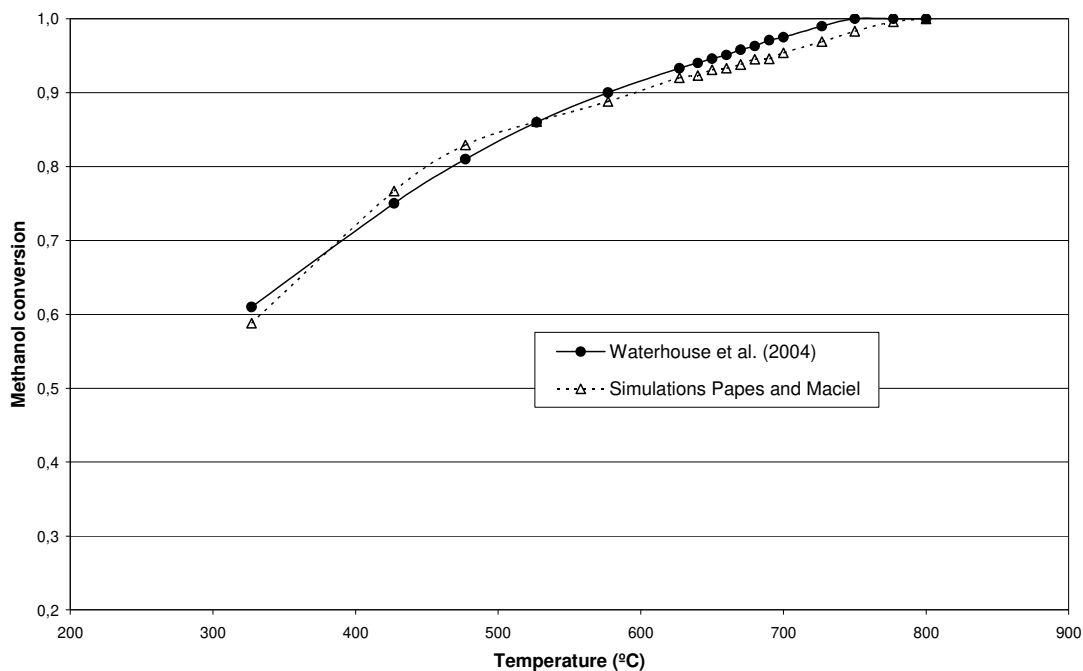


Figure 5: simulated conversion against experimental measurements from Waterhouse et al. (2004a).

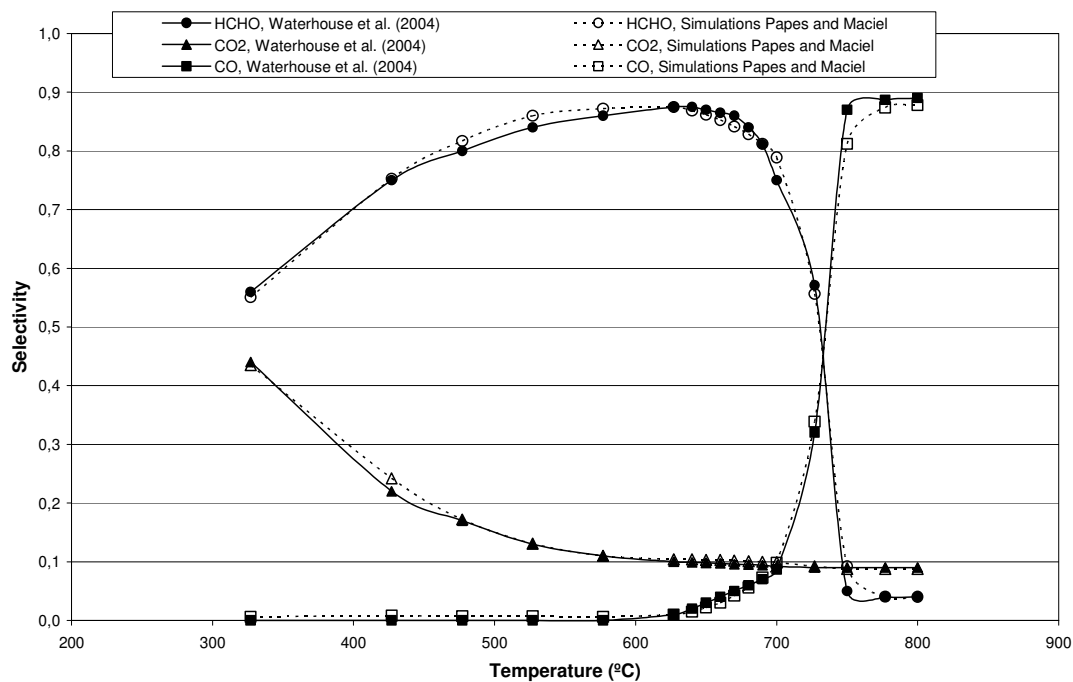


Figure 6: simulated selectivity against experimental measurements from Waterhouse et al. (2004a).

The explanation for the increase of formaldehyde selectivity with increasing temperatures below 600 °C is controversial. Lefferts et al (1986), Nagy et al (1998), Van Veen et al (2002) and Waterhouse et al. (2004a) explain the phenomena based on the influence of different oxygen species adsorbed throughout the silver surface on the reaction mechanism. Andreasen et al (2003, 2005), based on a reaction mechanism proposed by Wachs and Madix (1978), consider that a reaction in serial mode, where carbon dioxide is formed through formaldehyde oxidation, explains the selectivity phenomena, as the activation energy for methanol oxidation

is always larger than carbon dioxide formation one, making the rate of formaldehyde formation to increase faster than formaldehyde combustion with increasing temperature. Oxygen is rapidly consumed in the methanol oxidation reaction and smaller oxidant concentration inhibits further oxidation of formaldehyde. This behavior might be opposite (decrease on formaldehyde selectivity with increasing temperature) with rich oxygen mixtures, where the mechanism proposed by the researchers is believed to fail, since the unselective reaction routes seem to be suppressed (Cao and Gavriilidis, 2005).

The selectivity of carbon dioxide is high at lower temperatures and decreases consistently with increasing temperature. This effect reflects the increasing thermal instability and lower surface coverage of particular oxygen species on the catalyst surface at higher temperatures.

The formaldehyde decomposition is not significant at lower temperatures, but above 600 °C and with high formaldehyde availability, the selectivity towards carbon monoxide increase fast, associated with a drop on formaldehyde selectivity.

Temperatures below 327 °C are not representative and were not considered here. Negligible amounts of formic acid are formed under the conditions of the experiments and the selectivity toward this by-product was not simulated.

Analysis of variance over the simulated data shows sum of squares of the model (SQM) of 25.84 and sum of the squares of the residual (SQR) of 0.015. F-value, according to equation 12, is 1672, that is clearly significant indicating good fit (Box and Hunter, 1978).

$$F_{CALC} = \frac{SQM}{SQR} \quad (12)$$

The built-in training approach presented here was compared to the hybrid training approach developed in previous work (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007b). The hybrid training is an association of GA and Back-Propagation (BP), where the net was trained using rate of reaction data, extracted from experimental conversion and selectivity. The training starts with GA, adjusting the net weights from an initial random population and providing a solution believed to be close to the optimum. In the sequence, BP assumes the training task, starting from the GA solution, in order to refine it towards the optimum.

The rate of reaction data were not available for this comparative training and they had to be extracted from process data according to the procedure described by Papes Filho (2007): a simplified kinetic model was implemented into the reactor simulator and, for each process point, the model parameters were adjusted until the conversion and selectivity calculated by the simulator matched the experimental ones. Once the individual point was fit, the rate of reaction profile through the catalytic bed was saved with the associated local operational conditions. The adjustment on the simplified kinetic model was only valid for a single data point, but after repeating the procedure for all available experimental points, a huge set of rate of reaction data may be obtained (Papes Filho and Maciel Filho, 2007a).

The hybrid approach joins the advantages of GA (broader search, increasing the probability to find the global optimum) and BP (oriented training, faster than GA), but has the inconvenient of using the rate of reaction data, that have to be extracted by a complicated procedure. The built-in approach, in the other hand, uses directly measured data for ANN training, but it is much more time consuming.

Figure 7 shows a comparison between the simulated formaldehyde selectivity for Waterhouse's (2004a) experiments, by the built-in and hybrid approaches. For temperatures below 650 °C, the two methods calculate approximately the same values. For higher temperatures, the built-in approach estimates values closer to the experimental ones than the hybrid method.

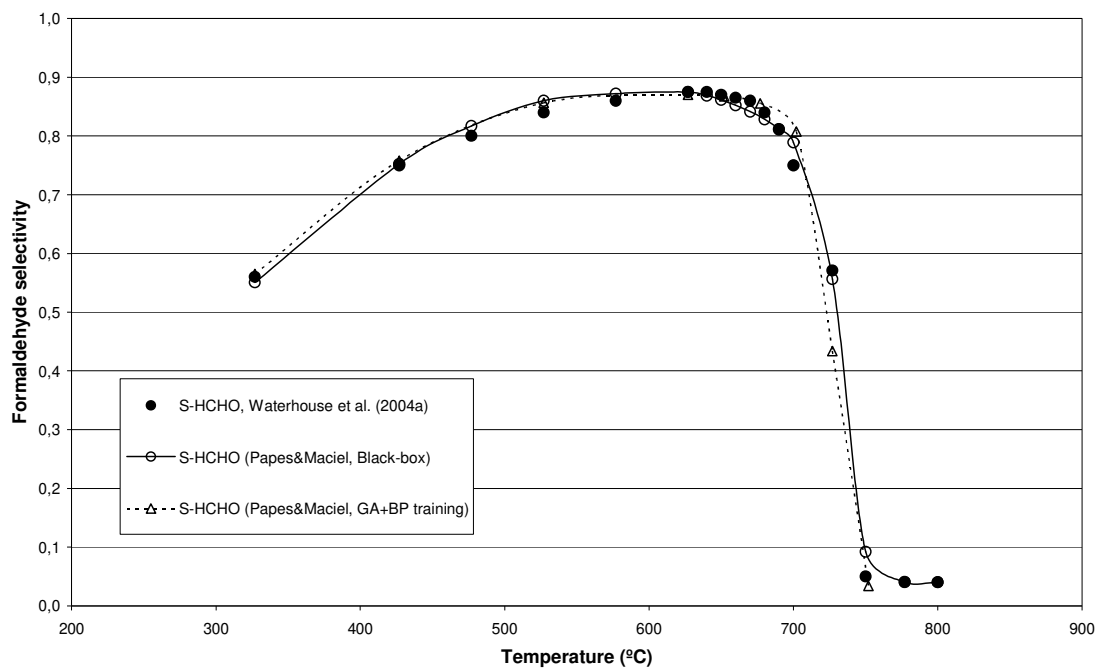


Figure 7: Simulated formaldehyde selectivity using different training approaches (hybrid method and black-box method) plotted against experimental values.

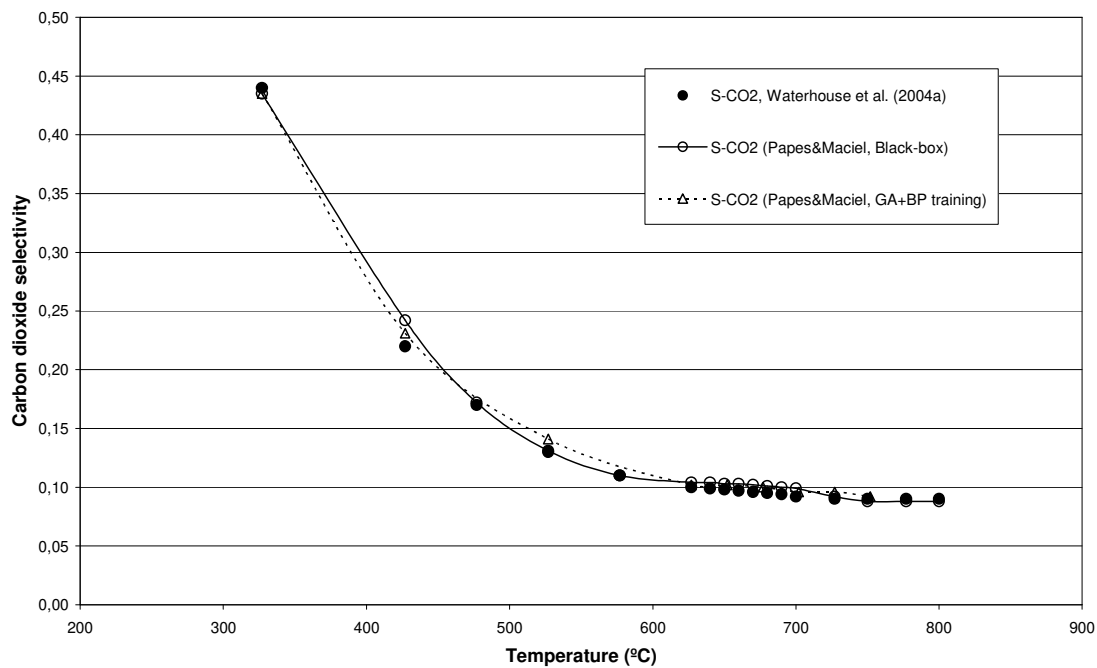


Figure 8: Simulated carbon dioxide selectivity using different training approaches (hybrid method and black-box method) plotted against experimental values.

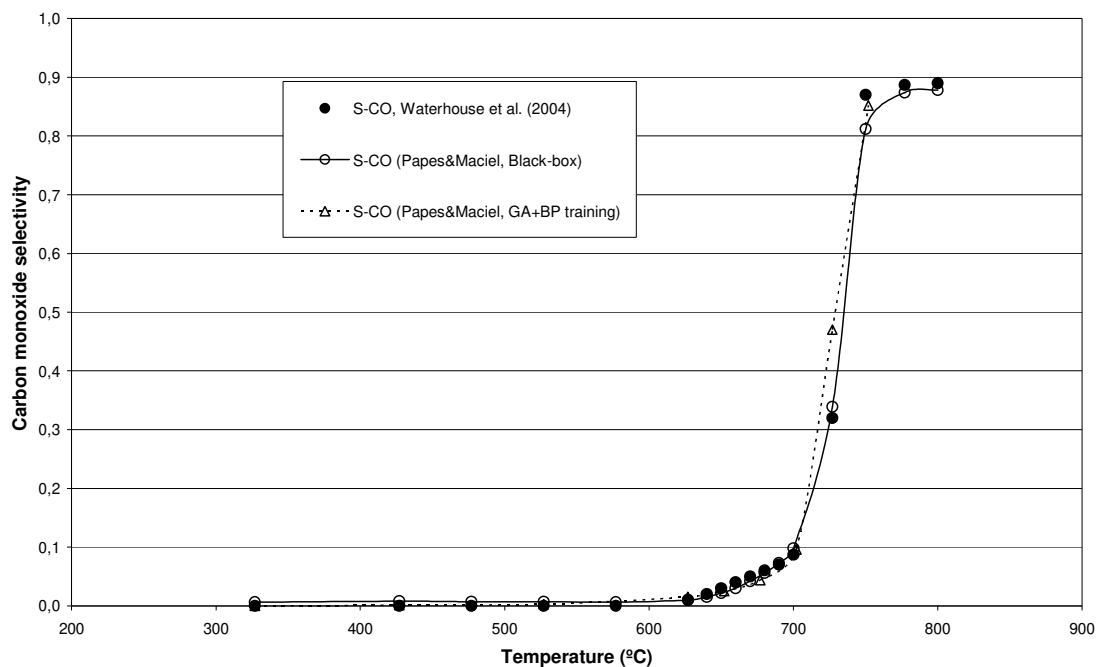


Figure 9: Simulated carbon monoxide selectivity using different training approaches (hybrid method and black-box method) plotted against experimental values.

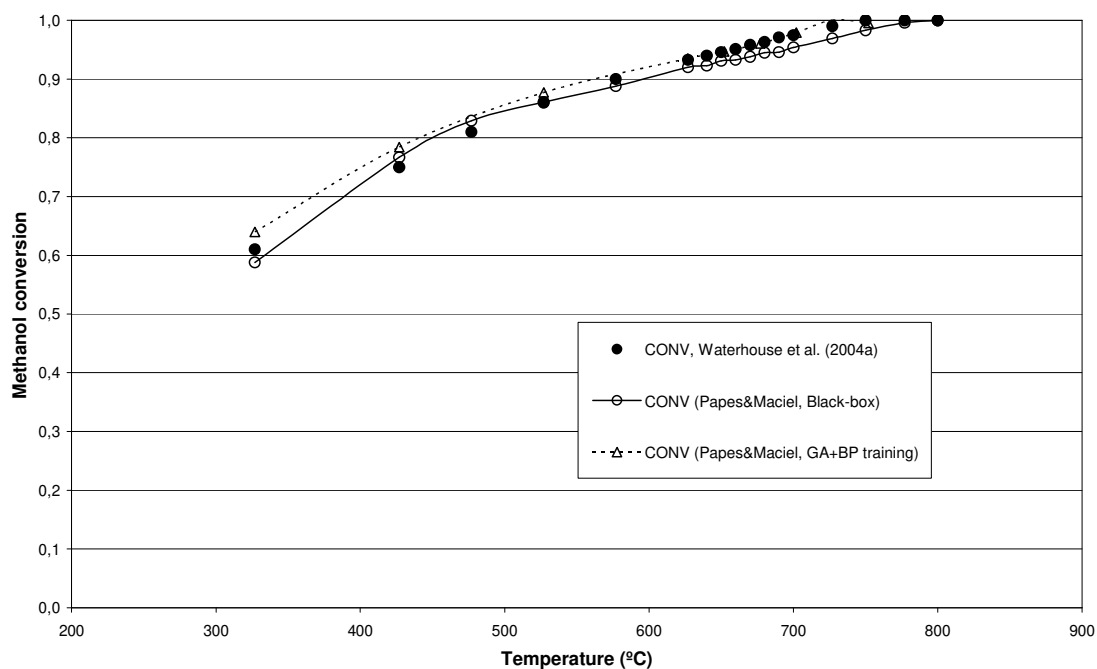


Figure 10: Simulated methanol conversion using different training approaches (hybrid method and black-box method) plotted against experimental values.

The same comparison was made for carbon dioxide selectivity (Figure 8), carbon monoxide selectivity (Figure 9) and methanol conversion (Figure 10) with very consistent approximation between the results with the two training methods. This is an outstanding achievement, once the built-in training method can reach the same performance of standard methods, using directly process data, with no need of rate of reaction data.

3.2. ANN training with industrial data;

In a second case, a set of 50 measured data was used to train the ANN for a reactor with 1.5 m diameter and 20 mm silver bed height in operation at an average size industrial formaldehyde plant with fresh catalyst. Collected data consisted in bed temperature, bed pressure, feed composition, conversion and selectivity. Actual operation data were extrapolated in order to obtain a broader range for the variables, allowing a wider analysis of the system. Temperature ranged from 580 to 720 °C, MeOH/O₂ molar ratio varied between 2.0 and 3.4, H₂O/MeOH molar ratio ranged from 0.07 to 0.44 and residence time from 4.7 to 8.8 msec. Reactor pressure was constant, at 1.2 atm. Oxygen was supplied as atmospheric air.

GA features used in this case were the same as the ones set for the previous case, with the ANN using 12 neurons at hidden layer accordingly. The training procedure was run for 1,000 GA generations, spending approximately 200 computing hours (Pentium-4, 2.66 GHz, 480MB RAM). Final model error (objective function “E”, as in Eq. 11) divided by the number of data points was $9.26 \cdot 10^{-5}$.

The ANN was trained according to the built-in procedure and the optimum weights for the particular reactor were stored in a data file. A control set of data (not used for training) was considered for validation purposes, comparing known conversion and selectivity values with simulated ones. Simulated results were plotted against the experimental ones on Figure 11, showing very good agreement. Conversions and CO₂ selectivity values showed good correlation (0.974 and 0.960 respectively), while selectivity towards HCHO and CO presented excellent correlation (> 0.99). All values are concentrated along the 45° line. Analysis of variance over the simulated data shows sum of squares of the model of 80.76 and sum of the squares of the residual of 0.019. F-value is 4361, that is very significant, indicating that the ANN model could successfully fit the measured data (Box and Hunter, 1978).

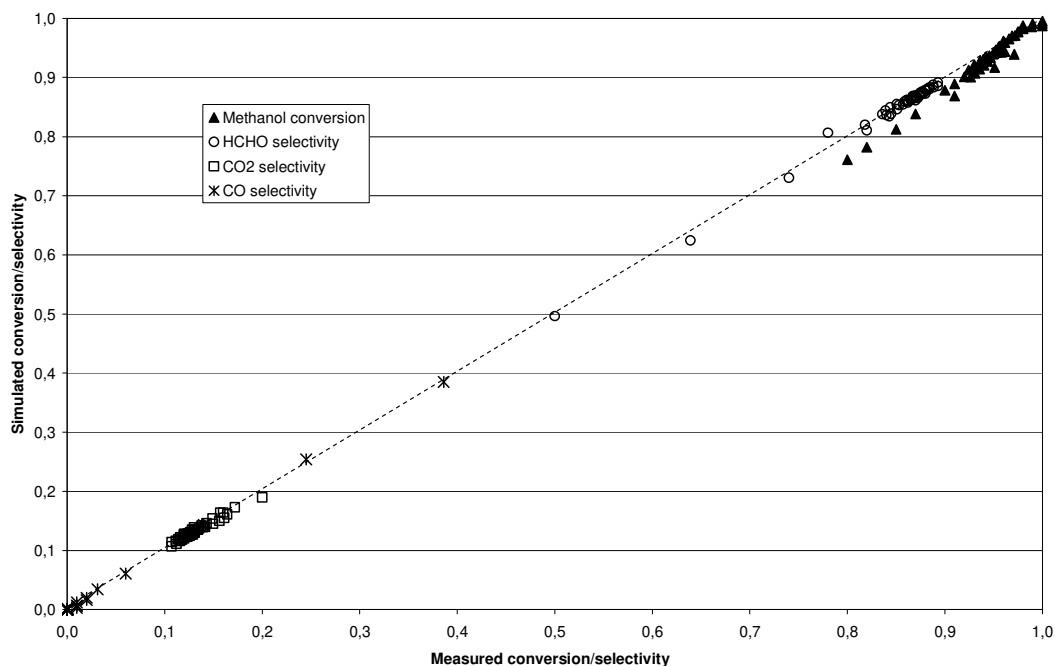


Figure 11: Simulated conversion and selectivity plotted against industrial measured values for control conditions (ANN training validation).

Industrial data used in this case is not as organized as the experimental data from Waterhouse et al. (2004a) and a complete comparison plot similar to Figures 5 and 6 is not possible. However, Figure 12 presents simulations in the temperature range from 580 to 720 °C, maintaining the other variables at the standard process conditions stated above, including the available measured information. Once again, good correlation was obtained, indicating good fit with the presented training algorithm. The trends for conversion and selectivity presented on Figure 12 are in accordance with the results reported on literature, well represented by Waterhouse et al. (2004a) studies and discussed above.

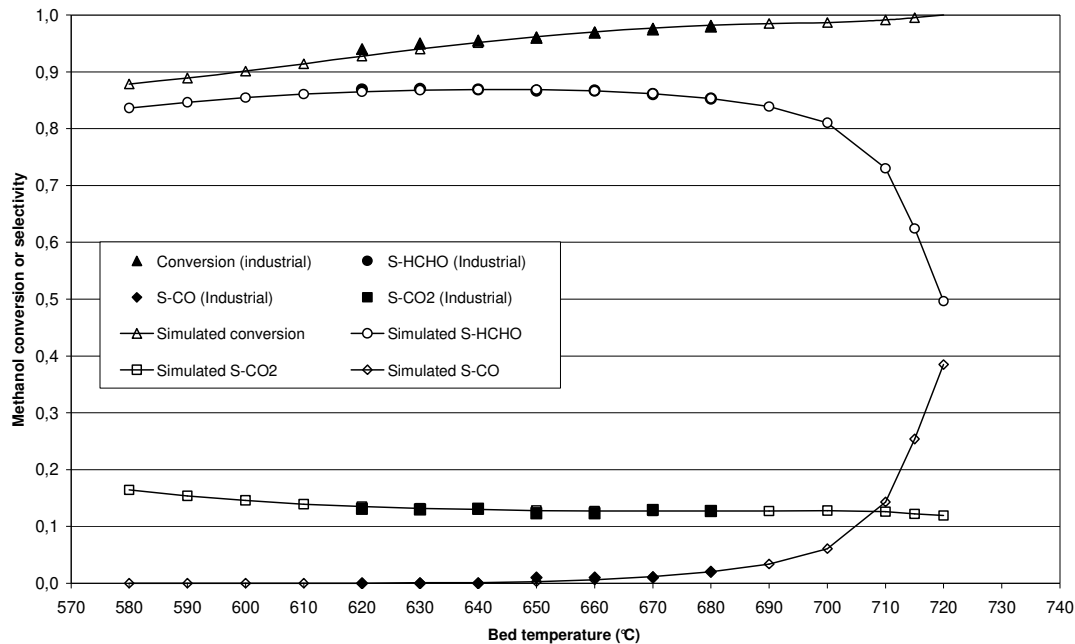


Figure 12: Simulated conversion and selectivity for various temperatures (other parameters remained constant) and measured values.

It is important to note that simulations based on trained ANN over a specific set of data are fully valid only for the reactor from which that data was obtained. The trends observed for conversion and selectivity as a function of all studied variables are valid for a wide variety of reactors operated under the same Silver process, however, precise simulation values may vary from one reactor to another, depending on the data set. The same warning applies to simulations with fresh and aged catalyst for a particular reactor.

For both cases considered as examples here, the built-in approach for ANN training provided good results concerning simulated reactor performance in comparison with experimental data (from literature or from industrial plant). This is a clear advantage for quick simulation of systems, once process data is generally available, while kinetic data (rate of reaction) is not. The built-in approach may take much longer computing times than other approaches, but nowadays computer capacity is much more available than headcounts.

ANN is a convenient model for the built-in approach, once it captures the essence of the data set, and there is no need to state hypothesis about mass transfer limitations on catalyst surface (kinetic regimen), reaction mechanism, limiting steps or catalyst activity homogeneity. This claim is not applicable to deterministic models, which fail when these hypotheses are not correctly formulated or when experimental data are incorrectly obtained.

3.3. Alternative search algorithm for the built-in training

It was tried to use another classical search algorithm (SQP – Sequential Quadratic Programming) to perform this task in the place of GA. Theoretically, if it is provided an initial estimative for all weights, SQP would be able to reach an optimum set of weights as GA did. A commercial routine from Fortran’s math library was used to optimize the GA weights, considering the simulator itself the objective function: the SQP routine defined the weights to be evaluated, which were saved in a data file, and the reactor simulator was run for all experimental data set, calculating the objective function “E” with the simulator outputs. The “E” value returned to the SQP routine to establish the new set of weights to be evaluated. The procedure was supposed to be repeated until the convergence of “E”, defining the best set of weights.

After several trials, changing many parameters of the SQP routine, it was proven to be impossible to use the SQP approach for training the ANN by the built-in method. After some iterations, SQP was not able to calculate the derivatives and it stopped with an error.

Here it was possible to verify in practice one of the disadvantages of SQP: when the function is complex it may not be able to properly calculate the derivatives and cannot indicate the search direction, consequently not reaching any optimum.

In the case of ANN, the model is extremely complex and the complexity varies depending on the number of neurons. The derivatives may be difficult to be estimated, what makes SQP a bad choice. In the other hand, GA has no constraints concerning ANN training besides the long computing time and has proven to be a robust method for this task.

4. Conclusion

A built-in training algorithm for Artificial Neural Network (ANN) was presented in this paper. The ANN was implemented inside a fixed-bed reactor simulator for calculating the rates of the three reactions involved on methanol oxidation to formaldehyde with silver catalyst: formaldehyde formation, oxidation and decomposition.

The ANN was trained as a black-box inside the simulator: the ANN weights were adjusted by a Genetic Algorithm (GA), minimizing the difference between simulator outputs and experimental conversion/selectivity, with no attempt to the ANN output (reaction rate) directly.

Using GA operators, the training starts with a random population of sets for ANN weights. For each of these sets (possible solutions or GA “individuals”), the reactor simulator is run for all experimental data points, calculating the error between the simulated conversion/selectivity and experimental ones. The best individuals are selected and mixed to generate a new population of possible solutions to be evaluated, according to GA operators. After a defined number of generations (iterations), the best set of weights allows the simulator to predict correct conversion and selectivity, while rate of reaction is believed to be right, once there are no experimental rates to compare. A classical search method – SQP – was tested in place of the genetic algorithm for this task and it did not performed well at all.

Successful results were obtained by training the ANN inside the simulator, with the built-in approach, using experimental data from literature and industrial data. Estimated values were very close to experimental ones in both cases. Comparison with standard ANN training procedure (BP) showed that equal or better performance can be achieved with the approach presented here.

The benefit of this training method is the simplicity of using directly measured data (conversion and selectivity) to train the ANN, with no need to calculate or measure rate of the reactions involved, which is a difficult and time consuming task. The disadvantage is the large computing time: the built-in training method may take several days, while the standard ANN training itself may take some hours. For plant personnel, the final balance is an advantage with the built-in method, once normally there is no available headcount to generate reaction rate data, and the computers can do the hard job.

The neural network algorithm has proven to be powerful for modelling the formaldehyde kinetics based on measured data, making possible the development of a simulator for the silver reactor applicable to industrial conditions. It captures the essence of the data set, and there is no need to state hypothesis about mass transfer limitations on catalyst surface (kinetic regimen), reaction mechanism, limiting steps or catalyst activity homogeneity.

Information provided by the simulations, presented on this paper, is essential for understanding the relationship between the operational variables and the reactor performance as an orientation for the optimized management of a silver reactor in order to increase plant profitability by reducing methanol consumption and pollutant by-product generation.

The reactor simulator, the ANN subroutine for the calculation of the rate of reaction and the GA training program were developed by the authors using Fortran code. To the best of our knowledge, this is the first time GA is used to train an ANN built-in a reactor simulator, employing only process macro information (conversion and selectivity) and not the rate of the reactions.

References

- ABRAF (Brazilian Association of Formaldehyde Manufacturers) report; "Panorama of productive chain", www.abraf.com.br, 2004.
- Andreasen, A.; Lynggaard, H.; Stegelmann, C. and Stoltze, P.; "A microkinetic model of the methanol oxidation over silver", *Surface Science*, 544, pp.5-23, 2003.
- Andreasen, A.; Lynggaard, H.; Stegelmann, C. and Stoltze, P.; "Simplified kinetic models of methanol oxidation on silver", *Applied Catalysis A: General*, 289, pp.267-273, 2005.
- Barteau, M and Madix, R.J.; *Surf. Sci*, 40, p.108, 1984.
- Bazilio, C.A.; Thomas, W.J.; Ullah, U. and Hayes, K.E.; "The catalytic oxidation of methanol", *Proc. R. Soc. Lond. A*, 399, pp.181-194, 1985.
- Bhagat, P.; "An Introduction to Neural Nets", *Chemical Engineering Progress*, August, p.55, 1990.
- Bhattacharyya, S.K.; Nag, N.K. and Ganguly, N.D.; "Kinetics of vapor-phase oxidation of methanol on reduced silver catalyst", *J. of Catalysis*, v.23, i.2, pp.158-167, 1971.
- Box, G.E.P and Hunter, J.S.; "Statistics for experimenters", Wiley and Sons, 1st ed., New York, 1978.
- Cao, E; Gavriilidis, A.; "Oxidative dehydrogenation of methanol in a microstructured reactor", *Catalysis Today*, 110, pp.154-163, 2005.
- Carrol, D.L.; "Chemical laser modeling with genetic algorithm", *AIAA Journal*, v.34, no 2, pp.338-346, 1996a.
- Carrol, D.; "Genetic Algorithms and Optimizing Chemical Oxygen-Iodine Lasers", *Developments in Theoretical and Applied Mechanics*, v.XVIII, pp.411-424, 1996b.
- Costa, C.B.B. and Maciel Filho, R.; "Evaluation of optimization techniques and control variable formulations for a batch cooling crystallization process", *Chemical Engineering Science*, v. 60, pp. 5312-5322, 2005.
- Crank, J. and Nicholson, P.; *Proc. Phil. Soc.*, v.43, p.50, 1947.
- Davis, L.; "Handbook of Genetic Algorithms", International Thomson Computer Press, Boston, 1991.
- Fogler, H.S.; "Elements of chemical reaction engineering", Prentice-Hall International, 2nd ed., New Jersey, p.71, 1992.
- Garrard, A. and Fraga, E.S.; "Mass exchange network synthesis using genetic algorithms", *Computers Chem. Engng.*, v.22, n.12, pp.1837-1850, 1998.
- Goldberg, D.E.; "Genetic Algorithms in Search, Optimization, and Machine Learning", Ed. Addison-Wesley Publishing Company, Inc, New York, 1989.
- Goldberg, D.E; Deb, K. and Clark, J.H.; "Genetic Algorithms, Noise and the Sizing of Populations", *Complex Systems*, 6, pp. 333-362, 1992.
- Gravilin, V.N and Popov, B.I; *Kinet. Catal.*, 6, p.799, 1965.
- Holland, J.H.; "Adaptation in natural and artificial systems", Ann Arbor: The University of Michigan Press, 1975.
- Holland, J.H.; "Adaptation", *Progress in theoretical biology*, 4, pp.263-293, 1976.
- Lefferts, L.; Ommen, J.G. and Ross, J.R.H.; "The oxidative dehydrogenation of methanol to formaldehyde over silver catalysts in relation to the oxygen-silver interaction", *Appl. Catal.*, 23, p.385, 1986.
- Lennox, B.; Montague, G.A.; Frith, A.M.; Gent, C. and Bevan, V.; "Industrial application of neural networks – an investigation", *Journal of Process Control*, v.11, pp.497-507, 2001.
- Nagy, A.; Mestl, G.; Ruhle, T.; Weinberg, G. and Schlogl, R.; "The dynamic restructuring of electrolytic silver during the formaldehyde synthesis reaction", *J. of Catalysis*, 179, pp.548-559, 1998.
- Nagy, A. and Mestl, G.; "High temperature partial oxidation reactions over silver catalysts", *Applied Catalysis A: General*, 188, pp.337-353, 1999.
- Papes Filho, A.C.; "Simulation and optimization of a silver formaldehyde reactor, using artificial intelligence techniques", PhD thesis (in English), UNICAMP – University of Campinas, Brazil, 2007.
- Papes Filho, A.C. and Cremasco, M.A.; "Correlation for estimation of diffusion coefficient for gases", *Proceedings of the 1st Brazilian Congress of Chemical Engineering – Scientific Initiation, UFSCar Ed.*, www.ufscar.br, 1995.
- Papes Filho A.C. and Maciel Filho R.; "Concurrent Engineering Reactor Design", *Computer Aided Chemical Engineering*, v.20 A, Edited by Luis Puijgagner and Antonio Espuña, Elsevier B.V., ISSN 1570-7946, pp.559-564, 2005.
- Papes Filho, A.C. and Maciel Filho, R.; "Novel approach for acquiring rate of reaction data from process information for neural network training: application to an industrial reactor for methanol oxidation to formaldehyde over silver catalyst process", to be published, 2007a.
- Papes Filho, A.C. and Maciel Filho, R.; "Hybrid training method for artificial neural networks using genetic algorithms: application to industrial methanol oxidation to formaldehyde over silver catalyst", to be published, 2007b.

- Papes Filho, A.C. and Maciel Filho, R.; "Hybrid simulation of a fixed-bed formaldehyde silver-catalyzed reactor using artificial neural networks", to be published, 2007c.
- Pham, D.T. and Pham, P.T.; "Artificial intelligence in engineering", *International Journal of Machine Tools & Manufacture*, v.39, pp. 937-949, 1999.
- Piccoli, R.L.; "Kinetic study of methanol selective oxidation to formaldehyde on iron molybdate catalyst", Master dissertation, Rijksuniversiteit Gent, Belgium, 1992.
- Press, W.H., Flannery, B.P., Teukolsky, S.A. and Vetterling, W.T.; "Numerical Recipes", Press Syndicate of the University of Cambridge, 1st ed., 1992.
- Psichogios, D.C. and Ungar, L.H.; "A hybrid neural network-first principles approach to process modeling", *AIChE Journal*, 38, 10, pp. 1499-1511, 1992.
- Qian, M.; Liauw, M.A. and Emig, G.; "Formaldehyde synthesis from methanol over silver catalysts", *Applied Catalysis A: General*, 238, pp.211-222, 2003.
- Reid, R.C.; Prausnitz, J.M. and Poling, B.E.; "The properties of gases and liquids", McGraw-Hill Book Company, 4th ed, New York., 1987.
- Rumelhart, D.E.; Hinton, G.E. and Williams, R.J.; "Learning internal representations by error propagation" in *Parallel distributed processing*, v.1, pp.318-362, 1986.
- Sandler, S.I.; "Chemical and engineering thermodynamics", John Wiley & Sons, New York, 1989.
- Santacesaria, E. and Morbidelli, M.; "Kinetics of the catalytic oxidation of methanol to formaldehyde", *Chem. Engng. Sci.*, v.36, pp.909-918, 1981.
- Syswerda, G.; "Uniform crossover in genetic algorithms", *Proceedings of the third international conference on genetic algorithms*. San Mateo, California, Morgan Kaufmann publishers, 1989.
- Treybal, R.E.; "Mass-transfer operations", McGraw-Hill International Editions, 3rd ed., Singapore, 1981
- Ullmann's Encyclopedia of Industrial Chemistry, v.A11, VHC Publishers, 5th ed., New York, 1988.
- Van Veen, A.C., Hinrichsen, O. and Muhler, M.; "Mechanistic studies on the oxidative dehydrogenation of methanol over polycrystalline silver using the temporal-analysis-of-products approach", *J. of Catalysis*, 210, pp. 53-56. 2002.
- Wachs, I.E. and Madix, R.; "The oxidation of methanol on a silver (110) catalyst", *Surface Science*, 76, pp. 531-558, 1978.
- Walker, J.F.; "Formaldehyde", Robert E. Krieger Publishing Company, 3rd Ed., New York, 1975.
- Wang, Q.J.; "Using Genetic Algorithms to Optimise Model Parameters", *Environmental Modelling & Software*, v.12, n.1, pp 27-34, 1997.
- Wasserman, P.D.; "Neural Computing: Theory and Practice", Editora van Nostrand Reinhold, 1st ed., New York, 1989
- Waterhouse, G., Bowmaker, G. and Metson, J.; "Mechanism and active sites for the partial oxidation of methanol to formaldehyde over an electrolytic silver catalyst"; *Applied Catalysis A*, 265, pp.85-101; 2004. (a)
- Waterhouse, G., Bowmaker, G. and Metson, J.; "Influence of catalyst morphology on performance of electrolytic silver catalysts for the partial oxidation of methanol to formaldehyde", *Applied Catalysis A*, 266, pp.257-273, 2004. (b)
- Welty, J.R.; Wicks, C.E. and Wilson, R.E.; "Fundamentals of momentum, heat and mass transfer", John Wiley & Sons editor, 3rd ed., New York, 1984.

5.3. Conclusões

Uma abordagem de treinamento para RNA acoplada foi apresentada nesse capítulo: a RNA foi implementada como uma sub-rotina do simulador para o reator de leito fixo, com o objetivo de calcular as taxas das três reações envolvidas na oxidação do metanol a formaldeído em catalisador de prata: formação, oxidação e decomposição do formaldeído.

A RNA foi treinada como uma “caixa-preta” dentro do simulador: os dados estimados pelo “software” foram comparados com os valores experimentais para conversão de metanol e seletividades para formaldeído, CO₂ e CO, sendo que os parâmetros da rede (pesos) foram ajustados utilizando-se algoritmo genético, sem que as taxas de reação calculadas por essa estivessem visíveis ao usuário.

Com o uso de operadores de AG, o treinamento iniciou-se com uma população aleatória de conjunto de pesos. Para cada um desses conjuntos (ou possíveis soluções ou indivíduos, no jargão do AG), o simulador do reator foi executado para todos os dados experimentais disponíveis, calculando-se o erro entre conversão/seletividade simulados e experimentais. Os melhores indivíduos são selecionados e misturados para criar uma nova população de possíveis soluções a serem avaliadas. Após certo número de iterações (ou gerações), o melhor conjunto de pesos permite ao simulador prever corretamente a conversão e seletividades, enquanto acredita-se que as taxas de reação estejam sendo corretamente calculadas, uma vez que não há dados experimentais de taxas para comparar ou validar.

Um método clássico determinístico de busca (SQP) foi testado para essa tarefa, sem sucesso.

O método de treinamento descrito nesse capítulo foi testado com dados experimentais de literatura e dados de processo industriais, com bons resultados. Valores estimados encontraram-se muito próximos dos dados experimentais em ambos os casos. Comparações com o método clássico de treinamento da RNA baseado nas taxas de reação (AG+BP) mostraram que o método acoplado apresenta desempenho igual ou superior no ajuste dos dados.

O benefício desse método de treinamento reside na simplicidade de usar diretamente dados de processo (conversão e seletividade), disponíveis em unidades industriais, para treinar a RNA, sem necessidade de calcular ou medir taxas de reação, que

é uma tarefa difícil e demorada. A desvantagem do método apresentado é o grande tempo computacional: a abordagem acoplada pode levar vários dias para ser executada, enquanto que o método clássico pode levar algumas horas. Para engenheiros e operadores de plantas, o balanço final representa uma vantagem para o método acoplado, uma vez que normalmente não há pessoal disponível para obter dados de taxa de reação, enquanto que computadores podem realizar a demorada tarefa de treinar a rede usando dados de processo.

A RNA mostrou mais uma vez seu poder para modelar a cinética do formaldeído baseada em dados experimentais, tornando possível o desenvolvimento de um simulador para o reator de prata, aplicável a condições industriais. A informação fornecida pelo simulador, apresentada nesse capítulo, é essencial para compreender as relações entre variáveis operacionais e o desempenho do reator como uma orientação para o gerenciamento otimizado da planta prata, melhorando sua rentabilidade com a redução do consumo de metanol e geração de poluentes.

O simulador do reator, a sub-rotina com a RNA para o cálculo das taxas de reação e o programa de treinamento baseado em AG foram desenvolvidos pelos autores em código Fortran. A RNA foi treinada de forma inédita com AG como uma caixa-preta dentro de um simulador de reator, empregando apenas informação macro de processo (conversão e seletividades), dispensando a necessidade de informação sobre as taxas de reação.

CAPÍTULO 6

SIMULAÇÃO HÍBRIDA DE UM REATOR DE LEITO FIXO DE FORMALDEÍDO, CATALISADO POR PRATA, USANDO REDES NEURAS ARTIFICIAIS

6.1. Introdução

Nesse Capítulo é descrito o desenvolvimento do simulador para o reator de formol com catalisador de prata, citado nos capítulos anteriores. Esse simulador pode ser considerado um modelo híbrido para o reator, uma vez que utiliza um modelo determinístico para o leito fixo e RNA para o modelo cinético.

A construção do simulador baseia-se na equação de balanço diferencial de massa, derivada da aplicação dos modelos pseudo-homogêneo, bidimensional e plug-flow para o reator tubular em estado estacionário.

A equação de balanço é aplicada às três reações de interesse, apresentadas no Capítulo 3, sendo que para cada uma determinou-se uma substância representativa: formaldeído para a reação de formação do formaldeído; CO₂ para a reação de oxidação do formaldeído e CO para a reação de decomposição do formaldeído.

As três equações diferenciais de balanço de massa são solucionadas simultaneamente, utilizando o método numérico de Crank-Nicholson. Esse método é uma variação das diferenças finitas, porém é semi-implícito e intrinsecamente estável, muito adequado para simuladores de reatores.

O reator (leito-fixo) foi considerado adiabático e isotérmico. Estudos de literatura e medições industriais corroboram a hipótese de operação adiabática. Cálculos de radiação e condução de calor pelo leito de prata, bem como medições industriais mostram que para efeitos práticos a diferença de temperatura entre a entrada e a saída do leito catalítico é pequena (da ordem de 10 °C), além disso, essa simplificação é essencial para obter um simulador estável e robusto, sem prejuízo para o desempenho do mesmo. A diferença na temperatura de entrada e saída do leito (1,5 % do set-point) é da ordem de grandeza do erro do instrumento de medição (cerca de 1%).

A corrente de alimentação do reator encontra-se a uma temperatura entre 100 e 150 °C. Antes de entrar no leito catalítico, a corrente é aquecida por radiação, completando o aquecimento na superfície do leito, onde a temperatura atinge 650 °C. Praticamente a totalidade do catalisador opera à temperatura constante de 650 °C.

A RNA foi previamente treinada com dados industriais, como apresentado nos capítulos anteriores, e é capaz de prever adequadamente as taxas de reação utilizando o conjunto ótimo de pesos arquivado.

Cálculos de equilíbrio termodinâmico mostram que as conversões de metanol podem atingir níveis de praticamente 100% e que a seletividade combinada para CO₂ e CO pode atingir 100%, demonstrando que os estudos cinéticos dessa reação são de suma importância para maximizar a geração da substância de interesse, uma vez que não é favorecida pelo equilíbrio termodinâmico.

Observou-se boa correlação entre os dados simulados e dados experimentais (conversão e seletividade). Com o “software” ajustado e validado, várias situações foram simuladas para demonstrar as interações entre as variáveis operacionais e o desempenho do reator, comparando-se com dados de literatura e dados industriais.

As variáveis operacionais estudadas foram a temperatura, a razão molar metanol-oxigênio, a razão molar água-metanol e o tempo de residência. O desempenho do reator engloba a conversão e seletividades.

As tendências encontradas foram discutidas com base em estudos publicados na literatura e no mecanismo da reação, demonstrando grande coerência.

6.2. Desenvolvimento.

O desenvolvimento desse capítulo é descrito no artigo intitulado “Hybrid Simulation of a Fixed-bed Formaldehyde Silver-catalyzed Reactor using Artificial Neural Networks”, apresentado a seguir, que será submetido para publicação em revista indexada internacional.

Hybrid Simulation of a Fixed-bed Formaldehyde Silver-catalyzed Reactor using Artificial Neural Networks

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Abstract

A hybrid simulator for formaldehyde silver-catalyzed reactor was developed in this work. The fixed-bed model was based on deterministic differential mass balance equations, solved numerically by the Crank-Nicholson algorithm. Rate of reaction data was calculated by an Artificial Neural Network (ANN), implemented as a sub-routine inside the simulator, using the trained weights based on industrial and experimental data. Detailed information about the simulator construction was reported, as well as its use for estimating operational conditions based on actual industrial data. A series of simulations were performed close to the set-point in order to illustrate the influence of bed temperature, feed molar ratio oxygen-to-methanol, feed molar ratio water-to-methanol and residence time, on the methanol conversion, selectivity towards formaldehyde, carbon dioxide and carbon monoxide. The trends obtained were compared to experimental data reported on literature, validating the simulator.

Key words: formaldehyde, silver, artificial neural networks, genetic algorithms, artificial intelligence, methanol oxidation, simulation.

1. Introduction

Formaldehyde is a key chemical intermediate for a variety of engineering products used by construction, metallurgy and automotive sectors. Despite recent health and safety concerns about the formaldehyde, it is still the most technical and economically viable alternative for the production of a series of adhesives employed on the manufacture of plywood, MDF, OSB, brake linings, brake pads, thermal insulation, foundry castings, refractory bricks, abrasives and many other materials (Walker, 1975; Pizzi, A., 1994; Pilato et al., 2000). It is the simplest aldehyde, ranked among the top 50 products of industrial organic chemistry, whose consumption has increased fast and tends to keep strong. In 2004, the worldwide production reached 32 million metric tones per year of formalin 37% solution basis (ABRAF, 2004).

Two main commercially available routes comprise almost all industrial formaldehyde production: the Formox and the Silver process. The Silver process is the classical route since the beginning of the twentieth century, where methanol-rich methanol-air-stream mixture is passed through a simple silver catalyst bed at 600 – 700 °C, at near atmospheric pressure. The Formox process (Santacesaria and Morbidelli, 1981; Piccoli, 1992), commercially available since 1950's uses iron-molybdenum oxides as catalyst in multitubular reactors, oxygen-rich feed and lower bed temperatures (300 – 400 °C). Formalin, an aqueous solution of formaldehyde, is obtained and commercialized as final product by these two processes.

Best selectivity towards formaldehyde is obtained with Formox process; in this sense, new plants are preferably built using this technology, but approximately 30 - 50% of the current world's capacity still rely on plants operated with Silver technology (Van Veen et al, 2002; Qian et al., 2003; Waterhouse et al., 2004b). Formox process supplied to new plants is normally licensed with technical assistance, including expert engineers, complete process manuals and simulators. Facilities based on Silver process are often operated according to the experience of plant personnel, with little or no availability of simulators, technical data or assistance from licensors. In this sense, every tool developed for assisting engineers and operators for Silver plants will be strategic for improving the efficiency of these plants, reducing operational costs and shortening the gap for the Formox operated plants. Even considered an old process, there are many Silver plants in operation with potential to improve raw-material costs, increasing the selectivity towards formaldehyde: even

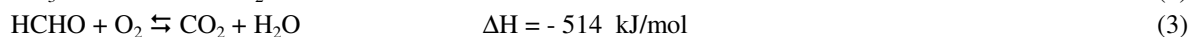
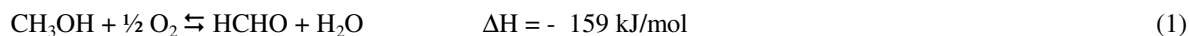
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small selectivity improvements are likely to be profitable to formaldehyde manufacturers, principally when methanol prices escalate due to global shortening.

Despite much work has been done worldwide to study the Silver process, there is no full mechanistic and kinetics understanding of methanol oxidation on silver surfaces under industrial conditions (Gravilin and Popov, 1965; Bazilio et al., 1985; Ullman, 1988; Van Veen et al., 2002; Andreasen et al., 2003; Waterhouse et al., 2004b; Cao and Gavriilidis, 2005). The formation of formaldehyde is generally the focus of the researchers, with little attention to the formation of by-products, principally carbon monoxide. The influence of temperature, methanol and oxygen concentrations and residence time at industrial conditions have not been fully reported.

Kinetic experiments are difficult to be performed, due to mass transfer limitations, non-isothermicity, deactivation and aging of silver catalyst in conventional reactors (Bazilio et al, 1985; Andreasen et al, 2003; Cao and Gavriilidis, 2005). Without good quality kinetic data, only a few simulators have been developed for the formaldehyde fixed-bed reactor with silver catalyst, most of them not applicable for industrial conditions.

Two parallel reactions account for the formaldehyde formation from methanol over the silver catalyst: methanol oxidation (1) and methanol dehydrogenation (2). The formaldehyde generated reacts with oxygen on the silver catalyst, forming carbon dioxide (3) and it may also decompose on gas phase to carbon monoxide at high temperatures (4). Reactions 3 and 4 reduce the selectivity towards the desired product. The oxidation reactions are extremely exothermic and the reactor has a high heat generation.



Several workers studied the balance between the oxidation and the dehydrogenation of methanol on formaldehyde formation (Thomas, 1920; Bazilio and al., 1984). Most of the important works in this area considers the mechanism proposed by Wachs and Madix (1978) as a base reference, in which the oxidation of methanol to formaldehyde goes through a methoxy intermediate and it cannot be divided into separate dehydrogenation and oxidation steps. In practice, the mechanism proposed considers that 50% of the formaldehyde is formed by each reaction. Experimental measurements of heat generation on industrial reactor confirm that reactions (1) and (2) do not take place alone: approximately 60% of the formaldehyde is generated by the first reaction (oxidation) and the second reaction do not happen in the absence of oxygen (it activates the catalyst).

Different hypothesis were found concerning the formation of carbon dioxide, believed to be generated by direct oxidation of methanol (Bazilio et al., 1985) or by further oxidation of formaldehyde (Robb and Harriot, 1974; Lefferts et al., 1986; Andreasen et al., 2003). Carbon dioxide is only formed by a further oxidation of formaldehyde through a formate intermediate, according to Wachs and Madix (1978) mechanism. Direct methanol combustion is absent according to experiments run by Lefferts et al (1986) and conclusions of Andreasen et al (2003). Under industrial conditions, the formed hydrogen or hydrogen adsorbed species may also react with excess adsorbed oxygen to form water, reducing the availability of the oxidant to the combustion of formaldehyde.

Carbon monoxide is formed by the gas-phase homogeneous decomposition of formaldehyde, above 650 °C (Lefferts et al., 1986; Irdan et al., 1993; Sauer and Emig, 1995; Qian et al., 2003; Waterhouse et al, 2004a). This reaction was not considered in the mechanism of Wachs and Madix (1978) and on Andeasen et al. (2003) microkinetic model, but it is extremely important to understand the formaldehyde yields at industrial conditions.

Recent discussions about global warming will certainly start the discussion about carbon emissions on formaldehyde plants. If simulators and process manuals are available, engineers will be able to respond faster to future requirements towards improving plant's environmental compliance.

The Silver process is found with two variations: *Methanol Ballast Process*, where only air and pure methanol are fed to the silver bed, featuring incomplete methanol conversion and requiring a distillation recovery of the raw material; and *Water Ballast Process, or BASF Process (1905)*, where extra water is fed with the reactant mixture to achieved reasonable selectivity towards formaldehyde (85 – 92% range) with high methanol conversion (98 – 100%).

Reaction temperature is one of the most important parameters that influence the methanol conversion and the selectivity. At low temperatures the reaction is inactive, with an ignition temperature seen on the range 177 - 277 °C (Gravilin and Popov, 1965; Lefferts et al., 1986; Nagy and Mestl, 1999; Andreasen et al, 2003; Waterhouse et al., 2004a; Cao and Graviilidis, 2005). The methanol conversion and selectivity towards formaldehyde are very sensible to temperature and higher yields are achieved in the range 600 – 700 °C, where the thermal decomposition of formaldehyde starts to be significant. In this sense, the rapid stream quench upon exiting catalyst bed is very important to prevent the loss of selectivity (Waterhouse et al., 2004a). The optimal reaction temperature is believed to be in the range 630 – 650 °C (Dai et al, 2004). The total reaction is highly exothermic and fast, requiring short contact time to guarantee good selectivity. Silver particles' sintering is observed at temperatures close to 700 °C (Pestryakov, 1996; Dai et al., 2004). Hot-spots may reach this temperature limit and block the catalyst, increasing the bed pressure drop.

The addition of water to the feed is essential for achieving high formaldehyde yields (Waterhouse et al, 2004a,b; Cao and Gavriilidis, 2005). Due to its high heat capacity, water vapor absorbs reaction heat, preventing detrimental overheating as well sintering of catalyst. Water also cleans the coke on catalyst surface to expose active sites, blocks specific surface sites and displaces the reaction mechanism, reducing the formation of undesirable by products (Barteau and Madix, 1984; Qian et al, 2003; Andreasen et al., 2003). It is not a consensus the participation of water in the reaction (Nagy and Mestl, 1999). Bazilio et al. (1985) and Bhattacharyya et al. (1971) reported a marked inhibiting effect of water addition to the inlet reactants on the rate of methanol oxidation.

Oxygen plays a key role on the reaction mechanism, keeping the catalyst active (Bhattacharyya et al., 1971). Its interaction with silver at different temperatures promotes the formation of different oxygen-adsorbed species (Cao and Gavriilidis, 2005), leading to different kinetic behaviors. The methanol to oxygen ratio controls the balance between the dehydrogenation and the oxi-dehydrogenation paths (Nagy and Mestl, 1999). High oxygen concentrations increase the methanol conversion but leave much remaining oxidant for formaldehyde combustion.

Formic acid is normally not produced when the catalyst is fresh. After deactivation (4 – 9 months), formic acid is formed at all temperatures, urging catalyst replacement (Schubert et al., 1994; Qian et al., 2003).

Andreasen et al. (2003, 2005) reported a microkinetic modeling (Lyngaard et al., 2004) based on a mechanism proposed by Wachs and Madix (1978), where many parameter relationships were studied. It is the most complete study on formaldehyde kinetics modeling on literature, with very good results compared to experimental data. The weaknesses of their model are: it does not properly describe the influence of water and there is no attempt to model the decomposition of formaldehyde to carbon monoxide. The development of kinetic models for the formaldehyde synthesis has proven to be a difficult task, remaining unsolved after 50 years of good studies. In cases where deterministic models are not available or fail in achieving desired data fit, Artificial Neural Networks have been successfully employed to quickly model the process (Psichogios and Ungar, 1992).

Artificial Neural Networks (ANN) were initially developed as mathematical models to explain how the human brains work, based on biology and psychology (Berne and Levy, 1990). The result was a complex and

long math equation, whose size may be adjusted for each studied problem, with powerful capacity to calculate multiple outputs from multiple inputs (MIMO system). In this sense, researchers of different areas of knowledge have used the ANN as a model for a variety of systems, from stock exchange market to weather forecast, with minor adaptations. ANN are different that a simple regression: the complex neuronal structure is able to capture de data pattern, tolerating hardware failures and data noise. A regression model is not necessary, once the ANN itself is the model (Lennox et al., 2001).

According to ANN lingo, it is not adjusted, but it is “trained”, capturing the pattern of the experimental data by means of a “training” algorithm, where a set of [input/output] data is presented to the net until it properly fits the data. The “knowledge” is stored into the ANN internal parameters, or “weights”, as a memory. This is the reason why ANN is considered part of the Artificial Intelligence field (Wasserman, 1989; Davis, 1991; Pham and Pham, 1999; Papes Filho and Maciel Filho, 2005).

Many training algorithms are available. The most employed for engineering problems is the back-propagation (BP), that uses the error on the output neurons (between calculated and experimental outputs) to calculate the adjustment of the weights on the previous network layer. The error is then back-propagated to the preceding layers until all weights are adjusted. The process is repeated until the net error is minimized. For the first iteration, the set of weights is chosen randomly and then the algorithm starts adjusting them with back-propagation of error (Rumelhart et al., 1986; Wasserman, 1989). Once the BP is a gradient-driven type of algorithm, the quality of the solution will heavily depend on the initial estimate, but as it is random, there is no guarantee that it will be a good one.

Hybrid methods may employ a Genetic Algorithm (GA) to perform an initial search for a good solution, more probable to be close to the global optimum (Davis, 1991; Goldberg, 1992; Wang, 1997). The solution from the GA training session is used as an initial estimate for BP algorithm that refines the solution in a timely fashion (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007b).

In this work, a hybrid reactor simulator was constructed, containing a deterministic model for simulation of a fixed-bed reactor and an ANN model to calculate the rate of the reaction for the methanol oxidation to formaldehyde with silver catalyst. The results were compared with experimental work reported on literature, as well as actual industrial data. To the best of our knowledge this is the first time that ANN has been used to model the kinetics of the methanol oxidation to formaldehyde with silver catalyst.

2. Methods

2.1. Artificial Neural Networks

The rate of reaction used by the reactor simulator presented here was calculated by a neural network with three layers. The schematic of the used ANN is shown on Figure 1.

The number of neurons at hidden layer was varied to obtain the optimum configuration, found to be 12, according to studies of Papes Filho (2007). A bias neuron connected to “1” was included to the input and hidden layers (Papes Filho and Maciel Filho, 2007c).

Three neurons compose the output layer, calculating the rate of the 3 reactions of interest: formaldehyde formation, formaldehyde combustion and formaldehyde gas-phase decomposition.

Each virtual neuron (perceptron) of the neural net sums the inputs from the previous layer, after being multiplied by the weight associated to the two neurons involved (the one that sends the value and the one that receives). The input layer only receives the external inputs and passes them to the hidden layer. The neurons at the hidden layer receive the signals from the input layer, calculate the outputs and pass them to the output layer. The same procedure is done with the output layer, which generates the ANN outputs (Rumelhart et al., 1986; Wasserman, 1989 and Bhagat, 1990).

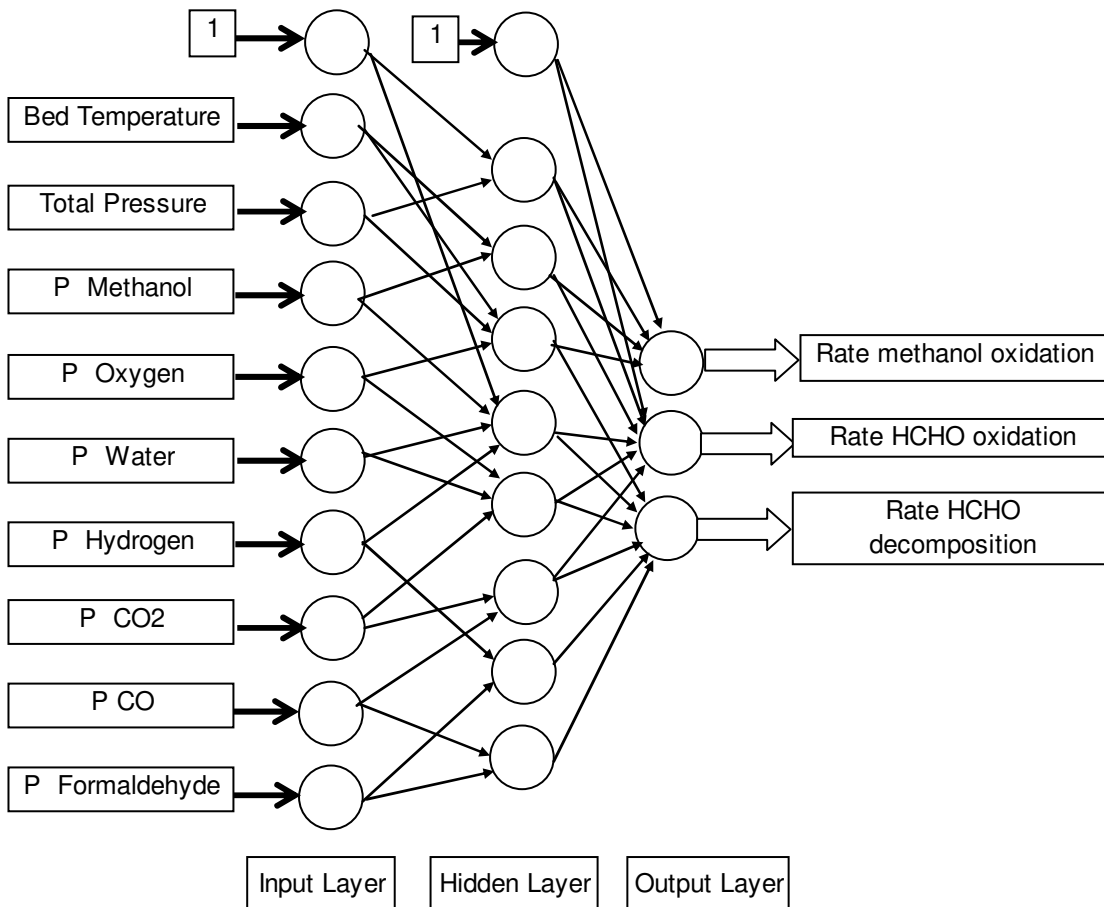


Figure 1: Schematic of the ANN used, where “P” means “partial pressure” (not all arrows were drawn, in order to make the picture clear)

The signal from each neuron is calculated by equation 5.

$$x_j^s = f\left(\sum_i (w_{ji}^s \cdot x_i^{s-1})\right) = f(I_j) \quad (5)$$

Where:

x_j^s is the signal from the neuron “j” at layer “s”

w_{ji}^s is the weight associated to the link between the neuron “j” at layer “s” and the neuron “i” at layer “s-1”

x_i^{s-1} is the signal from the neuron “i” at layer “s-1”

The signal from the neuron cannot be simply the sum of its input signals, once the final ANN would be simplified to a linear model (Wasserman, 1989). The sum presented on equation 5 must be transformed by means of a transfer function, typically a sigmoid, as in equation 6.

$$f(I_j) = \frac{1}{1 + \exp(-I_j)} \quad (6)$$

Provided input data to the ANN, as drawn on Figure 1, the net is able to calculate the output data for a particular set of weights. The ANN must be first trained or, in other words, the set of weights needs to be adjusted before it is able to predict the correct outputs.

2.2. Training

There are many training algorithms to adjust the internal ANN weights, using different approaches. For each case, a known set of input/output data is presented to the net and its internal parameters (weights) are tuned until the difference between the calculated outputs and the experimental ones is minimized.

Back-propagation algorithm is the most used training method for engineering problems. It calculates the adjustment to be done for each weight, based on the difference between the experimental output (d_m) and the calculated output (o_m), according to the global error function (E_n) associated to the neuron “n” of the output layer (equation 7).

$$E_n = 0.5 \cdot \sum_{m=1}^N \left((d_m - o_m)^2 \right) \quad (7)$$

Then, the raw local error of each neuron at output layer is given by equation 8 and the error is back-propagated to the previous layers by equation 9.

$$e_n^{out} = (d_m - o_m) \cdot o_m \cdot (1 - o_m) \quad (8)$$

$$e_j^s = x_j^s \cdot (1 - x_j^s) \cdot \sum_k \left(e_k^{s+1} \cdot w_{kj}^{s+1} \right) \quad (9)$$

Where,

e_n^{out} is the local error of neuron “n” of the output layer.

e_j^s is the local error of neuron “j” of layer “s”.

The weights are adjusted based on the local error, according to equation 10.

$$w_{ji}^{new} = w_{ji}^{old} + \alpha \cdot e_j^s \cdot x_i^{s-1} \quad (10)$$

Where “ α ” is the learning coefficient, usually ranging between 0.01 and 1.0, typically set as 0.5.

The ANN error defined by equation 7 is part of the BP algorithm, but for comparison reasons, the net error may also be calculated by equation 11, considering 3 output neurons, trained with a set of “N” data-pairs.

$$E_{TOT} = \frac{1}{N} \cdot \sum_{k=1}^3 \left(\sum_{m=1}^N \left((d_{m,k} - o_{m,k})^2 \right) \right) \quad (11)$$

For silver-catalyzed formaldehyde process, the ANN training cannot be directly performed with the measured data, once the ANN output (rate of reaction) is not available, but only conversion and selectivity data. The kinetic data had to be extracted from process data according to the procedure described by Papes Filho (2007): a simplified kinetic model was implemented into the reactor simulator and, for each process data point, the model parameters were adjusted until the conversion and selectivity calculated by the simulator matched the experimental ones. Once the individual point was fit, the rate of reaction profile through the catalytic bed was saved with the associated local operational conditions. The adjustment on the simplified kinetic model was only valid for a single data point, but after repeating the procedure for all available experimental points, a huge set of rate of reaction data may be obtained (Papes Filho and Maciel Filho, 2007a). The calculated rates were used to train the ANN by back-propagation.

Back-propagation (BP) algorithm starts from a random set of weights, refining them according to the equations above. The global error (E) is a complex function of the weights and many local minima may exist. As BP is a gradient driven method, it may be trapped into a local minimum, with no idea if better solutions do exist.

Novel search methods have been developed to overcome the weakness of gradient driven methods, as Genetic Algorithms. They perform a wide search on the whole universe of possible solutions, increasing the probability of finding the global optimum instead of climbing to a local one.

The Genetic Algorithm (GA) considers a population of solutions, which are evaluated according to specific criteria. Initially the population is set randomly, but the best solutions (individuals) are encouraged to survive and are mixed to generate new candidate solutions. The new generation of solutions is again evaluated and the procedure is repeated until the desired global error is achieved, mimicking the natural evolution of species. The algorithm seems to be a random search for good solutions, but it is indeed a complex method to mix intermediate good solutions in order to produce better ones.

Papes Filho (2007) presented a hybrid training method using Genetic Algorithm to perform the initial session of the training and back-propagation to refine the solution, with the same objective function exposed on equation 11. Rate of reaction data was used in this case, extracted from measured data (conversion and selectivity). The hybrid method increases the probability of reaching a global optimum due to the GA capabilities, keeping the computing times at an acceptable level due to the use of BP for refining the solution given by GA (Papes Filho and Maciel Filho, 2007b).

Other possible approach was reported by Papes Filho (2007), training the ANN as a built-in model inside the reactor simulator (Papes Filho and Maciel Filho, 2007c), adjusting the ANN weights using Genetic Algorithms, until the simulator outputs (and not the ANN outputs) – methanol conversion and formaldehyde selectivity – approached the experimental ones, according to equation 12 (evaluation function).

$$E = \sum_{i=1}^N \left(0.25 * (\chi_C - \chi_E)^2 + 0.25 * (S_C - S_E)_{HCHO}^2 + 0.25 * (S_C - S_E)_{CO_2}^2 + 0.25 * (S_C - S_E)_{CO}^2 \right) \quad (12)$$

Where: “E” is the fitting error; “N” is the number of experimental data points; “ χ ” is the methanol conversion; “S” is the selectivity; “C” stands for calculated values; “E” stands for experimental values; “HCHO” term refers to the selectivity towards formaldehyde; “CO₂” term refers to the selectivity towards carbon dioxide and “CO” term refers to the selectivity towards carbon monoxide.

These methods have shown advantages and disadvantages. The best approach was always seen to be a mix of all methods, in order to find the best fit to experimental values.

In this work, the ANN was trained based on actual industrial data and experimental data from literature. Rate of reaction data was extracted from the process data (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007a,b), translating measured conversion and selectivity into a set of 4050 data points, correlating temperature and partial pressures to the rate of reaction (formaldehyde formation, combustion and decomposition). The ANN was firstly trained with this data, refining the weights from a random set to an improved set. The built-in approach was then used on actual measured data to refine the weights based on GA approach (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007c).

2.3. Fixed-bed model

The reactor simulator was constructed with the deterministic model for the fixed-bed reactor, based on differential mass balance equation derived from the application of pseudo-homogeneous, bidimensional, plug-flow model for tubular reactor at steady-state operation. Equation 13 shows the differential mass transfer equation on cylindrical coordinates (Welty et al., 1984; Fogler, 1992) which was applied to the fixed-bed. Figure 2 shows a schematic of the silver reactor.

$$D_L \cdot \frac{\partial^2 C}{\partial z^2} + D_R \cdot \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial C}{\partial r} \right) - V_Z \cdot \frac{\partial C}{\partial z} + v_A \cdot R_V = 0 \quad (13)$$

Where, “C” is the substance concentration (kg/m³); “r” is the distance from the reactor central line or the radius on cylindrical coordinates (m); “z” is the distance from the reactor inlet or the axial distance on

cylindrical coordinates (m); “ D_L ” is the axial diffusion coefficient (m^2/s); “ D_R ” is the radial diffusion coefficient (m^2/s); “ V_z ” is the axial velocity (m/s); “ v_A ” is the stoichiometric coefficient for the studied substance (dimensionless); “ R_V ” is the rate of the reaction per reaction volume ($kg/m^3 \cdot s$).

This equation is better solved numerically if the variables are dimensionless, as in equation 14:

$$\frac{D_L}{L \cdot V_z} \cdot \frac{\partial^2 X}{\partial Z^2} + \frac{D_R \cdot L}{V_z \cdot R^2} \left(\frac{\partial^2 X}{\partial u^2} + \frac{1}{u} \cdot \frac{\partial X}{\partial u} \right) - \frac{\partial X}{\partial u} + \frac{v_A \cdot L}{C_o \cdot V_z} \cdot R_V = 0 \quad (14)$$

Where, “ X ” is the dimensionless concentration (C/C_o); “ Z ” is the dimensionless axial distance (z/L); “ u ” is the dimensionless radius (r/R); “ L ” is the reactor length (m); “ R ” is the reactor radius (m) and “ C_o ” is the inlet concentration of the substance (kg/m^3).

Equation 13 provides the bidimensional mass balance equation, as demonstrated in literature. The simulator was created by the authors containing this equation in order to produce a generic software that could deal with axial and radial flow, useful for a variety of problems. Nevertheless, in the case of the Silver formaldehyde reactor, the system is unidimensional, once the inlet stream is homogeneous, the reaction takes place homogeneously throughout the silver, there is no inlet/outlet streams along the bed and the catalyst bed is isothermal. In this sense, in practice, Eq. 13 is simplified by excluding the terms related to the radial flow.

According to previous works (Andreasen et al, 2003; Papes Filho, 2007), the reactions involved in the Silver process can be divided into three, as stated below:



In this sense, three differential mass balance equations have to be solved simultaneously, representing the advancement of these three reactions. Formaldehyde formation is representative of R_{HCHO} , carbon dioxide is representative of R_{CO_2} and carbon monoxide is representative of R_{CO} . There will be three differential equations similar to equation 14, applied to formaldehyde, carbon dioxide and carbon monoxide respectively. At every iteration, the mole fraction of all species is calculated using the partial pressures and total pressure.

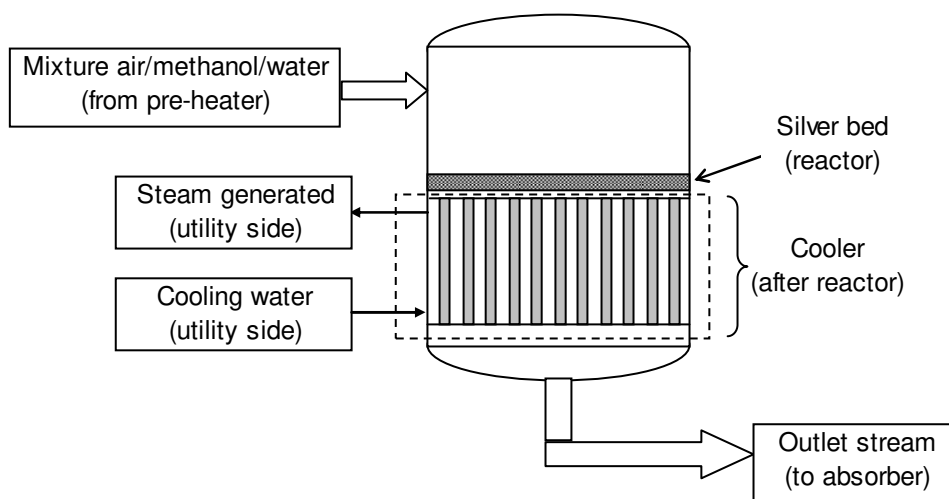


Figure 2: Scheme of a typical silver reactor, showing the fixed-bed, where reaction takes place, and the downstream cooler.

2.4. Energy balance and pressure drop

Formaldehyde silver reactors (fixed-bed) are known to operate adiabatically, once the catalyst bed is porous and thin (Bazilio et al., 1985; Van Veen et al., 2002). All work reported in literature considers this type of operation and industrial observations supply the same information. Normally, the bed starts the operation with almost zero pressure drop (50 mbar) when catalyst is fresh and, in this sense, pressure in the simulator model will be considered constant.

Only after some months of operation, pressure drop starts to increase and the bed must be replaced, mostly because of air compressor constraints than to catalyst low activity. The causes are: silver sintering (Dai et al., 2004), bed packing (fines generation due to friction between particles) and bed blocking by methanol impurities. With old catalyst, pressure drop along the bed is meaningful, but as it represents a little part of operating cycle, it will not be considered in this work.

Considering that the net reaction is extremely exothermic, the bed is thin, the catalyst is a heat conductor and the residence time is extremely short, it is very difficult to model the temperature profile in this type of reactor. The silver bed itself has no external heating or cooling and its temperature is in fact controlled by the feed temperature and methanol conversion. The reactants are normally fed to the reactor at 100 – 150 °C and the outlet stream leaves the bed at approximately 650 °C, being the temperature increase driven by the heat generated by the reaction. The inlet temperature is below the light-off reaction temperature, thus there certainly are radiation and conductive heat transfer phenomena that lead to the quick heating of inlet stream above 300 °C.

The simulator was originally built with heat transfer differential equation (equation 18), but it was found to be very unstable, once at inlet conditions (considered 300 °C) the simulated reaction is very slow and only in the final portion of the bed length the calculated temperature approaches the set-point (c. 650 °C): the rates increased exponentially, making difficult the numeric solution of the differential equations due to overflow errors.

$$k_L \cdot \frac{\partial^2 T}{\partial z^2} + k_R \cdot \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial T}{\partial r} \right) - \rho \cdot C_p \cdot V_z \cdot \frac{\partial T}{\partial z} - [\Delta H_R \cdot R_V]_{F,C,D} = 0 \quad (18)$$

Where: “ K_L ” is the axial effective thermal conductivity (W/m.K); “ K_R ” is the radial effective thermal conductivity (W/m.K); “ T ” is the local temperature (K); “ ρ ” is the local specific gravity (kg/m³); “ C_p ” is the heat capacity (J/kg.K) and “ ΔH_R ” is the heat of reaction (J/mol). The heat generated or consumed by all reactions must be taken into account: “F” for formaldehyde formation (Eq.15), “C” for formaldehyde combustion (Eq. 16) and “D” for formaldehyde decomposition (Eq. 17).

The first simulations were performed considering the radiation from the silver bed at normal operation conditions, heating the feed stream before entering the catalyst (equation 19), as well as the heat conductivity through the silver bed (Welty et. al, 1984). The calculations showed a temperature profile of 8 °C between the bed faces.

$$E = \epsilon_s \cdot \sigma \cdot T^4 \quad (19)$$

Where: “E” is the radiant energy (W/m²); “ ϵ_s ” is the silver emissivity (rough silver); “ σ ” is the Stefan-Boltzman constant and “T” is the bed temperature (K).

Industrial measurements were made, installing termocouples at the bed surface (inlet – upper side of the bed) and at the catalyst support (outlet – bottom side of the bed), obtaining temperature differences of 10 °C between them. The silver bed was observed through a sight glass at the top of reactor and the catalyst surface is clearly incandescent, showing that the surface is close to the operation set-point (650 °C). The industrial

observations are in phase with the heat balance calculations and we decided to simplify the model to an isothermal reactor based on:

- a 10 °C temperature profile (1.5% of the set-point) is about the order of magnitude of the instrument errors for the temperature measurements (1%);
- a 10 °C difference on temperature between bed surfaces will not significantly change the conclusions about formaldehyde reactor performance;
- the heat balance equations will introduce instability to the simulator.

2.5. Rate of reaction

The rate of the three reactions were calculated simultaneously by an ANN, previously trained (Papes Filho and Maciel Filho, 2007c), whose weights were stored in an external data file. The input variables are: bed temperature (K), total pressure (atm), local partial pressures for methanol, oxygen, water, hydrogen, formaldehyde, carbon dioxide and carbon monoxide.

Bed pressure and temperature are constant and given by the user. Partial pressures are calculated at every numerical algorithm step for the equation solving, considering the mole balance in the reactor:

$$\begin{aligned}
 \text{For formaldehyde:} & \quad n_1 = n_1^o + \xi_{HCHO} - \xi_{CO_2} - \xi_{CO} \\
 \text{For carbon dioxide} & \quad n_2 = n_2^o + \xi_{CO_2} \\
 \text{For carbon monoxide} & \quad n_3 = n_3^o + \xi_{CO} \\
 \text{For methanol} & \quad n_4 = n_4^o - \xi_{HCHO} \\
 \text{For oxygen} & \quad n_5 = n_5^o - 0.25 \cdot \xi_{HCHO} - \xi_{CO_2} \\
 \text{For water} & \quad n_6 = n_6^o + 0.5 \cdot \xi_{HCHO} + \xi_{CO_2} \\
 \text{For hydrogen:} & \quad n_7 = n_7^o + 0.5 \cdot \xi_{HCHO} + \xi_{CO} \\
 \text{For nitrogen:} & \quad n_8 = n_8^o
 \end{aligned}$$

Where “ n_i ” is the number of moles of the substance “ i ” at every numerical step; “ n_i^o ” is the initial number of moles of the substance “ i ”; “ ξ_{HCHO} ” is the advancement of the reaction of formaldehyde formation; “ ξ_{CO_2} ” is the advancement of the reaction of formaldehyde combustion and “ ξ_{CO} ” is the advancement of the reaction of formaldehyde decomposition.

Using the input parameters stated above and the trained weights, the ANN, by means of a sub-routine inside the reactor simulator, calculates the local rate of the three reactions simultaneously:

- The rate of methanol oxidation (r_{HCHO}), kmol/m³.h
- The rate of formaldehyde oxidation (r_{CO_2}), kmol/m³.h
- The rate of gas phase decomposition of formaldehyde (r_{CO}), kmol/m³.h

2.6. Inputs and outputs

The inputs to the simulator, given by the user, are: methanol flowrate (kg/h); air flowrate (kg/h); water flowrate (kg/h); bed temperature (°C) and bed pressure (atm).

Other information is also provided by the user, but it is not changed on simulations for the same reactor, are: reactor diameter (m); bed length (m); silver particle size (m) and oxygen concentration on air (mole %).

The outputs from the simulator are:

- Methanol conversion (%): $X = \frac{\xi_{HCHO}}{n_4^o}$
- Selectivity towards formaldehyde (%): $S_{HCHO} = \frac{\xi_{HCHO} - \xi_{CO_2} - \xi_{CO}}{\xi_{HCHO}}$
- Selectivity towards carbon dioxide (%): $S_{CO_2} = \frac{\xi_{CO_2}}{\xi_{HCHO}}$

- Selectivity towards carbon monoxide (%): $S_{CO} = \frac{\xi_{CO}}{\xi_{HCHO}}$

Formaldehyde yield, methanol specific consumption (tones of MeOH consumed per tone of formalin 37% produced) and the outlet stream composition may also be provided by the simulator.

- Formaldehyde yield = $X \cdot S_{HCHO}$
- Methanol specific consumption = $\frac{32 \times 0.37}{S_{HCHO} \cdot 30.03}$

Physical properties of the pure substances were obtained from the literature (Welty et al., 1984; Reid et al., 1987; Sandler, 1989), at reactor conditions. Diffusion coefficients were calculated by the correlation of Papes Filho and Cremasco (1995). Mixture properties were calculated according to Reid et al. (1987) for local conditions.

2.7. Numerical solving

The three mass balance differential equations (for formaldehyde, carbon dioxide and carbon monoxide) were solved simultaneously, using the Crank-Nicholson numeric algorithm (Crank and Nicholson, 1947; Press et al., 1992).

The iterated Crank-Nicholson method has become popular in engineering simulations, with the progress in computer processing capacity, making possible the rapid solution of big matrices. It is a finite difference method, semi-implicit and known to be intrinsically stable, very suitable for reactor simulators. The method involves taking the derivative half way between the beginning and the end of the “z” direction (length of reactor) and the price paid for the high accuracy and unconditional stability is having to invert a tridiagonal matrix at each space-step.

Final composition (moles or partial pressures) from the last “z”-step of Crank-Nicholson algorithm (bed outlet) allows the calculation of the methanol conversion and selectivity towards formaldehyde, carbon dioxide and carbon monoxide.

The workflow inside the simulator is summarized on Figure 3. About hundreds of million simulations were run in this work without errors on the numerical solving, proving the stability of Crank-Nicholson method.

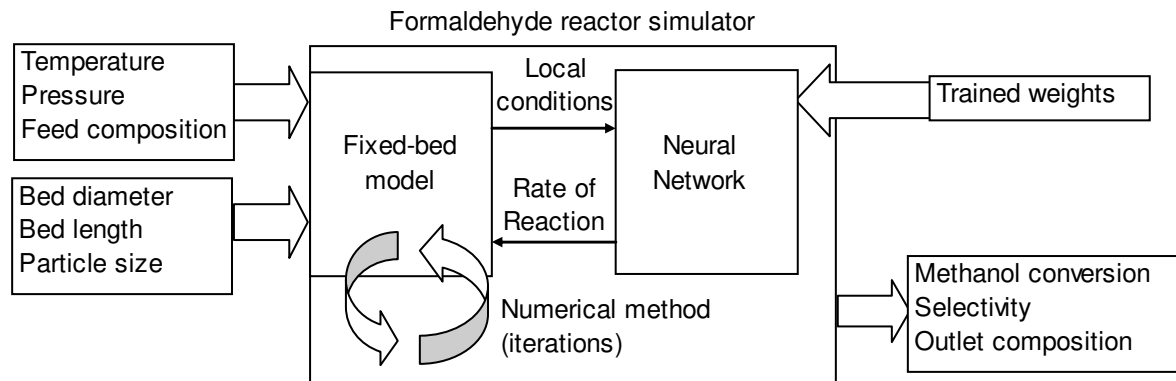


Figure 3: Workflow inside the reactor simulator

Boundary conditions for the model solving are: radial symmetry (equation 20), homogeneous profile at reactor inlet (equation 21) and no mass transfer through the reactor walls (equation 22).

$$\frac{\partial C}{\partial r} = 0 \Big|_{r=0} \quad (20)$$

$$C = C_0 \text{ at } z = 0 \quad (21)$$

$$\frac{\partial C}{\partial r} = 0 \Big|_{r=R} \quad (22)$$

The control limits for the Silver reactor are the limits of the portion of the equipment containing the catalyst (fixed-bed): the “z” direction is limited by the top catalyst surface (bed inlet, or $z = 0$) and bottom surface (bed outlet, or $z = L$); the “r” direction is limited by the reactor center line ($r = 0$) and the reactor walls ($r = R$).

3. Results and Discussion

The ANN was trained by the hybrid algorithm (GA+BP) and built-in approach, using process data from an industrial Silver plant in operation with fresh catalyst (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007a,b,c). The optimum set of weights was stored in a data file for proceeding to simulation of new cases. For validation purposes, a set of actual conditions (not used for training) was considered to simulate control cases, comparing known conversion and selectivity values with simulated ones. Results are shown on Figure 4, indicating that the simulated conversions and selectivity are pretty much consistent with actual measured data, validating the ANN training. Conversions and CO₂ selectivity values showed good correlation (0.974 and 0.960 respectively), while selectivity towards HCHO and CO presented excellent correlation (> 0.99). All values are concentrated along the 45° line. Analysis of variance over the simulated data shows sum of squares of the model (SQM) of 80.76 and sum of the squares of the residual (SQR) of 0.019. F-value, as in Eq.23, is 4361, that is very significant, indicating that the ANN model could successfully fit the measured data (Box and Hunter, 1978).

$$F_{CALC} = \frac{SQM}{SQR} \quad (23)$$

The Crank-Nicholson numerical method was run with 500 steps along the “z” direction in all cases.

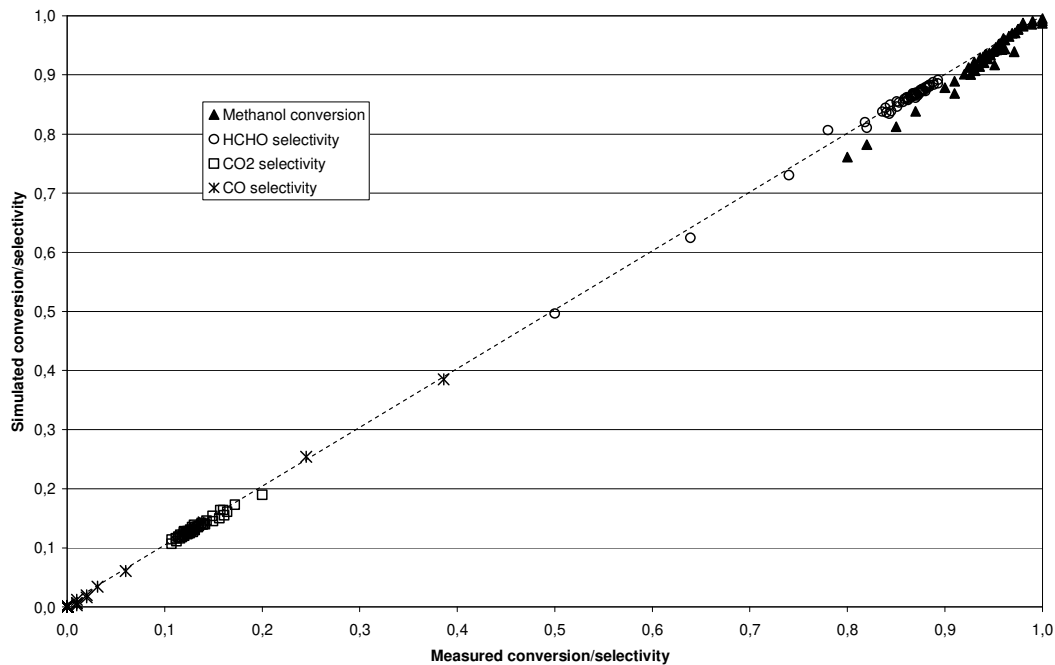


Figure 4: Simulated conversion and selectivity plotted against measured values for control conditions (ANN training validation).

Using the validated ANN trained weights, the simulator can now be employed to predict new conditions for better understanding the influence of process parameters on the performance of the formaldehyde reactor. The goal is to simulate different conditions close to the industrial set-point, in order to illustrate the influence of bed temperature, feed molar ratio oxygen-to-methanol, feed molar ratio water-to-methanol and residence time on the conversion and selectivity. Results were validated by comparing the trends to lab experimental work reported on literature.

Base conditions for the simulations presented here are: bed temperature of 630 °C, pressure of 1.2 atm, air flowrate at 6060 kg/h, methanol flowrate at 3681 kg/h, water flowrate at 364 kg/h, reactor diameter of 1.5 m, bed length of 20 mm and catalyst size of 0.6 mm.

At the conditions above, the molar ratio methanol to oxygen (MeOH/O₂) is 2.6 and the molar ratio water to methanol (H₂O/MeOH) is 0.18. The simulated methanol conversion is 94.0%, with a formaldehyde selectivity of 86.8 % and carbon dioxide selectivity of 13.2%. Formaldehyde yield is 81.6% and carbon dioxide yield is 12.4 %. Carbon monoxide selectivity and yield are very low. Exit composition contains 39.2% nitrogen, 11.4% hydrogen, 3.4% carbon dioxide and 0.01% carbon monoxide. The heat generated from the reaction is in the range 3700 to 4300 Mcal/h (exothermic), depending on the extent of the reaction between hydrogen and oxygen in the reactor.

Equilibrium constants calculated for the three reactions by means of the Gibbs free energy and formation enthalpy (Sandler, 1989) allow the determination of the equilibrium composition at the operation condition stated above, indicating that methanol conversions of practically 100% are possible and carbon monoxide plus carbon dioxide selectivity may approach 100% (Papes Filho, 2007). In this sense, it is clear the importance of the kinetic studies for the formaldehyde reactions in order to optimize the desired product formation once it is not favored by the thermodynamic equilibrium (Schubert et al., 1994; Sauer and Emig, 1995).

The simulator was run for a series of operational conditions, varying one parameter at a time in order to generate the profiles for conversion and selectivity over the studied range for the variables.

3.1. Influence of reactor temperature

Simulations were performed on the temperature range of 580 °C to 720 °C, keeping the other variables at the set-points presented above. The results were shown on Figure 5. Normal operating temperatures seen in industrial processes are in the range 600 – 700 °C, depending on the particular conditions of the plants. Typical values vary from 620 to 650 °C on optimized plants.

In the studied case, simulated methanol conversion increases monotonically with increasing temperature, approaching 100% close to 700 °C. Conversions close to 90% are obtained at 600 °C and close to 95% at 650 °C. This behavior is well reported on literature (Nagy and Mestl, 1999; Waterhouse et al., 2004a; Cao and Gavriilidis, 2005).

Selectivity towards formaldehyde shows different behaviors at high and low temperatures. While the formaldehyde decomposition to carbon monoxide is not significant, at temperatures below 650 °C, the selectivity to formaldehyde increases with increasing temperature. Above this value, the gas-phase decomposition develops fast and the formed formaldehyde is converted in carbon monoxide, decreasing the desired selectivity in a fast pace.

The maximum formaldehyde selectivity in this case (86.9 %) is found on the range 630 – 660 °C, where normally a plateau is seen with no sensible variation on the selectivity. This plateau range may vary for different plants, but it is believed to have its center on the interval 620 – 650 °C, flat enough to allow a stable operation at the optimum point on plants with a reasonable temperature control on the reactor bed.

In the studied case, the simulated selectivity decreases slowly to 83.6% when temperature decreases to 580 °C. Above 660 °C, the selectivity decreases slowly to 85.3% at 680 °C and drops quickly above this temperature due to the gas-phase decomposition of formaldehyde. The selectivity towards carbon dioxide

decreases from 16.4% at 580 °C to 13.5% at 620 °C, and maintains at this approximate level over the upper temperature range.

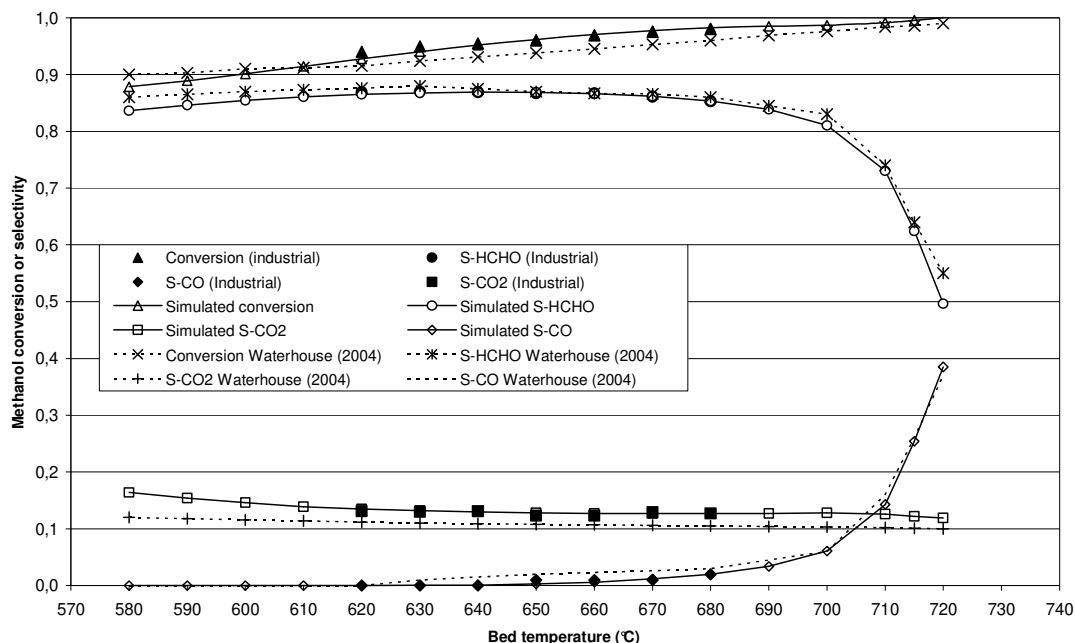


Figure 5: Effect of temperature on methanol conversion, selectivity towards formaldehyde (S-HCHO), carbon dioxide (S-CO₂) and carbon monoxide (S-CO). Simulations performed according to the base industrial operational conditions, varying the bed temperature, compared to some industrial and literature data (Waterhouse et al, 2004a).

These results from the simulations have good agreement with industrial and experimental work from literature, as could be observed on Figure 5.

Waterhouse (2004a) reported maximum formaldehyde selectivity at 630 °C (c. 88%), with a plateau on the range 600 – 650 °C. Selectivity as high as 92% is reported to be feasible in optimized plants (Nagy and Mestl, 1999).

According to literature, carbon dioxide selectivity is higher at lower temperatures, reaching around 40% at 350 °C (Nagy and Mestl, 1999; Waterhouse et al., 2004a), but this condition is much far from industrial temperatures. At the range 580 – 720 °C, Waterhouse’s experiments reported selectivity between 12 and 10%, with the same trends as the simulations presented here, also shown on Figure 5. Qian’s experiments (2003) showed nearly constant selectivity at c. 10% over the temperature range. The decrease in the selectivity to carbon dioxide with increasing temperature reflects the increasing thermal instability and lower surface coverage of particular oxygen species on the catalyst surface at higher temperatures.

Formaldehyde selectivity drops fast at lower temperatures (< 525 °C) and decreases sharply above 700 °C due to the homogeneous decomposition of formaldehyde to carbon monoxide and hydrogen (Schubert et al., 1994; Nagy et al., 1998; Qian et al., 2003; Cao and Gavriilidis, 2005). Optimum formaldehyde yield was reported to be 84.3% at 650 °C (Waterhouse et al, 2004a), while an optimum of 84.2% at 670 °C was found in the simulations, comparable with typical values from industrial manufacture. Dai et al (2004) reported optimal reaction temperature at 630 °C; Qian et al (2003) reported maximum yield at 650 °C.

The explanation for the increase of formaldehyde selectivity with increasing temperatures, below 600 °C, is controversial. Lefferts et al (1986), Nagy et al (1998), Van Veen et al (2002) and Waterhouse et al. (2004a)

explain the phenomena based on the influence of different oxygen species adsorbed throughout the silver surface on the reaction mechanism. Andreasen et al (2003, 2005) consider that a reaction in serial mode, where carbon dioxide is formed through formaldehyde oxidation, explains the selectivity phenomena, as the activation enthalpy for methanol oxidation is always larger than carbon dioxide formation one, making the rate of formaldehyde formation to increase faster than formaldehyde combustion with increasing temperature. Oxygen is rapidly consumed in the methanol oxidation reaction and smaller oxidant concentration inhibits further oxidation of formaldehyde. This behavior might be opposite (decrease on formaldehyde selectivity with increasing temperature) with oxygen-rich mixtures, where the mechanism proposed by the researchers is believed to fail, since the unselective reaction routes seem to be suppressed (Cao and Gavriilidis, 2005).

3.2. Influence of oxygen

Formaldehyde studies manage the molar ratio methanol to oxygen instead of the oxygen concentration alone. The simulator was run on the molar ratio range of 2.0 to 3.4, keeping the other variables at the industrial set-point presented above. Results are plotted on Figure 6, where is clear that the simulations are in agreement with industrial and literature data. At molar ratio of 2.26, the simulated conversion is 97.4% and the formaldehyde selectivity is 82.0%, while at molar ratio of 3.05, the conversion is 83.7% and the selectivity is 86.9%. Industrial reactors operate at fuel-rich conditions, on the upper edge of the flammability limits for methanol-air mixtures. Typical molar ratios are reported to be on the range 2.3 – 3.0.

Simulated methanol conversions showed decreasing behavior with increasing MeOH/O₂ ratio. The higher the oxygen availability, the higher the methanol consumption due to the acceleration of methanol oxidation and formaldehyde combustion reactions, based on Le Chatellier equilibrium principles and catalyst activation features. Waterhouse et al. (2004a) reported methanol conversion close to 100% below 2.0 molar ratio, decreasing fast above 2.25 ratio, as plotted on Figure 6.

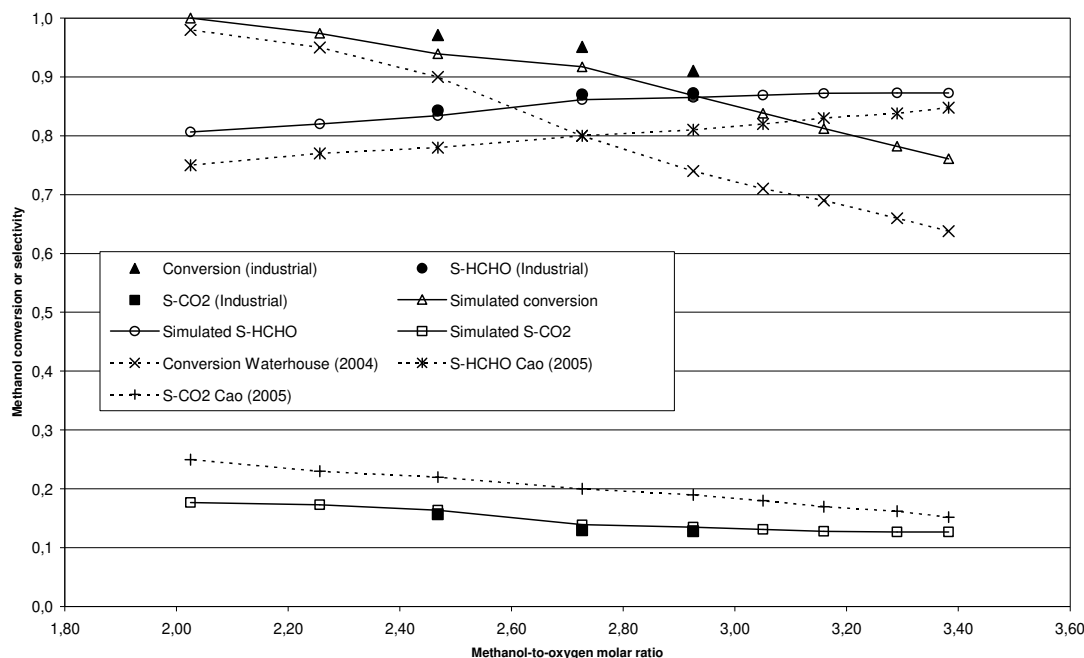


Figure 6: Effect of methanol/oxygen molar ratio on methanol conversion, selectivity towards formaldehyde (S-HCHO) and carbon dioxide (S-CO₂). Simulations performed according to the base industrial operational conditions, varying the molar ratio, compared to some industrial and literature data (Waterhouse et al, 2004a; Cao and Gavriilidis, 2005).

The simulations also predicted that formaldehyde selectivity increases with increasing MeOH/O₂ ratio, while carbon dioxide selectivity decreases. Small changes on simulated selectivity were seen above molar ratio of

3.0. These trends are explained by the reaction mechanism, where the higher the oxygen availability, the higher the rate of formaldehyde combustion.

Waterhouse et al. (2004a) report quick increase on formaldehyde selectivity from 1.50 to 2.25 molar ratio, remaining practically constant at a level of 87% above the molar ratio of 2.25. The selectivity towards carbon dioxide presents the complementary behavior (practically constant at 10% level on the studied range, not shown on Figure 6), while the selectivity to carbon monoxide is kept at very low levels. Higher carbon dioxide selectivity is reported by the authors at low molar ratio, believed to be caused by localized catalyst heating and sintering.

The operational conditions used on the present simulations differ from Waterhouse's experimental conditions, carried out with diluted oxygen ($O_2/He = 2.7/97.3$) and excess water ($H_2O/MeOH = 0.75$) at 650 °C, what could explain the differences presented above. The results below 2.25 molar ratio reported by Waterhouse et al. (2004a) were not compared once they are far from industrial conditions studied here.

Nagy and Mestl (1999) reported that formaldehyde selectivity increases with increasing $MeOH/O_2$ ratio. The same behavior was reported by Lefferts et al., 1986 and Wang et al, 1999.

Cao and Gavriilidis (2005) ran experiments in a quartz tube reactor, varying the molar ratio in the range 2.2 to 5.0, observing decreasing conversion, increasing formaldehyde selectivity and decreasing CO_2 selectivity with increasing molar ratio, as plotted on Figure 6. The formaldehyde selectivity was not found to level at high molar ratios as observed in Waterhouse's experiments (2004a), and c. 80% selectivity is found at 2.9 molar ratio (it should be noted that the experiments were run at 347 °C, much lower than industrial bed temperatures). The same researchers ran experiments in microreactors with oxygen-richer conditions (molar ratio from 0.1 to 2.9) and the formaldehyde selectivity was observed to increase monotonically with increasing molar ratio (Cao and Gavriilidis, 2005).

Simulated carbon monoxide selectivity was small at the set-point temperature (630 °C) and it was not included on Figure 6. CO selectivity is not expected to show a dependence with oxygen concentration as it is formed by the homogeneous decomposition of formaldehyde (Lefferts et al., 1986; Waterhouse et al., 2004a).

3.3. Influence of water

The molar ratio water to methanol is used on formaldehyde studies in place of water concentration alone. Simulations here were performed on the molar ratio range of 0.07 to 0.44, maintaining the other variables at their set-points stated above. At molar ratio of 0.15, the simulated conversion is 94.2% and the formaldehyde selectivity is 86.6%, while at molar ratio of 0.4, the conversion is 92.2% and the selectivity is 88.8%.

There is a lack of quantitative information on literature concerning the influence of water on the formaldehyde reaction at industrial conditions. The simulations done here are well in accordance with industrial qualitative information, but poor comparison could be done with literature data.

Observing Figure 7, the simulations show a clear indication that the inclusion of water to the reactor feed increases the selectivity towards the desired product, decreasing the methanol specific consumption. This behavior is in accordance with industrial practices and experiments reported by Waterhouse et al. (2004a).

Simulations also show that methanol conversion decreases with increasing molar ratio, also in accordance with industrial observations and conclusions of Bhattacharrya et al. (1971) and Bazilio et al. (1985). The poisoning effect of water is believed to be due to its competitive adsorption on the catalyst surface.

Qian et al. (2003) ran experiments varying the molar ratio from 0 to 2.0, at 550 °C, using an O_2/N_2 mixture with molar ratio of 10/90. They reported that the methanol conversion increases with increasing molar ratio, while the carbon dioxide selectivity decreases. Formaldehyde selectivity was reported to increase achieving a maximum at molar ratio of 0.75 and decreasing above this point.

Interestingly, the behavior for methanol conversion reported by Qian et al. (2003) is different than the simulations done in this work, based on industrial data, and the conclusions of Bhattacharya et al (1971) and Bazilio et al. (1985), probably due to differences on the experimental conditions. Industrial observations in many plants agree with the simulation, as far as only water/methanol ratio is varied, keeping bed temperature constant (in many cases, when water is added to the feed, bed temperature is increased to compensate the loss on conversion, and a different conclusion may be drawn, considering that two variables were changed simultaneously).

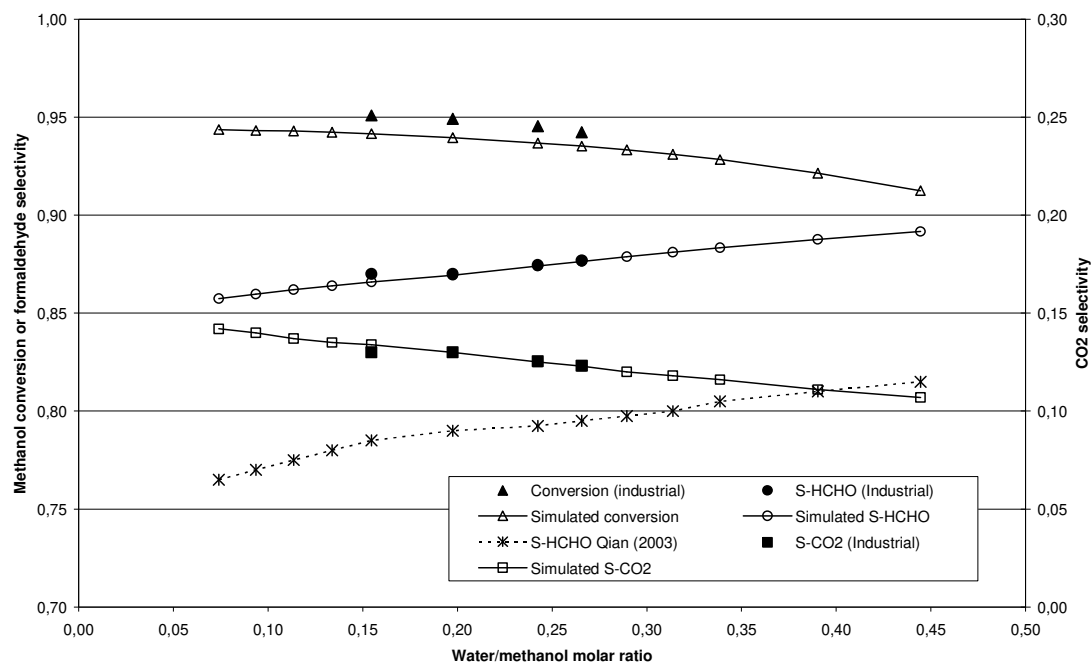


Figure 7: Effect of water/methanol molar ratio on methanol conversion, selectivity towards formaldehyde (S-HCHO) and carbon dioxide (S-CO₂). Simulations performed according to the base industrial operational conditions, varying the molar ratio, compared to some industrial and literature data (Qian et al., 2003).

The simulations done here were run at molar ratios below the maximum at 0.75 reported by Qian et al. (2003). In this range, the formaldehyde selectivity trends were similar (see Figure 7), but the absolute values are different due to particular experimental conditions. Once the industrial conditions are reported to be in the studied region, the opposite behavior above 0.75 is not seen in formaldehyde plants. Water Ballast process is known to achieve higher formaldehyde selectivity than Methanol Ballast process, in industrial plants.

The formaldehyde report from SRI International (1978) states that a maximum formaldehyde yield occurs at a molar ratio water/methanol of 1.19, which is an impractical operational condition once the formaldehyde produced would be too dilute.

Carbon monoxide selectivity presented small values on the studied range and the results were not plotted on the graph.

The water to methanol molar ratio used industrially is observed to vary depending on the particular distillation constraints of each plant. Values as low as 0.15 – 0.20 are found in industrial plants and a limit is supposed to exist between 0.65 and 0.75.

3.4. Influence of residence time

All studies agree that longer residence time increases the methanol conversion, the carbon dioxide and carbon monoxide selectivity, consequently decreasing the formaldehyde selectivity (Qian et al., 2003; Andreasen et

al., 2003; Waterhouse et al., 2004a; Cao and Gavriilidis, 2005; Andreasen et al., 2005). The conversion versus selectivity relationship (Figure 10) is due to the increasing quantity of formaldehyde formed with increasing conversion, as long as more contact time with the catalyst is allowed. The higher the formaldehyde availability in the reaction mixture, the higher is the rate of formaldehyde combustion and decomposition, a classical effect of a consecutive reaction mechanism (Andreasen et al., 2005).

Besides residence time, the corresponding space velocity is also widely used in formaldehyde studies. These two parameters were calculated using the ratio of reactor volume containing catalyst to gas volumetric flowrate at reaction temperature. In the base simulation performed here, the residence time was 6.2 msec and space velocity $5.8 \cdot 10^5 \text{ h}^{-1}$.

Table 1: residence time conditions on reported experiments

Researcher	Residence time (msec)	Space velocity (h^{-1})
Lefferts et al. (1986)	60	60,000
Nagy and Mestl (1999)	10	363,000
Qian et al. (2003)	240	15,000
Waterhouse et al. (2004a)	29	125,000
Cao et al. (2005)	5 – 25	145,000 – 720,000
Papes and Maciel Filho (2007)	6.2	585,000

Simulated trends (Figure 8) are in accordance with experimental data from Qian et al. (2003), plotted on Figure 9. Values vary depending on different operation conditions, as shown on Table 1. Simulated values on Figure 8 are very much consistent with industrial measurements.

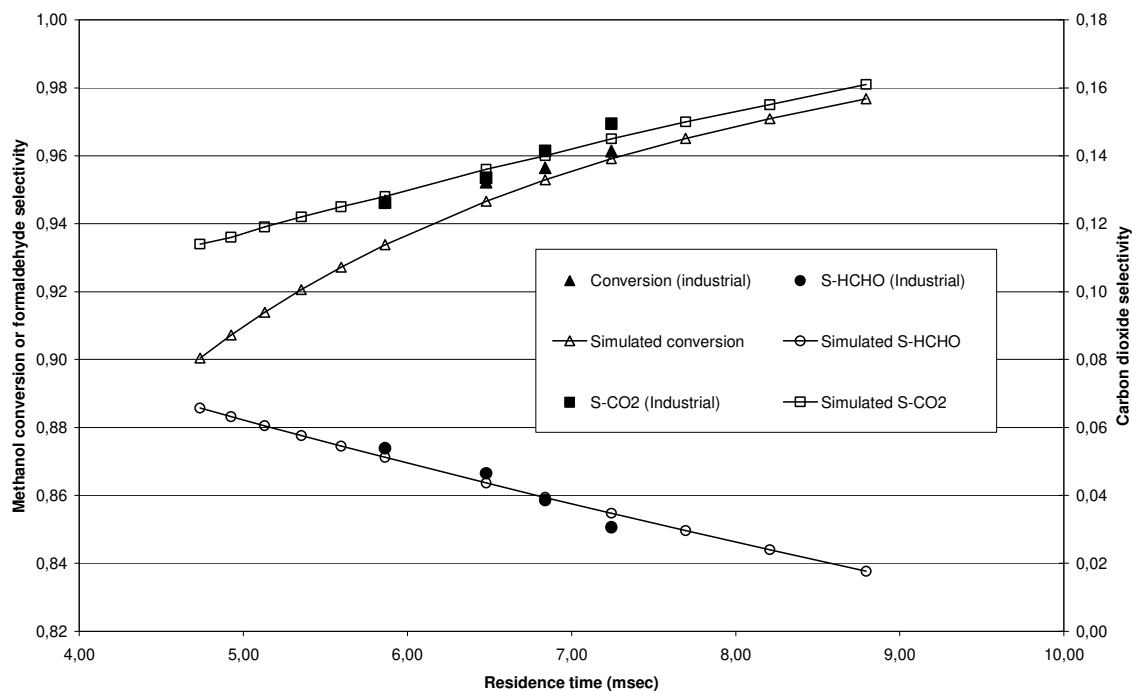


Figure 8: Effect of residence time on methanol conversion, selectivity towards formaldehyde (S-HCHO) and carbon dioxide (S-CO2). Simulations performed according to the base industrial operational conditions, varying the total flow.

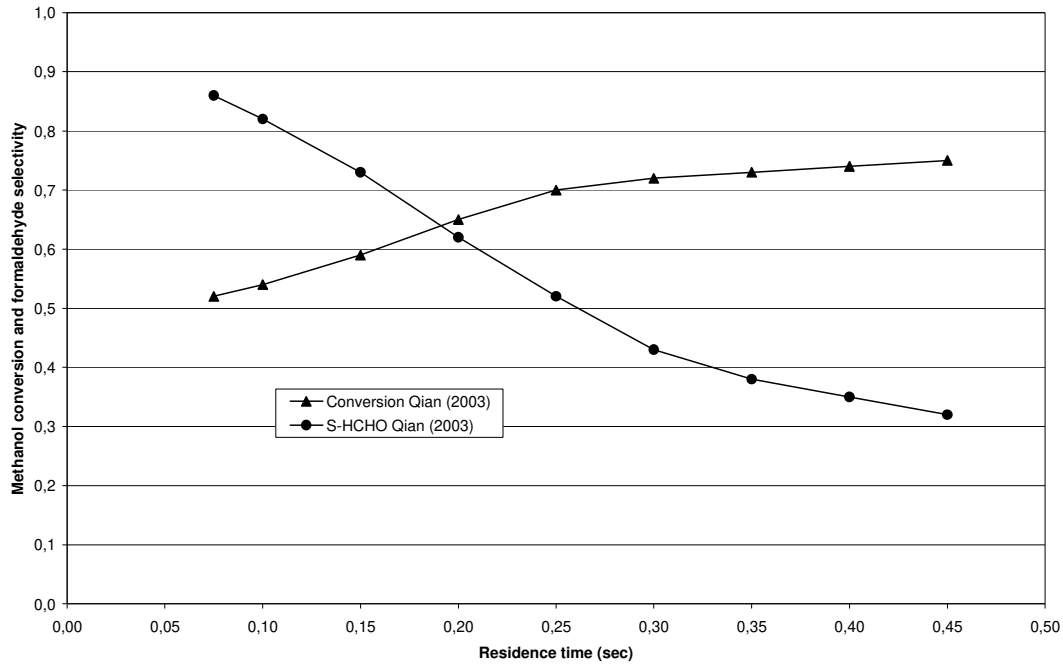


Figure 9: Effect of residence time on methanol conversion and selectivity towards formaldehyde (S-HCHO). Experiments from Qian et al. (2003).

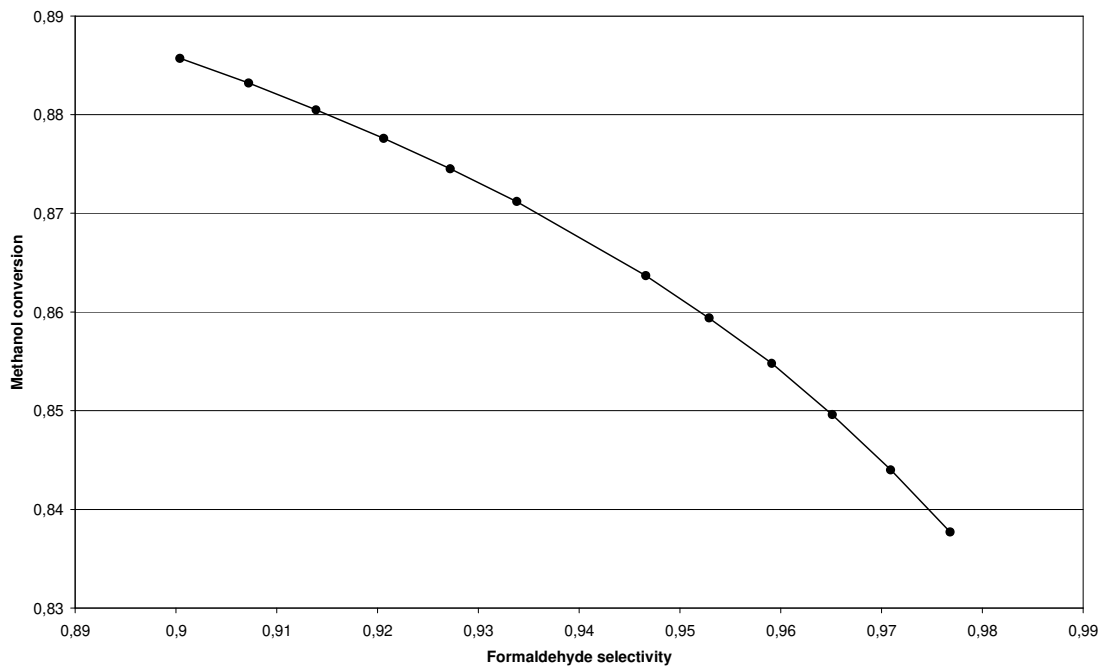


Figure 10: Simulated methanol conversion plotted against simulated formaldehyde selectivity.

4. Conclusion

In this paper, a simulator for a formaldehyde silver reactor was presented, based on a hybrid model. The fixed-bed reactor was modelled by deterministic mass transfer differential balance equation and the rates of the reactions were calculated by an artificial neural network, running together with the reactor model. Heat transfer calculations and industrial measurements indicated that isothermal approximation is feasible for the reactor simulator. The simulator and the ANN subroutine were developed by the authors in Fortran code.

The neural network was trained with industrial and experimental data, presenting successful results, validated by a control data set. New training approaches based on Genetic Algorithms improved the training performance, increasing the probability of reaching an optimum set of weights. A built-in approach, also based on Genetic Algorithms, allowed the net training using available measured data (conversion and selectivity). Results from previous works corroborate the examples given here.

Simulations performed near industrial operation conditions, using the trained neural network, indicated the influence of operational variables (temperature, methanol-to-oxygen molar ratio, water-to-methanol molar ratio and residence time) on the reactor performance (methanol conversion, selectivity towards formaldehyde, carbon dioxide and carbon monoxide). The trends were compared to literature information and industrial data, with excellent agreement.

It is important to note that simulations based on trained ANN over a specific set of data are fully valid only for the reactor from which that data was obtained. The trends observed for conversion and selectivity as a function of all studied variables are valid for all reactors operated under the same Silver process, however, precise simulation values may vary from one reactor to another, depending on the data set. The same warning applies to simulations with fresh and aged catalyst for a particular reactor.

The neural network algorithm has proven to be powerful for modelling the silver-formaldehyde kinetics based on measured data and made possible the development of a simulator for the silver reactor applicable to industrial conditions, presented here, differently than former simulators found in literature. Once the ANN learns the data pattern, there is no need to state hypothesis about mass transfer limitations on catalyst surface (kinetic regimen), reaction mechanism, limiting steps or catalyst activity homogeneity. This is not applicable to deterministic models, which have failed in simulating the kinetics for the Silver process.

If the kinetic behavior changes depending on the operational conditions, as stated by many researchers, the ANN still captures the different patterns through the experimental data. This task would be much more complex with deterministic approach, once different models would have to be considered depending on the operational condition.

Information provided by the simulations, presented on this paper, is essential for understanding the relationship between the operational variables and the reactor performance as an orientation for the optimized management of a silver reactor in order to increase plant profitability by reducing methanol consumption and pollutant by-product generation.

References

- ABRAF (Brazilian Association of Formaldehyde Manufacturers) report; "Panorama of productive chain", www.abraf.com.br, 2004.
- Andreasen, A.; Lynggaard, H.; Stegelmann, C. and Stoltze, P.; "A microkinetic model of the methanol oxidation over silver", *Surface Science*, 544, pp.5-23, 2003.
- Andreasen, A.; Lynggaard, H.; Stegelmann, C. and Stoltze, P.; "Simplified kinetic models of methanol oxidation on silver", *Applied Catalysis A: General*, 289, pp.267-273, 2005.
- Barteau, M and Madix, R.J.; *Surf. Sci*, 40, p.108, 1984.
- Bazilio, C.A.; Thomas, W.J.; Ullah, U. and Hayes, K.E.; "The catalytic oxidation of methanol", *Proc. R. Soc. Lond. A*, 399, pp.181-194, 1985.
- Berne, R. M. and Levy, M. N.; "Fisiologia", Editora Guanabara, 2nd ed., 1990.
- Bhagat, P.; "An Introduction to Neural Nets", *Chemical Engineering Progress*, August, p.55, 1990.
- Bhattacharyya, S.K.; Nag, N.K. and Ganguly, N.D.; "Kinetics of vapor-phase oxidation of methanol on reduced silver catalyst", *J. of Catalysis*, v.23, i.2, pp.158-167, 1971.
- Box, G.E.P and Hunter, J.S.; "Statistics for experimenters", Wiley and Sons, 1st ed., New York, 1978.
- Cao, E; Gavriilidis, A.; "Oxidative dehydrogenation of methanol in a microstructured reactor"; *Catalysis Today*, 110, pp.154-163, 2005.
- Crank, J. and Nicholson, P.; *Proceedings of Cambridge Phil. Soc.*, v.43, p.50, 1947.
- Dai, W.L., Cao, Y, Ren, L.P., Yang, X.L., Xu, J.H., Li, H.X., He, H.Y. and Fan, K.N.; "Ag-SiO₂-Al₂O₃ composite as highly active catalyst for the formation of formaldehyde from the partial oxidation of methanol", *Journal of Catalysis*, 228, pp. 80-91, 2004.
- Davis, L.; "Handbook of Genetic Algorithms"; International Thomson Computer Press, Boston, 1991.

- Fogler, H.S.; "Elements of chemical reaction engineering", Prentice-Hall International, 2nd ed., New Jersey, p.71, 1992.
- Goldberg, D.E; Deb, K. and Clark, J.H.; "Genetic Algorithms, Noise and the Sizing of Populations", Complex Systems, 6, pp. 333-362, 1992.
- Gravilin, V.N. and Popov, B.I; Kinet. Catal., 6, p.799, 1965.
- Irdam, E.A.; Kiefer, J.H.; Harding, L.B. and Wagner, A.F.; "The formaldehyde decomposition chain mechanism", International Journal of Chemical Kinetics, v.25, pp.285-303, 1993.
- Lefferts, L.; Ommen, J.G. and Ross, J.R.H.; "The oxidative dehydrogenation of methanol to formaldehyde over silver catalysts in relation to the oxygen-silver interaction", Appl. Catal., 23, p.385, 1986.
- Lennox, B.; Montague, G.A.; Frith, A.M.; Gent, C. and Bevan, V.; "Industrial application of neural networks – an investigation", Journal of Process Control, v.11, pp.497-507, 2001.
- Lynggaard, H.; Andreasen, A.; Stegelmann, C. and Stoltze, P.; "Analysis of simple kinetic models in heterogeneous catalysis", Progress in Surface Science, 77, pp.71-137, 2004.
- Nagy, A.; Mestl, G.; Ruhle, T.; Weinberg, G. and Schlogl, R.; "The dynamic restructuring of electrolytic silver during the formaldehyde synthesis reaction", J. of Catalysis, 179, pp.548-559, 1998.
- Nagy, A. and Mestl, G.; "High temperature partial oxidation reactions over silver catalysts", Applied Catalysis A: General, 188, pp.337-353, 1999.
- Papes Filho, A.C.; "Simulation and optimization of a silver formaldehyde reactor, using artificial intelligence techniques", PhD thesis (in English), UNICAMP – University of Campinas, Brazil, 2007.
- Papes Filho, A.C. and Cremasco, M.A.; "Correlation for estimation of diffusion coefficient for gases", Proceedings of the 1st Brazilian Congress of Chemical Engineering – Scientific Initiation, UFSCar Ed., www.ufscar.br, 1995.
- Papes Filho A.C. and Maciel Filho R.; "Concurrent Engineering Reactor Design", Computer Aided Chemical Engineering, v.20 A, Edited by Luis Puijagner and Antonio Espuña, Elsevier B.V., ISSN 1570-7946, pp.559-564, 2005.
- Papes Filho, A.C. and Maciel Filho, R.; "Novel approach for acquiring rate of reaction data from process information for neural network training: application to an industrial reactor for methanol oxidation to formaldehyde over silver catalyst process", to be published, 2007a.
- Papes Filho, A.C. and Maciel Filho, R.; "Hybrid training method for artificial neural networks using genetic algorithms: application to industrial methanol oxidation to formaldehyde over silver catalyst", to be published, 2007b.
- Papes Filho, A.C. and Maciel Filho, R.; "A Built-in Training Method for Universal Kinetic Models Trough Neural Networks and Genetic Algorithms: Application to Industrial Methanol Oxidation to Formaldehyde over Silver Catalyst", to be published, 2007c.
- Pestryakov, A.N.; "Modification of silver catalyst for oxidation of methanol to formaldehyde", Catalysis Today, 28, pp. 239-244, 1996.
- Pham, D.T. and Pham, P.T.; "Artificial intelligence in engineering", International Journal of Machine Tools & Manufacture, v.39, pp. 937-949, 1999.
- Piccoli, R.L.; "Kinetic study of methanol selective oxidation to formaldehyde on iron molybdate catalyst", Master dissertation, Rijksuniversiteit Gent, Belgium, 1992.
- Pilato, L.A., Knop, A. and Gardziella, A.; "Phenolic resins", Springer, 2nd ed., New York, 2000.
- Pizzi, A.; "Advanced wood adhesives technology", Marcel Dekker Inc., 1st ed., New York, 1994.
- Press, W.H., Flannery, B.P., Teukolsky, S.A. and Vetterling, W.T.; "Numerical Recipes", Press Syndicate of the University of Cambridge, 1st ed., 1992.
- Psichogios, D.C. and Ungar, L.H.; "A hybrid neural network-first principles approach to process modeling", AIChE Journal, 38, 10, pp. 1499-1511, 1992.
- Qian, M.; Liauw, M.A. and Emig, G.; "Formaldehyde synthesis from methanol over silver catalysts", Applied Catalysis A: General, 238, pp.211-222, 2003.
- Reid, R.C; Prausnitz, J.M and Poling, B.E.; "The properties of gases and liquids", McGraw-Hill Book Company, 4th ed., New York, 1987.
- Robb, D.A. and Harriot, P; "The kinetics of methanol oxidation on a supported silver catalyst", J. of Catalysis, 35, pp.176-183, 1974.
- Rumelhart, D.E; Hinton, G.E. and Williams, R.J.; "Learning internal representations by error propagation" in Parallel distributed processing, v.1, pp.318-362, 1986.
- Sandler, S.I.; "Chemical and engineering thermodynamics", John Wiley & Sons, New York, 1989.
- Santacesaria, E. and Morbidelli, M.; "Kinetics of the catalytic oxidation of methanol to formaldehyde", Chem. Engng. Sci., v.36, pp.909-918, 1981.
- Sauer, J and Emig, G.; "The catalyzed dehydrogenation of methanol to formaldehyde at high temperatures", Chemical Engineering Technology, 18, pp. 284-291, 1995.

- Schubert, H; Tegtmeier, U. and Schlogl, R.; "On the mechanism of the selective oxidation of methanol over elemental silver", *Catalysis Letters*, 28, pp.383-395, 1994.
- SRI International; "Formaldehyde", Report n° 23A, Menlo Park, 1978.
- Thomas, M.D.; "Preparation of formaldehyde", *Journal of the American Chemical Society.*, 42, p. 867, 1920.
- Ullmann's Encyclopedia of Industrial Chemistry, v.A11, 5th ed., VHC Publishers, New York, 1988.
- Van Veen, A.C, Hinrichsen, O. and Muhler, M.; "Mechanistic studies on the oxidative dehydrogenation of methanol over polycrystalline silver using the temporal-analysis-of-products approach", *J. of Catalysis*, 210, pp. 53-56. 2002.
- Wachs, I.E. and Madix, R.; "The oxidation of methanol on a silver (110) catalyst", *Surface Science*, 76, pp. 531-558, 1978.
- Walker, J.F; "Formaldehyde", Robert E. Krieger Publishing Company, 3rd ed., New York, 1975.
- Wang, Q.J.; "Using Genetic Algorithms to Optimise Model Parameters", *Environmental Modelling & Software*, v.12, n.1, pp 27-34, 1997.
- Wasserman, P.D.; "Neural Computing: Theory and Practice", van Nostrand Reinhold ed., 1st ed., New York, 1989
- Waterhouse, G., Bowmaker, G. and Metson, J.; "Mechanism and active sites for the partial oxidation of methanol to formaldehyde over an electrolytic silver catalyst", *Applied Catalysis A*, 265, pp.85-101; 2004 (a).
- Waterhouse, G., Bowmaker, G. and Metson, J.; "Influence of catalyst morphology on performance of electrolytic silver catalysts for the partial oxidation of methanol to formaldehyde", *Applied Catalysis A*, 266, pp.257-273, 2004(b).
- Welty, J.R.; Wicks, C.E. and Wilson, R.E.; "Fundamentals of momentum, heat and mass transfer", John Wiley & Sons editor, 3rd ed., New York, 1984.

6.3. Conclusões

Nesse capítulo apresentou-se um simulador híbrido para o reator de formaldeído catalisado por prata. O leito fixo foi modelado pela equação diferencial de balanço de massa e as taxas de reação foram calculadas por uma RNA, executada em conjunto com o modelo do reator. Cálculos de transferência de energia e medições industriais indicaram que o modelo isotérmico é adequado para esse caso. O simulador e a sub-rotina com RNA foram desenvolvidos pelos autores em código Fortran.

A RNA foi treinada com sucesso a partir de dados industriais e experimentais, validada pela comparação com um conjunto de dados de controle. Novos métodos de treinamento baseados em AG aprimoraram o desempenho do aprendizado, aumentando a probabilidade de atingir-se o conjunto ótimo de pesos para a rede. O método tipo “acoplado”, também baseado em AG, permitiu o treinamento da rede usando dados de processo disponíveis em uma planta industrial (conversão e seletividades). Os resultados dos capítulos anteriores corroboram os exemplos do presente capítulo.

As simulações realizadas em condições operacionais próximas às industriais, usando a RNA treinada, detalharam a influência de variáveis operacionais (temperatura, razão molar metanol/oxigênio, razão molar água/metanol e tempo de residência) no desempenho do reator (conversão e seletividades). As tendências foram comparadas com informações de literatura, bem como com dados industriais, com excelente correspondência.

A abordagem com RNA mostrou-se bastante conveniente para modelar a cinética do formaldeído-prata, baseando-se em dados experimentais, e tornou possível o desenvolvimento de um simulador para este processo, aplicável a condições industriais, apresentado nesse capítulo, diferentemente dos simuladores encontrados na literatura. Uma vez que a RNA “aprende” o padrão dos dados, não há necessidade de formular hipótese acerca de limitações na transferência de massa na superfície do catalisador (regime cinético), mecanismos, etapas limitantes ou homogeneidade da atividade do catalisador. Essa característica não é aplicável aos modelos determinísticos, que têm falhado em simular a cinética do processo prata.

Se o comportamento cinético sofre alteração dependendo das condições operacionais, como declaram vários pesquisadores, a RNA continua apta a capturar os diferentes padrões através dos dados experimentais. Essa tarefa seria muito mais

complicada com abordagem determinística, uma vez que modelos diferentes teriam que ser considerados dependendo das condições operacionais.

A informação gerada pelas simulações apresentadas nesse capítulo é essencial para compreender as relações entre as variáveis operacionais e o desempenho do reator, como uma orientação para o gerenciamento otimizado do reator de prata, aumentando a rentabilidade da planta através da redução do consumo de metanol e geração de subprodutos poluentes.

CAPÍTULO 7

OTIMIZAÇÃO DO REATOR DE FORMALDEÍDO - PRATA USANDO ALGORITMO GENÉTICO (AG) E PROGRAMAÇÃO QUADRÁTICA SUCESSIVA (SQP)

7.1. Introdução

Nesse Capítulo, foi descrito o desenvolvimento de um programa de otimização baseado em AG e SQP, aplicado ao reator de leito fixo de oxidação do metanol a formaldeído em catalisador de prata. O processo de otimização matemática foi realizado com o auxílio do simulador para o reator estudado, descrito e validado nos Capítulos anteriores.

Estudos de otimização para diferentes casos foram realizados, comparando-se o desempenho dos dois métodos: AG e SQP. As variáveis manipuladas nesse estudo foram:

- Temperatura do leito ($^{\circ}\text{C}$);
- Vazão de ar (kg/h);
- Vazão da mistura água/metanol (kg/h);
- Fração mássica da água na mistura (%).

A variável otimizada foi o consumo específico de metanol (minimizado), uma medida diretamente relacionada à seletividade para formaldeído (maximizada) e ao custo de fabricação (minimizado). As restrições foram os limites para cada variável manipulada, bem como a conversão mínima. Baixas conversões de metanol requerem uma etapa de destilação para que o produto final esteja dentro da especificação, uma vez que o metanol tem efeito inibidor de reatividade em várias aplicações do formol. Dessa forma, a mínima conversão possível do reator dependerá da capacidade de destilação da planta.

Os casos estudados basearam-se em circunstâncias comuns em uma planta química:

- Caso I: restrições na capacidade de destilação, traduzidas como restrições na conversão mínima; como exemplo foram estudadas as restrições com conversão mínima de 85%, 90%, 92%, 95% e 98%;
- Caso II: restrição na capacidade do compressor de ar, traduzida como um menor valor máximo da vazão de ar;
- Caso III: restrição na capacidade de injeção da mistura água-metanol;

- Caso IV: restrições na programação de produção, traduzidas como restrições na alimentação de metanol na planta, em três níveis.

Foi realizada uma análise de sensibilidade em um dos pontos ótimos de operação encontrados, com o objetivo de verificar se a condição indicada é possível de ser mantida com os controles encontrados em uma planta química.

O trabalho de otimização com o AG foi comparado com o SQP, apresentando-se as vantagens e desvantagens de cada, bem como a proposta de associação desses dois algoritmos para extrair o máximo desempenho em projetos de otimização.

Finalmente, foi realizada uma análise comparativa entre uma condição padrão de operação industrial e as condições otimizadas apresentadas nesse capítulo, destacando os benefícios econômicos e ambientais.

7.2. Desenvolvimento.

O desenvolvimento desse capítulo é descrito no artigo intitulado “Optimization of a Fixed-bed Formaldehyde Silver Reactor using Genetic Algorithms and Sequential Quadratic Programming”, apresentado a seguir, a ser submetido para publicação em revista indexada internacional.

Optimization of a Fixed-bed Formaldehyde Silver Reactor using Genetic Algorithms and Sequential Quadratic Programming

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Abstract

The mathematical optimization of a formaldehyde silver reactor was presented in this work. The catalytic reactor simulator was built by the authors, using a hybrid model based on the mass balance differential equations for the fixed-bed and neural networks for calculating the rate of reaction. The artificial neural network was successfully trained and validated, as reported by the authors in previous works. An optimization tool, based on genetic algorithm, was developed here to optimize the reactor simulator, comparing the results to a classical gradient-driven optimization algorithm: sequential quadratic programming (SQP).

Many cases were studied, with different constraints and objectives in order to report optimum working conditions for a variety of circumstances found in the industrial operation of this process. The optimization results using genetic algorithm always indicated an operational condition believed to be the global optimum, but with longer computing times. The classical SQP, in the other hand, produced results very close to genetic algorithm, but this performance was dependant on the initial estimate: sometimes the algorithm converged to a solution that was clearly not the global optimum. The advantages and disadvantages of the two methods were considered and an association of them is believed to be the best approach for optimization studies.

The optimized conditions found in this work were analyzed according to the known relationships between operational parameters and reactor performance, reported in previous works, with very consistent results. The indications of this work have already started to be implemented in industrial plant with successful results.

Key words: formaldehyde, silver, artificial neural networks, genetic algorithms, artificial intelligence, methanol oxidation, optimization, sequential quadratic programming.

1. Introduction

Formaldehyde is industrially produced worldwide using one of the two available routes: the Formox and the Silver process. Both processes are based on the methanol oxidation under air stream, obtaining an aqueous solution of formaldehyde (formalin), using different reactor configurations. In 2004, production of this important chemical intermediate reached 32 million metric tones per year of formalin 37% solution basis (ABRAF, 2004), consumed basically for the manufacture of a series of adhesives, employed on wood products, brake linings, thermal insulation, foundry castings, refractory bricks and many other materials (Walker, 1975; Pizzi, A., 1994; Pilato et al., 2000).

The Formox is a relatively new technology (1950's), employed in practically all plants built in the recent decades. It uses an iron-molybdenum oxide as catalyst, packed in multitubular reactors, with oxygen-rich feed and low temperatures (300 – 400 °C). High methanol conversion (no distillation required) and high formaldehyde selectivity (90 – 93%) are achieved with this process (Santacesaria and Morbidelli, 1981; Piccoli, 1992).

The Silver technology is in use since the beginning of the XXth century, working with a thin silver catalyst bed at 600 – 700 °C, with methanol-rich feed. The fixed-bed is not cooled and rapid quenching of the reacted stream is required to prevent formaldehyde decomposition. Two variations are industrially used: *Methanol Ballast Process*, where only air and pure methanol are fed to the silver bed, featuring incomplete methanol conversion and requiring a distillation recovery of the raw material; and *Water Ballast Process, or BASF Process*, where extra water is fed with the reactant mixture, and higher methanol conversion (98-100%) may be achieved with reasonable selectivity towards formaldehyde (85 – 92% range).

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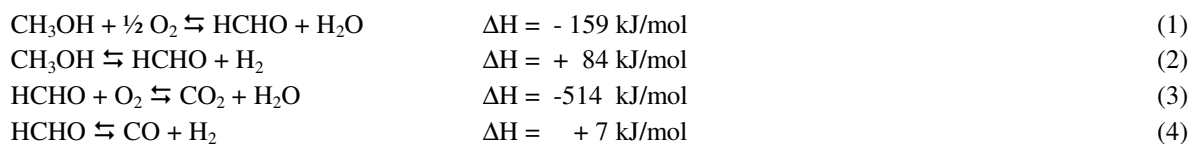
Besides new plants are built with Formox technology, having better selectivity and lower operational costs, approximately 30 - 50% of the current world's capacity still relies on plants operated with Silver process (Van Veen et al, 2002; Qian et al., 2003; Waterhouse et al., 2004b). Many researchers have devoted their work to study the Silver process but there is still no full mechanistic and kinetics understanding of methanol oxidation on silver surfaces under industrial conditions (Gravilin and Popov, 1965; Bazilio et al., 1985; Ullman, 1988; Van Veen et al., 2002; Andreasen et al., 2003; Waterhouse et al., 2004ab; Cao and Gavriilidis, 2005). In this sense, a little information exists about the formation of by-products and the influence of the operational parameters on the reactor performance.

Formox plants are supplied with process manuals and technical assistance from licensors, including plant simulators. Silver plants are far behind concerning competitiveness, once they naturally have lower formaldehyde selectivity (consumes more methanol per formaldehyde unit produced) and there are few tools to help in improving its performance. Any simulator or process information that aids Silver plant personnel to optimize the process will be a strategic key to minimize the gap for the Formox plants and guarantee the continuity of the business.

Process simulators applicable for all industrial conditions are not available in literature and deterministic models cannot be developed due to the lack of measured kinetic data, caused by difficulties in avoiding mass transfer limitations (kinetic regimen), non-isothermicity, deactivation and aging of silver catalyst in conventional reactors (Bazilio et al, 1985; Andreasen et al, 2003; Cao and Gavriilidis, 2005).

Papes Filho and Maciel Filho (2007d) proposed a hybrid model for a Silver formaldehyde reactor, using classical deterministic approach for modeling the fixed-bed and neural networks for calculating the rate of reaction. The same authors also presented a method for using macro experimental data (reactor conversion and selectivity), instead of kinetic data (rate of reaction), to fit the neural network (Papes Filho and Maciel Filho, 2007a,b,c). Good results were obtained for several tested conditions, comparing the outputs of the hybrid simulator with measured data from literature and industrial measurements, as reported by Papes Filho (2007)

The simulator was based on four relevant reactions that account for the formation of formaldehyde and by-products. Two parallel reactions are involved in formaldehyde formation from methanol on the silver catalyst: methanol oxidation (1) and methanol dehydrogenation (2). The formed formaldehyde reacts with oxygen on the silver catalyst, forming carbon dioxide (3) and it may also decompose on gas phase to carbon monoxide, at high temperatures (4). Reactions 3 and 4 reduce the selectivity towards the desired product. The oxidation reactions are extremely exothermic and the reactor has a high heat generation.



Carbon dioxide is only formed by a further oxidation of formaldehyde through a formate intermediate, according to Wachs and Madix (1978) mechanism (Andreasen et al, 2003). Carbon monoxide is formed by the gas-phase homogeneous decomposition of formaldehyde, above 650 °C (Lefferts et al., 1986; Sauer and Emig, 1995; Qian et al., 2003; Waterhouse et al, 2004b).

Simulations from previous works of Papes Filho and Maciel Filho (2007d) and information from literature allows establishing the relationships between process variables and reactor performance.

Reaction temperature is one of the most important parameters that influence the methanol conversion and the selectivity. At low temperatures the reaction is inactive, with an ignition temperature seen on the range 177 - 277 °C (Gravilin and Popov, 1965; Lefferts et al., 1986; Nagy and Mestl, 1999; Andreasen et al, 2003; Waterhouse et al., 2004a; Cao and Gavriilidis, 2005). The methanol conversion and selectivity towards

formaldehyde are very sensible to temperature and higher yields are achieved in the range 600 – 700 °C, where the thermal decomposition of formaldehyde starts to be significant.

At lower temperatures (below 600 °C), the formaldehyde selectivity increases with increasing temperature, up to a maximum, believed to lie in the range 630 – 650 °C (Dai et al, 2004). Above this limit, the selectivity drops fast due to the gas-phase decomposition of formaldehyde, forming carbon monoxide. A plateau is seen between 580 and 650 °C (the plateau range may vary depending on the process), where the selectivity to formaldehyde shows little variation with temperature. Carbon dioxide selectivity is higher at lower temperatures, reaching values of 40% at 350 °C (Nagy and Mestl, 1999; Waterhouse et al., 2004a), but decreasing to the level of 10% at the temperature range of 580 – 720 °C. The decrease in the selectivity to carbon dioxide with increasing temperature reflects the increasing thermal instability and lower surface coverage of particular oxygen species on the catalyst surface at higher temperatures (Andreasen et al., 2003). Methanol conversion increases monotonically with increasing temperature, approaching 100% in the range 650 – 700 °C.

The explanation for the increase of formaldehyde selectivity with increasing temperatures below 600 °C is controversial (Papes Filho, 2007). Lefferts et al (1986), Nagy et al (1998), Van Veen et al (2002) and Waterhouse et al. (2004a) explain the phenomena based on the influence of different oxygen species adsorbed throughout the silver surface on the reaction mechanism. Andreasen et al (2003, 2005) consider that a reaction in serial mode, where carbon dioxide is formed through formaldehyde oxidation, explains the selectivity phenomena, as the activation enthalpy for methanol oxidation is always larger than carbon dioxide formation one, making the rate of formaldehyde formation to increase faster than formaldehyde combustion with increasing temperature. Oxygen is rapidly consumed in the methanol oxidation reaction and smaller oxidant concentration inhibits further oxidation of formaldehyde. This behavior might be opposite (decrease on formaldehyde selectivity with increasing temperature) when oxygen-rich mixtures are used, where the mechanism proposed by the researchers is believed to fail, since the unselective reaction routes seem to be suppressed (Cao and Gavriilidis, 2005).

As observed by Papes Filho and Maciel Filho (2007c,d), the addition of water to the feed is essential for achieving high formaldehyde yields (Waterhouse et al, 2004a; Cao and Graviilidis, 2005): it has high heat capacity and removes the reaction heat, preventing overheating as well sintering of catalyst. Water also blocks specific surface sites and displaces the reaction mechanism, reducing the formation of undesirable by products (Barteau and Madix, 1984; Qian et al, 2003; Andreasen et al., 2003). It has an inhibiting effect on the methanol conversion but improves the selectivity towards formaldehyde (decreases the selectivity towards carbon dioxide). In general, the conversion reduction with water addition is compensated operating the bed with higher temperature. Molar ratios water/methanol as low as 0.15 – 0.20 are found in plants equipped with distillation column (for separating the non-reacted methanol), where better selectivity can be achieved with lower conversion. Molar ratios close to 0.5 are found in complete conversion plants, operating the plant at higher temperatures. A limit is supposed to exist between 0.65 and 0.75.

Oxygen plays a key role on the reaction mechanism, keeping the catalyst active (Bhattacharyya et al., 1971; Papes Filho, 2007). High oxygen concentrations increase the methanol conversion but leave much remaining oxidant for formaldehyde combustion. Simulated methanol conversions showed decreasing behavior with increasing methanol/oxygen ratio. The higher the oxygen availability, the higher the methanol consumption due to: the acceleration of methanol oxidation and formaldehyde combustion reactions, Le Chatellier equilibrium principles and catalyst activation features. Waterhouse et al. (2004a) reported methanol conversion close to 100% below 2.0 molar ratio, decreasing fast above 2.25 ratio. The simulations also predicted that formaldehyde selectivity increases with increasing methanol/oxygen ratio, while carbon dioxide selectivity decreases. Small changes on simulated selectivity were seen above molar ratio of 3.0. These trends are explained by the reaction mechanism, where the higher the oxygen availability, the higher the rate of formaldehyde combustion. CO selectivity is not expected to show a dependence with oxygen concentration as it is formed by the homogeneous decomposition of formaldehyde (Lefferts et al., 1986; Waterhouse et al., 2004a).

The residence time has a direct effect on the reactor performance. When residence time increases, there is an increase on methanol conversion and a decrease on the selectivity towards formaldehyde. An increase on the selectivity towards carbon dioxide and carbon monoxide is also observed.

Formic acid is normally not produced when the catalyst is fresh. After deactivation (4 – 9 months), formic acid is generated at all temperatures, urging catalyst replacement (Schubert et al., 1994; Qian et al., 2003). In this sense, formic acid is not considered an important by-product in this work.

Besides the relationships between the process variables (temperature, methanol/oxygen molar ratio, water/methanol molar ratio and residence time) and reactor performance have been presented (Papes Filho, 2007), it is difficult to predict the optimum operational condition that allow maximum formaldehyde selectivity, given a minimum methanol conversion, limited by product specifications, distillation capabilities and process constraints. The effects of the single variables on the reactor performance are not linear and there are synergistic effects between two or more variables that impair the use of one-variable-at-a-time plots to optimize the reactor. In this case, optimization programs are more suitable to find the optimum operation conditions.

There are many optimization algorithms available, but the most used in engineering problems is the sequential quadratic programming (SQP), a gradient-driven deterministic method based on an initial guess for the parameters to be optimized (Boggs and Tolle, 1996). The SQP is a classical method with solid theoretical foundation and commercially available programs, but it depends heavily on the initial guess: the algorithm may be trapped into a local optimum or the derivatives may not be determined.

Alternative techniques from artificial intelligence field, like the Genetic Algorithms (GA), have become very popular recently to solve optimization problems. GA do not depend on an initial estimative and they perform a wide search for best solutions throughout the whole parameters ranges, having higher probability to find the global optimum instead of being trapped into a local one (Garrard and Fraga, 1998). They do not need derivatives to calculate the solutions, overcoming the disadvantages of the deterministic gradient-driven methods, as SQP. The disadvantage is the huge computational requirement, demanding a great amount of mathematical operations and long run times. In the past, this fact made impracticable the use of GA methodology, but with the evolution of computer machines, nowadays every home desktop is able to perform a GA optimization with reasonable computing times, especially if real time operation is not an issue.

GA do not calculate the solutions, but they drive the best solutions to be kept and mixed to obtain even better solutions. They require that the solutions can be evaluated with defined criteria, in order to have them ranked from the best to the worst one. The process simulates the natural evolution of species, where the best individuals (solutions) survive and procreate, forming a new generation of solutions that will be evaluated in the same fashion.

The goal of the present work is to add value to the formaldehyde industry by studying the optimization of a Silver reactor for a series of cases in order to help engineers of industrial plants to define operational policies. Another important objective is to demonstrate the potential of GA for this task, in comparison with a classical SQP optimization algorithm. A sensitivity study was also performed at the optimum condition for one of the studied cases in order to verify the operation stability.

Considering the potential market demand for formaldehyde and strong competition, economic incentives do exist to optimize the process: methanol cost represents more than 80% of the production cost of formaldehyde and an improvement of 1 percentage point on the selectivity in an average size plant means saving about 200,000 US\$ per year on methanol purchasing. Environmental pressure is also a driver to optimize this process, once the carbon emissions generated by formaldehyde plants (carbon dioxide and carbon monoxide) will have to be reduced soon in order to comply with world's efforts against global warming (Papes Filho, 2007).

2. Methods

2.1. Formaldehyde Silver reactor simulator

A formaldehyde Silver reactor simulator was developed by the authors and presented in previous work (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007d), using Fortran code. In a hybrid approach, the fixed-bed was represented by a deterministic model and the rate of reactions were calculated by an artificial neural network, implemented inside the simulator code.

The fixed-bed model was based on the differential mass balance equation derived from the application of pseudo-homogeneous, bidimensional, plug-flow model for tubular reactor at steady-state operation. Equation 5 shows the differential mass transfer equation on cylindrical coordinates (Welty et al., 1984; Fogler, 1992). Figure 1 shows a schematic of the silver reactor.

$$D_L \cdot \frac{\partial^2 C}{\partial z^2} + D_R \cdot \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial C}{\partial r} \right) - V_Z \cdot \frac{\partial C}{\partial z} + \nu_A \cdot R_V = 0 \quad (5)$$

In this equation “C” is the substance concentration (kg/m³); “r” is the distance from the reactor central line or the radius on cylindrical coordinates (m); “z” is the distance from the reactor inlet or the axial distance on cylindrical coordinates (m); “D_L” is the axial diffusion coefficient (m²/s); “D_R” is the radial diffusion coefficient (m²/s); “V_z” is the axial velocity (m/s); “ν_A” is the stoichiometric coefficient for the studied substance (dimensionless); “R_V” is the rate of the reaction per reaction volume (kg/m³.s).

Equation 5 provides the bidimensional mass balance equation, as demonstrated in literature. The simulator was created by the authors containing this equation in order to produce a generic software that could deal with axial and radial flow, useful for a variety of problems. Nevertheless, in the case of the Silver formaldehyde reactor, the system is unidimensional, once the inlet stream is homogeneous, the reaction takes place homogeneously throughout the silver, there is no inlet/outlet streams along the bed and the catalyst bed is isothermal. In this sense, in practice, Eq. 5 is simplified by excluding the terms related to the radial flow.

According to studies of Papes Filho and Maciel Filho (2007d), for practical purposes, the reactor (fixed-bed) operates adiabatically and isothermally. The differential mass transfer equation was applied to the three reactions of interest in the Silver reactor (Andreasen et al, 2003; Papes Filho and Maciel Filho, 2007a), as presented on equations 6-8:



The three equations are solved simultaneously, calculating the advancement of each one. The substances representative of these three reactions are: formaldehyde for R_{HCHO}, carbon dioxide for R_{CO₂} and carbon monoxide for R_{CO}.

The Crank-Nicholson numerical algorithm was used to solve the equations (Crank and Nicholson, 1947; Press et al., 1992). It is a finite difference method, semi-implicit and known to be intrinsically stable, very suitable for solution of a system of differential partial equations. The method involves taking the derivative half way between the beginning and the end of the “z” direction and the price paid for the high accuracy and unconditional stability is having to invert a tridiagonal matrix at each space-step.

At every step of the numerical method, the concentration of all species is calculated, as well as the physical properties for all components (Welty et al., 1984; Reid et al., 1987; Sandler, 1989; Papes Filho and Cremasco, 1995).

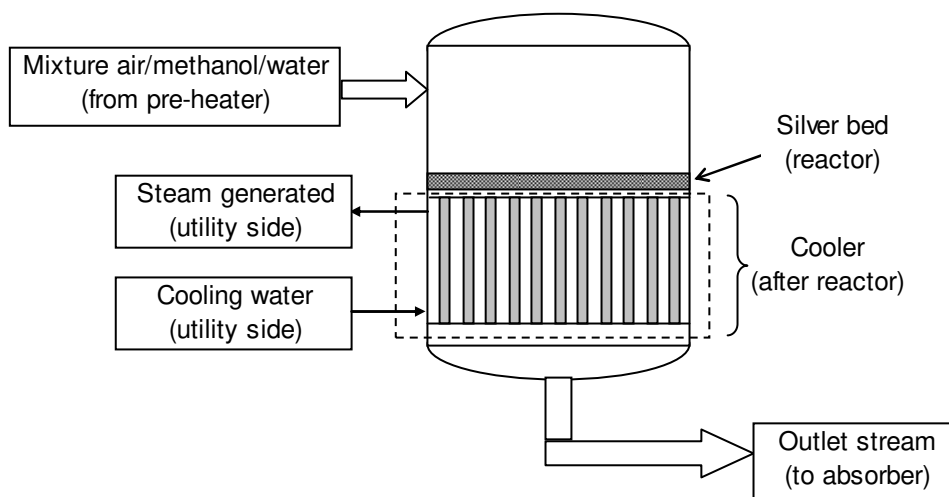


Figure 1: Scheme of a typical silver reactor, showing the fixed-bed, where reaction takes place, and the downstream cooler.

The rates of reaction are calculated by means of an artificial neural network (ANN), as shown on Figure 2, where the input and output parameters are identified. The ANN used has 3 layers and 12 neurons at hidden layer. A bias neuron connected to “1” was included to the input and hidden layers. Three neurons compose the output layer, calculating the rate of the 3 reactions of interest: formaldehyde formation, formaldehyde combustion and formaldehyde gas-phase decomposition. At every solving step, when the rates are requested by the simulator, the ANN calculates them using the temperature and partial pressures provided by the fixed-bed model for that iteration.

The ANN used for the current optimization studies was trained according to the works of Papes Filho (2007). In the training process, the ANN internal parameters (weights) are adjusted in order to minimize the difference between the values calculated by the net and experimental values, provided that a set of input-output experimental (measured) data is available for the fitting process. Once the difference lies below an established limit, the ANN is considered trained and the best set of weights is stored in a data file. Using the stored weights, the ANN is able to calculate outputs (rates for the three reactions) for new process conditions (Papes Filho and Maciel Filho, 2007c).

While ANN training is time consuming (may take several hours), it calculates the outputs very fast when the weights are defined (less than one second). In this sense, a trained ANN will not add computing times constraints for optimization studies. Details about ANN and ANN training may be found in literature (Rumelhart et al., 1986; Wasserman, 1989; Bhagat, 1990; Lennox et al., 2001; Psychogios and Ungar, 1992; Papes Filho and Maciel Filho, 2005; Papes Filho and Maciel Filho, 2007d).

The inputs to the simulator are: methanol flowrate (kg/h); air flowrate (kg/h); water flowrate (kg/h); bed temperature ($^{\circ}\text{C}$) and bed pressure (atm). If methanol and water are fed together as a solution, the solution flowrate (kg/h) and the water content on the solution (%) may be considered. Other information, also provided by the user, but not changed on simulations for the same reactor are: reactor diameter (m); bed length (m); silver particle size (m) and oxygen concentration on air (mole %).

The outputs from the simulator can be calculated using the concentrations of the substances from the last step of the numerical method (reactor outlet) or the advancement of the three reactions, as defined below, where “ ξ_{HCHO} ” is the advancement of formaldehyde formation reaction; “ ξ_{CO_2} ” is the advancement of the formaldehyde combustion reaction and “ ξ_{CO} ” is the advancement of the formaldehyde decomposition reaction.

- Methanol conversion (%): $X = \frac{\xi_{HCHO}}{n_4^o}$
- Selectivity towards formaldehyde (%): $S_{HCHO} = \frac{\xi_{HCHO} - \xi_{CO_2} - \xi_{CO}}{\xi_{HCHO}}$
- Selectivity towards carbon dioxide (%): $S_{CO_2} = \frac{\xi_{CO_2}}{\xi_{HCHO}}$
- Selectivity towards carbon monoxide (%): $S_{CO} = \frac{\xi_{CO}}{\xi_{HCHO}}$

Formaldehyde yield, methanol specific consumption (tones of MeOH consumed per tone of formalin 37% produced) and the outlet stream composition may also be provided by the simulator.

- Formaldehyde yield = $X \cdot S_{HCHO}$
- Methanol specific consumption = $\frac{32 \times 0.37}{S_{HCHO} \cdot 30.03}$

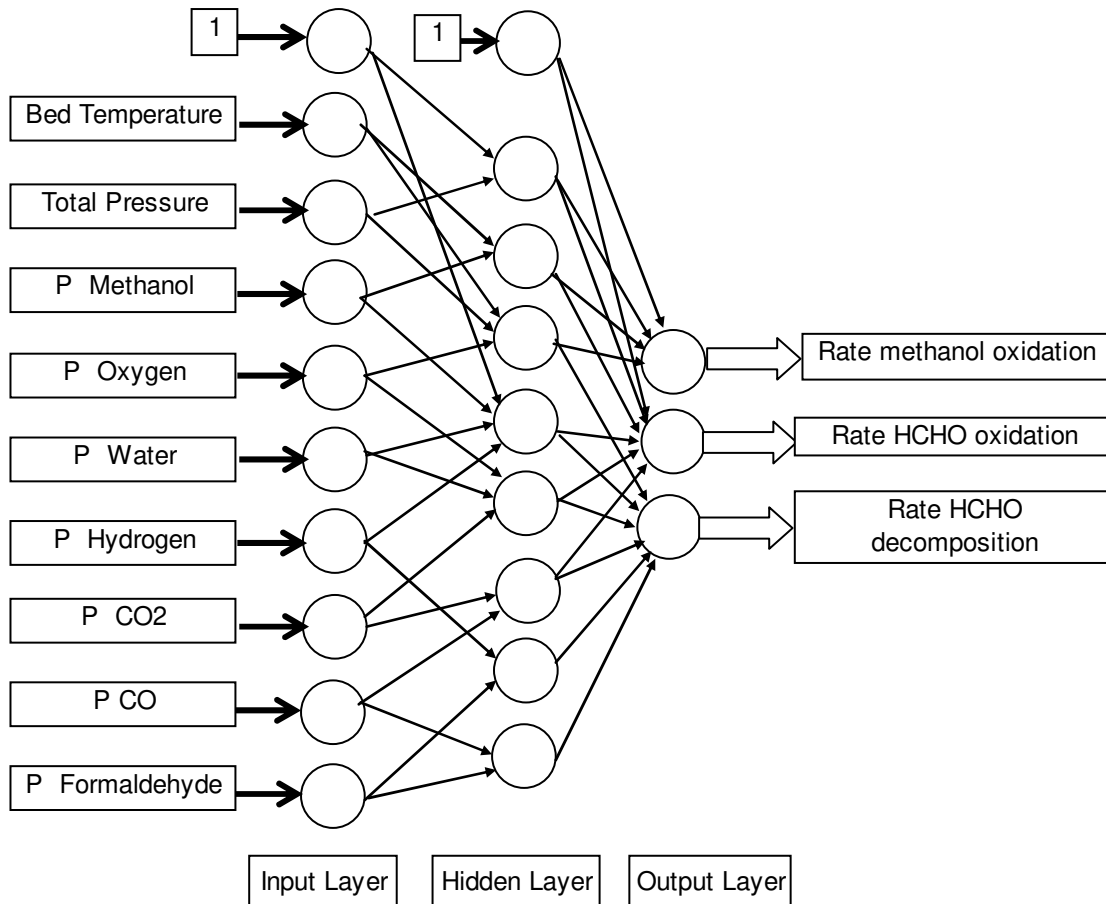


Figure 2: Schematic of the ANN used (not all arrows were drawn, in order to make the picture clear). “P” stands for partial pressure.

Having the ANN weights defined, the simulator can calculate correctly the conversion and selectivity for desired process conditions, defined by a temperature, pressure, air flowrate, methanol flowrate and water flowrate, given by the user.

2.2. Genetic Algorithms

Genetic Algorithms (Holland, 1976; Wang, 1997) have proven to be a powerful tool for a variety of optimization problems. They are based on natural evolution and considered part of the Artificial Intelligence field (Pham and Pham, 1999). The algorithm deals with a population of possible solutions and it does not calculate them, but encourages the best ones to survive generation after generation, while new solutions are created by a mixture of the best solutions of previous generation, always maintaining variability among the solutions

Population size is kept constant throughout generations and this parameter must be optimized to have best precision with reasonable computing time. The larger the population, the higher the probability of finding a better individual in smaller number of generations. There are methodologies available for calculating population size, but in practice it is set as large as computing time allows (Goldberg et al., 1992; Carrol, 1996a; Carrol, 1996b).

The individuals of the population, or possible solutions, are a mathematical representation of a chromosome. In practice, it is a vector with the parameters of the studied model. In the case of an optimization problem, the chromosome will contain as much genes as the parameters to be optimized. As an example, if the studied problem comprises 6 variables to be optimized, the chromosome vector will contain 6 genes or positions (Figure 3).

Gene	Gene	Gene	Gene	Gene	Gene
1	2	3	4	5	6

Figure 3: Example of a chromosome vector

For a small number of parameters to be optimized (less than 4, arbitrarily), it is difficult to apply the GA operators to create new possible solutions (the crossover operator has small efficiency). In this case, each gene, or parameter, should not be represented by its true value, but as a binary representation or Binary Code (Goldberg, 1989; Davis, 1991). The studied range for each parameter is divided into " N_{bin} " discrete values and a sequential number is assigned to each one. Instead of using the true value of the parameter, the associated sequential number is used, but in the binary representation (sequence of "1" and "0"). If higher precision on the estimate is required, a higher number of divisions (N_{bin}) is needed and a binary representation with more digits has to be used. If a large number of parameters is considered for optimization (more than 5, arbitrarily), the true values for the parameters can be used to fill the chromosomes' genes (Real Code).

Initially, the algorithm starts with a population of chromosomes whose values are chosen randomly. In the first iteration, or generation, the initial set of random solutions is evaluated, using a model according to the studied problem. It is very important to evaluate the individuals (solutions), once it is necessary to rank the solutions to identify the fittest individuals, which will survive and procreate.

The model in this work is the reactor simulator itself, where its input parameters are the ones to be optimized (temperature, methanol flowrate, air flowrate and water flowrate). The evaluation criteria will be the methanol specific consumption (SC), as it is directly related to the formaldehyde production cost, given that the methanol conversion will be considered a constraint.

Once the individuals of the first generation are evaluated (lower SC), the best solutions (parents) are combined to create the new solutions (children). The next generation is then composed by children of the individuals from the previous generation. The best solution of a generation is usually maintained in the new generation, in order to prevent losing this good solution in case of the children are less able than the parents (elitism). The parents may be selected by "selection of best individuals" or "tournament".

In the first case, the best individuals of a generation are selected to be the parents of the new generation. The best individuals are the ones with lower SC. A specific number of parents selected to mate may be defined or a limit may be considered (the selected parents are the ones with SC better than certain limit). The selected individuals are grouped in pairs to generate children. The pairing method may vary: priority to the best individuals or random pairing.

In the tournament, two pairs are randomly chosen. The best individual of each pair is selected and the two selected individuals generate a child. Two new pairs are chosen and the process is repeated until the new generation is completed.

The children are formed from the mixture of the parents' chromosomes. The pair of parents is selected by the methods above and then the child chromosome is created by "single-point crossover" or "uniform crossover".

In the single-point crossover, the chromosome from one of the parents is copied to the child (e.g.: "abcde"). If the chromosome of the second parent is "ABCDE", a random point of it is selected as cross-over point, as an example, between genes "C" and "D". Then, part of the second parent's chromosome is copied over the chromosome of the child and the result is "abcDE".

The uniform crossover (Syswerda, 1989) considers a combination of any order with the parents' chromosomes, as: "aBcDe" or "AbcdE" or "abcDE".

Usually, the children may be formed by both methods, with probabilities for each case (uniform or single). Carrol (1996a) defined equal probabilities for them. Generally, one child is formed per parents' pair, but some papers (Carrol, 1996a; Costa and Maciel Filho, 2005) used 2 children per pair. An interesting property of crossover is that children may be radically different from the parents and it will not introduce differences for a gene in a position where both parents have the same value for the gene. Crossover is an extremely important component of a genetic algorithm. Many researchers believe that if we exclude it from a GA the result is no longer a GA and performance is degraded on a variety of problems. This claim has not been made for mutation operators (Davis, 1991).

As occurs in nature, a mutation on a gene of some children may take place. It is simulated in two ways: *Creep Mutation* or *Jump Mutation*. In the *Creep Mutation*, one gene (parameter) of a created individual may be slightly changed. As an example, a child with a chromosome "abCdE" may mutate to a chromosome "abCdF", where "F" is not a gene from any of the two parents, but is similar. In the *Jump mutation*, the mutation is larger. An individual with a chromosome "abCdE" may mutate to "abCdP", where "P" is a gene very different from the parents'.

The probability for each type of mutation may be changed to improve the algorithm. As a reference, the probability for Creep mutation may be set as "1/n" and the probability for Jump mutation as "2/n", where "n" is population size (Carrol, 1996a). The probability of mutation for each gene of an individual is the same.

Using the crossover and mutation operators, the new generation of individuals is composed by children, whose chromosomes were formed by mating the parents' chromosomes. All individuals are evaluated again and ranked, in order to select the fittest to pair for the next generation.

The GA operators (crossover and mutation) are essential to keep the variability of the population, to avoid converging to the same solution: if all individuals of the population are equal, there is no sense in finding a better solution.

GA may be run for a defined number of generations or until a certain objective (SC) is achieved. The optimized solution, in this case, will be the best individual of the last generation.

In this work, the optimization with GA was performed using a program developed in Fortran language by the authors, employing the concepts explained above.

2.3. Sequential Quadratic Programming

The sequential quadratic programming (SQP) is a deterministic method that has become widely used as a reference on optimization studies for nonlinear problems. It has been validated in numerous works and plenty of computational SQP routines are currently available.

The SQP method models the system to be optimized at a local approximate solution point, transforming the complex problem into a quadratic local subproblem. The solution of the subproblem is the new local point for the next subproblem iteration. The algorithm creates a sequence of approximations that will converge to the solution, or the optimum value of the system.

This method has similarities with Newton-like methods, including the advantage of rapid convergence when the approximations are close to the solution, and the disadvantage of possible erratic behavior. SQP, like Newton-like methods are gradient-driven and they will find an optimum that may be a local one and not the global, in cases where multiple maximum or minimum exists, what is feasible in complex nonlinear functions.

The problem is simplified locally to produce a quadratic objective function and linear constraints: a quadratic Taylor series approximation is used to represent the Lagrangian at the estimative “ x^n ”. The Lagrangian function is defined by Eq 9:

$$L(x, u, v) = f(x) + u^t \cdot h(x) + v^t \cdot g(x) \quad (9)$$

where “L” is the Lagrangian, “f(x)” is the function to be minimized, “h(x)” is a equality constraint, “g(x)” is an inequality constraint, “u” and “v” are multiplier vectors and “t” denotes transposed vector.

The constraints are linearized as shown on equations 10:

$$\begin{aligned} \nabla h(x^n)^t \cdot dx + h(x^n) &= 0 \\ \nabla g(x^n)^t \cdot dx + g(x^n) &\leq 0 \end{aligned} \quad (10)$$

The quadratic approximation of the Lagrangian involves the Hessian and the Jacobian of the functions. The solution of the simplified system of equations defines the search direction and the step-length, which are used to calculate the new estimate for the properties to be optimized. The procedure is repeated on the new estimate “ x^{n+1} ”, until the convergence is achieved (Boggs and Tolle, 1996; Costa and Maciel Filho, 2005).

The procedure is highly dependent on the initial estimate. A bad initial estimate can take the method to a local optimum or to an intermediate approximation where the gradients cannot be calculated, even numerically. Complex and high nonlinear problems, as simulator models, have high probability to contain multiple maxima or minima, high gradients and discontinuities, what can make difficult the use of SQP algorithms.

In this work, the SQP optimization was performed using a commercial routine in Fortran language.

2.4. Optimization problem

A generic optimization problem may be represented as: find the parameter values for “x”, “y” and “z” that minimize the function $f(x,y,z)$, subjected to “k” equality constraints $h(x)$ and “m” inequality constraints $g(x)$, as represented by equations 11.

$$\begin{aligned}
& \min_{x,y,z} f(x, y, z) \\
& h_k(x, y, z) = 0 \\
& g_m(x, y, z) \leq 0
\end{aligned}
\tag{11}$$

Considering that the goal here is to minimize the raw-material expenses in the formaldehyde plants, the selectivity towards formaldehyde must be maximized or, in other words, the methanol specific consumption must be minimized. In this sense, the function “f” is a complex function, represented by the reactor simulator itself. The parameters to be optimized are the simulator inputs: bed temperature, methanol flowrate, water flowrate and air flowrate. The combination of the flowrates will define important properties that influence the reactor performance: methanol-oxygen molar ratio, water-methanol molar ratio, oxygen concentration, methanol concentration, water concentration and the residence time. The methanol specific consumption, a simulator output, is the parameter to be optimized.

Some constraints must be added to the system, as the minimum and maximum possible values for the input parameters and minimum conversion. Flowrates may be restrained by pumps capacities, control valves and pipes diameters. Temperature may be limited by equipment project constraints. If the plant is not equipped with distillation column, the conversion must be kept above certain limit to guarantee the quality of the produced formalin. In this sense, the constraints may be written as in equations 12:

$$\begin{aligned}
T_{\min} & \leq \text{Bed_Temperature} \leq T_{\max} \\
\text{MeOH}_{\min} & \leq \text{Methanol_flowrate} \leq \text{MeOH}_{\max} \\
W_{\min} & \leq \text{Water_flowrate} \leq W_{\max} \\
\text{AIR}_{\min} & \leq \text{Air_flowerate} \leq \text{AIR}_{\max} \\
X_{\min} & \leq \text{Methanol_conversion} \\
\text{OBJECTIVE} & = \text{maximize}(S_{\text{HCHO}})
\end{aligned}
\tag{12}$$

3. Results and Discussion

Using the formaldehyde Silver reactor simulator, the system was optimized in order to achieve minimum methanol specific consumption (maximum formaldehyde selectivity) by changing the operational parameters — temperature, methanol flowrate, air flowrate and water flowrate — for a specific reactor configuration, subjected to defined constraints. The optimization methods were SQP and GA, whose performances were compared. A sensitivity analysis was also run to verify the reactor stability at the optimum operation point.

The reactor simulator was validated after a series of comparative simulations reported by the authors in previous works (Papes Filho, 2007; Papes Filho and Maciel Filho, 2007a,b,c,d). Simulator outputs showed good correlation with literature and industrial measured data, as the example presented on Figure 4. The fixed-bed reactor was configured in this work with 1.5m diameter, 20mm length and catalyst silver particle size of 0.6 mm (typical industrial data). The Crank-Nicholson numerical method was set with 500 steps on the “z” direction.

Some cases were run to illustrate the methodology, comparing SQP with GA for different optimization approaches: different minimum conversion, air flow limitations, methanol flow limitations, water flow limitations and throughput decisions.

The reference condition, representative of a current operation of a proprietary industrial reactor, is defined by bed temperature of 630 °C, air flowrate of 6060 kg/h, methanol flowrate of 3681 kg/h, water flowrate of 364 kg/h and pressure of 1.2 atm. At this condition, the MeOH/O₂ ratio is 2.60 and the H₂O/MeOH ratio is 0.18, achieving conversion of 94.0%, formaldehyde selectivity of 86.8%, CO₂ selectivity of 13.2%, CO selectivity of 0.0% and methanol specific consumption of 0.455 kg/kg.

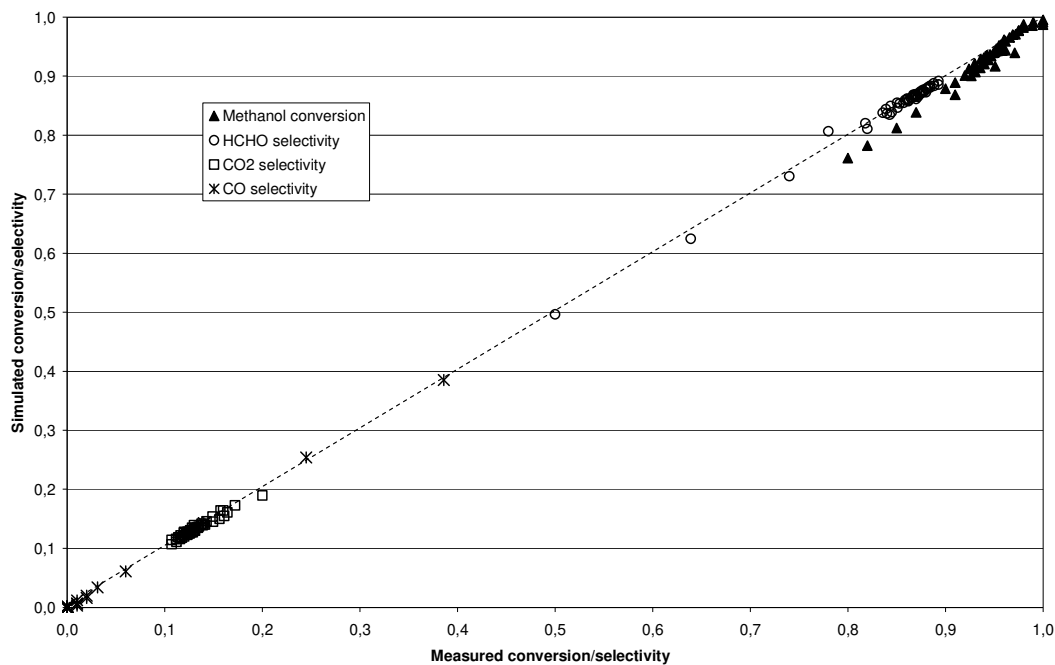


Figure 4: simulator validation: simulated conversion and selectivity plotted against measured values for control conditions.

Supporting software was created by the authors in Fortran code to run the optimizations with SQP, according to Figure 5. The algorithm starts with an initial guess given by the user, which is normalized using the maximum and minimum values also given by the user. The commercial SQP subroutine is run, and it defines the points where the objective function must be evaluated: in practice, they are operational conditions (temperature and flowrates), saved into the reactor input file. The supporting software runs the simulator itself (the simulator is the objective function) and the simulation outputs are saved in a data file, which is read by the SQP subroutine, assigning the function value (methanol specific conversion) to the operational conditions. The SQP subroutine calculates the next operational conditions to be evaluated and the algorithm is repeated until convergence is achieved.

The GA simulator was entirely built by the authors and its application is exemplified on Figure 6. The optimization software contains the GA principles and firstly it defines the initial population of operational conditions. For each individual of the population, the associated operational condition is saved in the reactor input file and the program runs the simulator automatically. The simulator outputs, including the variable to be optimized (methanol specific consumption) are saved in a data file, read by the GA program that assigns the operational condition with the specific consumption. The GA operators are run to create the next generation of operational conditions, which are evaluated in a new cycle. The procedure is repeated for a specified number of cycles. GA parameters used in this work are stated on Table 1.

In general, the results obtained with SQP agreed with the ones obtained with GA, as shown on Tables 2 and 3, provided that an appropriate initial estimative was considered for SQP. Only small differences were seen on temperature, solution flowrate and water content but they did not significantly change the objective function (methanol specific consumption) or the selectivity. Only the first 3 decimal digits are significant on the specific consumption, according to industrial practice.

Population size and the number of cycles were set as high as possible to reach the desired precision within a reasonable computing time. The best population size in the cases studied here was found to be 200, considering 300 generations.

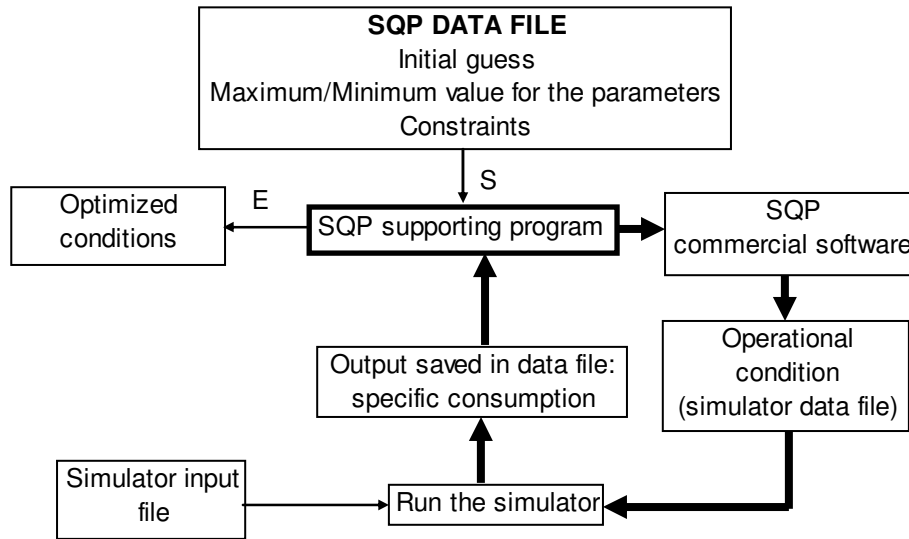


Figure 5: Optimization system with SQP (“SQP supporting program” controls the execution of the system; “S” and “E” indicate the starting and end points, respectively; large arrows indicate the software loop)

The best 50 individuals of a generation were selected to be the parents for the new generation. If this number is small and the best individuals of a generation are much similar one to the other, the crossover operator will be less likely to improve the solution and the algorithm will count on the chance of a successful mutation to occur in order to produce a better solution. In this case, this number may be increased to include in the parents set other individuals that are not so good, but add variability to enhance the crossover operator. In our studies, the parents set was started with 10% of the population size, arbitrarily, and it was increased to 25% to improve GA performance.

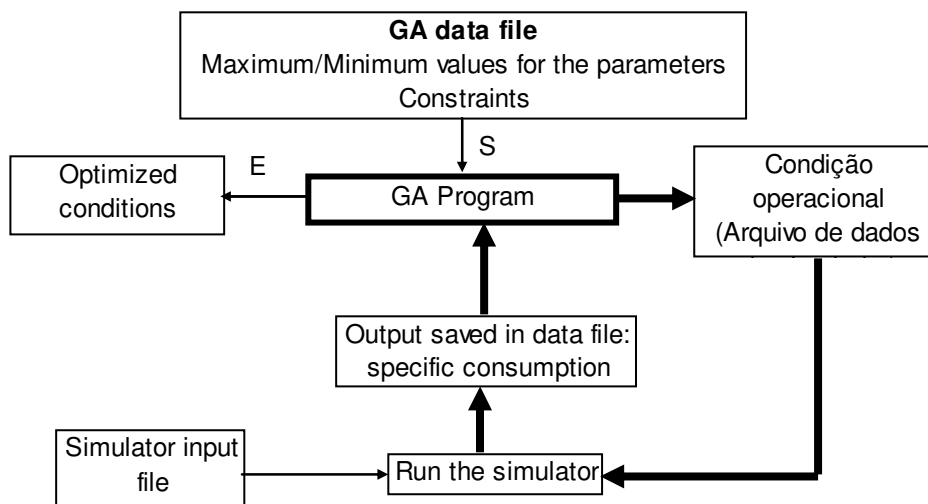


Figure 6: Optimization system with GA (“GA program” controls the execution of the system; “S” and “E” indicate the starting and end points, respectively; large arrows indicate the software loop)

Table 1: GA parameters

Parameter	Set-point
Population size	200
Maximum number of generations	300
Code	Real
Number of children per pair of parents	1
Number individuals selected to procreate	50
Elitism	Yes
Single point crossover probability	50%
Uniform crossover probability	50%
Creep mutation probability	6.6%
Severity of creep mutation	$\pm 10\%$ of gene value
Jump mutation probability	3.4%
Severity of jump mutation	$\pm 80\%$ of gene value

The single-point crossover probability was set equal to the uniform crossover probability, according to the studies of Carrol (1996a). The jump mutation probability was set as half of the creep mutation probability (Carrol, 1996a), starting with an approximate probability of “1/n” (“n” is the population size) and increasing this value if the algorithm takes too many generations to produce a better individual. In this study, the jump mutation probability was increased from 0.5% to 3.4% in order to achieve a good algorithm performance.

In the case of a mutation, the gene values were changed by the percentages stated above ($\pm 10\%$ and $\pm 80\%$). These values were defined as default after several GA studies performed by the authors with different applications.

Four optimization cases were studied and presented below. All cases produced conditions with significant improvement on the reactor performance compared to the standard operational condition.

3.1. Case I: conversion limitations

The reactor was optimized considering limitations on methanol conversion at five different levels (85%, 90%, 92%, 95% and 98%), with good flexibility on the air, water and methanol flowrates (wide ranges). Temperature was allowed to vary from 600 to 700 °C, air flowrate from 5000 to 7000 kg/h, methanol/water solution from 4000 to 6000 kg/h and water content on this mixture from 5 to 50%. Results are presented on Table 2.

In all cases, the optimum air flowrate was found to be the maximum possible value, in order to achieve minimum residence time. The methanol flowrate and water flowrate (equivalent to the solution flowrate and its water content) were balanced to obtain maximum MeOH/O₂ ratio, with as high water content as possible, without producing methanol conversion below the specified limit. Higher solution flowrate will also lead to minimum residence time. The temperature was set as high as possible to compensate the inhibiting effect of the water on conversion, but not so high in order to prevent excessive decomposition of formaldehyde to carbon monoxide.

When the limiting conversion is defined at lower values (from 98% towards 85%), the solution flowrate may assume higher values, as well as the water content. Differently, the temperature may assume lower values. Consequently, the MeOH/O₂ ratio and the H₂O/MeOH ratio are higher. In all cases, the resulting residence time was the same (3.7 msec). Regarding the reactor performance, the lower the limiting conversion, the higher the formaldehyde selectivity, and the lower the by-products selectivity (in other words, the methanol specific consumption is smaller).

The optimization results are in line with the relationships between process conditions and reactor performance described by Papes Filho and Maciel Filho (2007d) in previous work: higher MeOH/O₂ ratio, higher H₂O/MeOH ratio, lower temperature and lower residence time favor the selectivity towards formaldehyde.

Lower MeOH/O₂ ratio, lower H₂O/MeOH ratio, higher temperature and higher residence time favor the methanol conversion.

The higher the methanol conversion, the lower the formaldehyde selectivity due to the increasing quantity of formaldehyde formed, as long as more contact time with the catalyst is allowed. The higher the formaldehyde availability in the reaction mixture, the higher is the rate of formaldehyde combustion and decomposition, a classical effect of a consecutive reaction mechanism (Andreasen et al., 2005).

Table 2: case I- optimized conditions for the formaldehyde reactor considering methanol constraints.

Parameter	X _{MeOH} ≥ 85 %		X _{MeOH} ≥ 90 %		X _{MeOH} ≥ 92 %		X _{MeOH} ≥ 95 %		X _{MeOH} ≥ 98 %	
	SQP	GA	SQP	GA	SQP	GA	SQP	GA	SQP	GA
Temperature	649.7	649.3	659.0	660.4	663.7	666.5	672.6	672.8	682.1	683.1
Air flowrate	7000	7000	7000	7000	7000	7000	7000	7000	7000	7000
Solution flowrate	5530	5528	5205	5230	5091	5126	4947	4948	4839	4863
Water content	23.7	23.7	19.6	19.9	18.0	18.6	16.0	16.0	14.5	14.9
MeOH/O ₂ ratio	2.58	2.58	2.56	2.57	2.55	2.56	2.54	2.54	2.53	2.53
H ₂ O/MeOH ratio	0.39	0.39	0.43	0.44	0.39	0.41	0.34	0.34	0.30	0.31
Conversion	85.0	85.0	90.0	90.0	92.0	92.0	95.0	95.0	98.0	98.0
S-HCHO	91.6	91.6	91.5	91.5	91.4	91.4	91.2	91.2	90.9	90.9
S-CO ₂	7.5	7.5	7.3	7.2	7.2	7.0	6.9	6.9	6.6	6.5
S-CO	0.9	0.9	1.2	1.3	1.4	1.6	1.9	1.9	2.5	2.6
Spec cons	0.431	0.431	0.432	0.432	0.432	0.432	0.433	0.433	0.434	0.434
Residence time	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7

Note: Temperature is in °C, flowrates in kg/h, water content in mass%; MeOH/O₂ and H₂O/MeOH ratios are molar basis; methanol conversion (X_{MeOH}), formaldehyde selectivity (S-HCHO), carbon dioxide selectivity (S-CO₂) and carbon monoxide selectivity (S-CO) are in mole%. Methanol specific consumption is in kg_{MeOH}/kg_{formaldehyde} 37% and residence time is in msec.

3.2. Case II: air flowrate constraint

The reactor was optimized considering a constraint on the air flowrate at 6500 kg/h, with minimum conversion of 94%. Temperature was allowed to vary from 600 to 700 °C, methanol/water solution from 4000 to 6000 kg/h and water content on this mixture from 5 to 50%. Results are presented on Table 3.

The air flowrate reached the maximum, while the solution flowrate, water content and temperature were set by the program to keep the MeOH/O₂ ratio (2.55) constant and guarantee the minimum conversion. With lower gas flowrate, the residence time increased when compared to case I, what lead to lower formaldehyde selectivity and higher specific consumption.

3.3. Case III: solution flowrate constraint

The reactor was optimized considering a constraint on the solution flowrate at 4500 kg/h, with minimum conversion of 94%. Temperature was allowed to vary from 600 to 700 °C, air flowrate from 5000 to 7000 kg/h and water content on the water/methanol mixture from 5 to 50%. Results are presented on Table 3.

The optimized air flowrate and the water content were adjusted accordingly by the program to keep the MeOH/O₂ ratio at 2.55. The temperature and the water content were tuned to obtain the minimum specified conversion with maximum formaldehyde selectivity in this case, similar to case II. Residence time was a little bit higher than case II and significantly higher than case I.

3.4. Case IV: throughput constraints

The reactor was optimized considering a constraint on the methanol flowrate or formaldehyde throughput (due to commercial production programming, for example), maintaining minimum conversion of 94%. Temperature was allowed to vary from 600 to 700 °C and water content on the methanol/water solution from

10 to 50%. Case IV-A considered a methanol feed of approximately 3500 kg/h, case IV-B of c. 3900 kg/h and case IV-C of c. 4200 kg/h, simulating approximately 10% increase on methanol feed or formaldehyde throughput between them. Results are presented on Table 3.

Table 3: cases II, III, IV- optimized conditions for formaldehyde reactor considering different constraints.

Parameter	Case II		Case III		Case IV-A		Case IV-B		Case IV-C	
	SQP	GA	SQP	GA	SQP	GA	SQP	GA	SQP	GA
Temperature	664.7	665.0	660.4	660.3	658.4	658.0	664.7	664.0	670.4	670.2
Air flowrate	6500	6500	6209	6218	5800	5800	6500	6500	7100	7100
Solution flowrate	4700	4698	4500	4500	4303	4295	4700	4685	5050	5042
Water content	17.6	17.7	17.9	17.8	19.5	19.4	17.6	17.4	16.4	16.4
Methanol feed	3872	3866	3695	3699	3464	3462	3873	3870	4222	4215
MeOH/O ₂ ratio	2.55	2.55	2.55	2.55	2.56	2.56	2.55	2.55	2.55	2.55
H ₂ O/MeOH ratio	0.38	0.38	0.39	0.39	0.43	0.43	0.38	0.38	0.35	0.35
Conversion	94.0	94.0	94.0	94.0	94.0	94.0	94.0	94.0	94.0	94.0
S-HCHO	90.9	90.9	90.7	90.7	90.4	90.4	90.9	90.9	91.3	91.3
S-CO ₂	7.5	7.5	7.9	7.9	8.2	8.2	7.5	7.6	7.0	7.0
S-CO	1.6	1.6	1.4	1.4	1.4	1.4	1.6	1.5	1.7	1.7
Spec cons	0.434	0.434	0.435	0.435	0.437	0.437	0.434	0.434	0.433	0.433
Residence time	4.0	4.0	4.2	4.2	4.5	4.5	4.0	4.0	3.7	3.7

The flowrates were once again set by the program to maintain the MeOH/O₂ ratio at the same level. The lower the methanol flowrate, the lower the air flowrate and consequently the higher the residence time, what would lead to higher conversion but poorer formaldehyde selectivity. In this sense, the water content and temperature were increased to keep the formaldehyde selectivity, guaranteeing the minimum conversion. The water and temperature compensation are not enough to prevent lower formaldehyde selectivity at lower throughput, due to the strong effect of residence time, but the loss on specific consumption would be worse in a reactor running out of optimized conditions: if the reactor was moved from condition IV-C to IV-A without optimization, the formaldehyde selectivity would be 86.5%, with a specific consumption of 0.457 kg_MeOH/kg HCHO-37%.

3.5. Sensitivity analysis

One important task on optimization studies is to guarantee that the optimum operation condition is a stable situation, as far as plant control is concerned. In other words, this condition cannot be significantly affected if minor variations on the process parameters occur. If the optimum point is not stable, the operators will spend a great deal of time to control the plant, otherwise the process oscillation will take the process to a deviated condition that may be much worse than expected.

Taking Case II as an example, small changes on the optimum process conditions were introduced and the simulator was run in each case to check the reactor performance. Table 4 shows the results.

The deviation considered for the process parameters were: ± 5 °C for temperature, ± 100 kg/h for air and methanol flowrates and ± 50 kg/h for water flowrate. The consequences were: variation on methanol conversion of -2.3 to + 0.9 p.p.; variation of formaldehyde selectivity of -1.5 to +0.0 p.p. and variation of specific consumption of +8 to 0 kg/kg (“p.p.” stands for percentage points). The variations on conversion and selectivity are relevant and may affect the production costs of the plant studied here.

These results show that it is possible to operate the reactor at the optimum condition stated on case II, but methanol and air flowrate control must be more accurate than the example given to keep the reactor stable at the optimum point, in this order of importance. A methanol flowrate precision of ± 100 kg/h (represents 2.7% of the measure) seems to be high for the system and a more precise control instrument must be used, what is feasible for industrial measurement equipment. Besides the deviations influences on conversion and

selectivity, the optimum point cannot be said unstable, from the operability and safety stand point. However, better reactor control is required to extract the best performance from the reactor.

The discussion presented here was based on information of a proprietary industrial plant, as an example, but the methodology may be applied to any Silver reactor.

Table 4: sensitivity analysis of case II.

Parameter	Base	Temperature (°C)		Air (kg/h)		Methanol (kg/h)		Water (kg/h)	
		- 5	+ 5	- 100	+ 100	- 100	+ 100	- 50	+ 50
Conversion	94.0	93.2	94.9	94.7	92.7	91.7	94.4	94.7	93.3
S-HCHO	90.9	90.9	90.8	90.3	90.6	89.4	89.4	90.8	91.0
S-CO ₂	7.5	7.8	7.3	8.5	7.4	8.1	9.7	7.7	7.4
S-CO	1.6	1.3	1.9	1.2	2.0	2.5	0.9	1.5	1.6
Spec cons	0.434	0.434	0.435	0.438	0.436	0.442	0.442	0.435	0.434

3.6. Comparison SQP x GA

The advantages and disadvantages of both methods were pointed out in this work. SQP is extremely dependent on the initial estimate and it can be trapped into a local maximum.

As an example, in case III, SQP was run using the initial temperature estimate at 650 oC, and the results are presented on Table 5, as SQP-A. If the initial temperature estimate was 625 oC, the optimum condition presented by the SQP algorithm would be much worse (SQP-B on Table 5) than the real optimum condition, confirmed by GA optimization (GA on Table 5).

Other similar cases were found during the optimization runs made here, achieving different results depending on the initial guess, while GA always led to the same point.

Table 5: Influence of initial estimate on SQP performance

Parameter	Case III		
	SQP - A	SQP - B	GA
Temperature	660.4	600.0	660.3
Air flowrate	6209	7000	6218
Solution flowrate	4500	4176	4500
Water content	17.9	12.5	17.8
Methanol feed	3695	3654	3699
MeOH/O ₂ ratio	2.55	2.23	2.55
H ₂ O/MeOH ratio	0.39	0.26	0.39
Conversion	94.0	94.0	94.0
S-HCHO	90.7	84.5	90.7
S-CO ₂	7.9	15.4	7.9
S-CO	1.4	0.1	1.4
Spec cons	0.435	0.467	0.435
Residence time	4.2	4.0	4.2

In the current study, SQP has showed very good stability, but for complex functions it may fail in defining the derivatives and the program stops (Papes Filho and Maciel Filho, 2007c). GA, on the other hand, is totally stable as it does not depend on derivatives. GA's disadvantage is the high computing time to reach a solution with desired precision. Here, it took 300 generations with a 200 population size to properly achieve the desired solution (convergence on the third decimal digit of the specific consumption), spending approximately 3 hours using a Pentium-4, 2.66 GHz, 480MB RAM.

Observing the parameters of the best individual from each generation, recorded by the GA program, it is clear that after approximately 20 generations, the intermediate solution is very close to the optimum and a large number of generations is still needed just to obtain the desired precision. Therefore, instead of trying to

identify the best optimization technique, it is interesting to consider that a hybrid approach is more feasible, once GA may perform the initial search with a reduced number of generations and the GA approximation is then used as an initial guess by SQP. This approach takes the advantage of GA (higher probability of achieving the global optimum) and SQP (fast), using more efficiently the computing resources.

The cases presented above were run again with this principle — the best solution of the 20th generation of GA was used as initial guess for SQP — and it was observed that this hybrid approach enhances the optimization performance: computing times were reduced to 20 minutes and the solution was always in line with GA results, indicating good probability of having reached the global optimum. Convergence on the specific consumption was achieved on the fourth decimal digit (more precise than required).

3.7. Industrial optimization

The full implementation of the optimum conditions found in this work depends on investments in the plants, in order to have the capability of feeding the right flowrates of air, methanol and water, independently. In this sense, the complete optimization of a real Silver plant with the information presented here is not implemented yet.

Partial optimization was done industrially, manipulating the bed temperature and water flowrate, achieving practical results consistent with the information presented above. The implementation of the optimized conditions provided by the program resulted in sensible improvement on the methanol specific consumption and reduced catalyst sintering, contributing to lower production costs.

Figure 7 shows a comparison between the standard industrial operational condition and the optimized scenarios described above, considering the methanol conversion and formaldehyde selectivity. The methanol cost to produce formalin 37% was also shown on Figure 7. In the simulated cases, the minimum conversion was set at 94% due to distillation constraints, however if distillation tower is revamped, the reactor may operate with lower conversion, achieving even better formaldehyde selectivity.

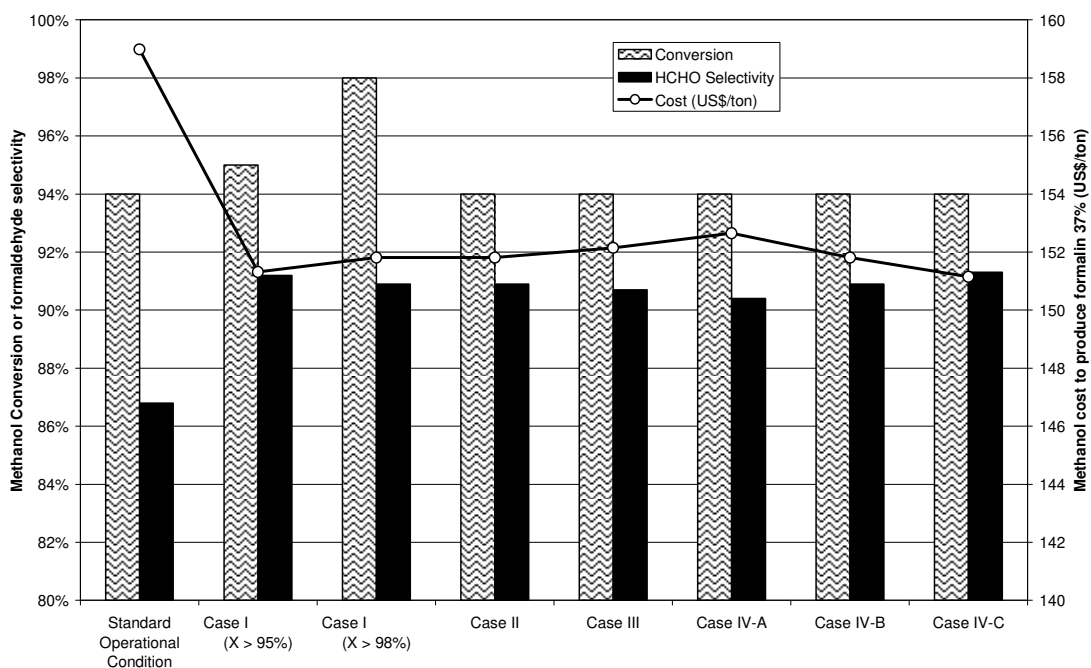


Figure 7: standard industrial operational condition compared to the optimized scenarios, considering methanol conversion (“X”) and formaldehyde selectivity, as well as the cost of methanol used to produce 1 ton of formalin 37% basis.

The results show that it is possible to improve about 4 percentage points on the selectivity towards formaldehyde in an optimized plant operated with Silver Water Ballast technology. Such performance improvement represents a reduction of US\$ 7.00/ton (- 3.7%) on the variable cost of production of formalin 37% basis (189.8 US\$/ton, according to estimations of Papes Filho, 2007). If the optimization results shown in this work are implemented in an average size Silver plant, the economy in methanol purchasing is expected to reach about US\$ 700,000 per year.

Other benefit of the improved performance is the reduction on the selectivity towards carbon dioxide and carbon monoxide, representing a yearly pollutant reduction of about 2,500 ton to the atmosphere, very significant to the environment.

4. Conclusions

In this paper, a mathematical optimization of a formaldehyde silver reactor was performed. The reactor simulator was built by the authors and presented in previous work, using a hybrid approach: the fixed-bed reactor was modelled by deterministic mass transfer differential balance equation and the rate of the reactions were calculated by an artificial neural network, running together with the reactor model. The artificial neural network was trained and validated with experimental and industrial conditions, as reported by the authors in previous works.

An optimization tool was developed in this work to optimize the reactor, using the simulator, by Genetic Algorithms and a hybrid procedure proposed by the authors, where GA and SQP were coupled. The objective function made use of the model equation through the simulator itself and the methanol specific consumption was selected as the parameter to be minimized, subjected to a minimum methanol conversion (constraint). Lower specific consumption means less methanol spent in the operation and lower production cost, promoting better competitiveness of silver plants. The parameters manipulated were: bed temperature, air flowrate, methanol flowrate and water flowrate.

Results from GA optimization were compared to the results of an SQP program over the same simulator. Both methods got practically to the same conditions, with insignificant deviations, provided that the appropriate initial estimate was considered on SQP optimization. SQP proved to be a stable, robust and quick (less than 1 minute) optimization method, but the performance is heavily affected by the initial estimate, once sometimes the result was clearly not the global optimum. GA proved to be very stable and always got to the point believed to be the global optimum, but computing times are long (3 hours). A better approach has proven to be an association of both methods, running GA for approximately 20 generations and taking the best estimate as the initial one for SQP, which runs faster and converges to the solution with desired precision. After 20 generations, we observed that the best individual on GA optimizations is very close to the optimum, most likely the global one.

Many cases were studied, with different constraints and objectives in order to report optimum working conditions for a variety of circumstances found in the industrial operation of this process. The optimized conditions found in this work were analyzed according to the known relationships between operational conditions and reactor performance, reported in previous works (Papes Filho, 2007), showing very consistent results. Higher conversions are associated with lower formaldehyde selectivity. The molar ratio methanol/oxygen seems to be the most important variable to be optimized. Optimum air flowrate was generally the maximum limit, in order to reach minimum residence time, while methanol flowrate was adjusted accordingly to keep the methanol/oxygen ratio at high values. Water flowrate goes to the maximum possible value, restrained by the methanol/oxygen ratio and the minimum conversion (water has an inhibiting effect on methanol conversion and positive effect on formaldehyde selectivity). Lower conversions due to high water content and high methanol/oxygen ratio were compensated by increasing bed temperature.

A sensitivity analysis was performed in one of the optimum conditions defined in this work, in order to verify if it was a stable operational point for an industrial plant. Different deviations on temperature and flowrates for air, methanol and water were simulated, showing that the optimized conditions are industrially feasible.

However, it was clear that a good control of the variables is essential for keeping the plant at the optimum conditions and extracting more value from the methanol specific consumption savings.

GA proved to be an efficient tool for the optimization of complex systems like the formaldehyde Silver reactor. Its association with SQP enhances the response time without loss of search efficiency in finding the global optimum. There is strong demand for optimization tools, as the one developed in this work, for fixed-bed reactors in several areas, including formaldehyde Silver reactors, with the objective to improve the economical viability of the process and minimize pollution. The indications produced in this work have already started to be implemented in an industrial plant with successful results.

References

- ABRAF (Brazilian Association of Formaldehyde Manufacturers) report; "Panorama of productive chain", www.abraf.com.br, 2004.
- Andreasen, A.; Lynggaard, H.; Stegelmann, C. and Stoltze, P.; "A microkinetic model of the methanol oxidation over silver", *Surface Science*, 544, pp.5-23, 2003.
- Andreasen, A.; Lynggaard, H.; Stegelmann, C. and Stoltze, P.; "Simplified kinetic models of methanol oxidation on silver", *Applied Catalysis A: General*, 289, pp.267-273, 2005.
- Barteau, M and Madix, R.J.; *Surf. Sci*, 40, p.108, 1984.
- Bazilio, C.A.; Thomas, W.J.; Ullah, U. and Hayes, K.E.; "The catalytic oxidation of methanol", *Proc. R. Soc. Lond. A*, 399, pp.181-194, 1985.
- Bhagat, P.; "An Introduction to Neural Nets", *Chemical Engineering Progress*, August, p.55, 1990.
- Bhattacharyya, S.K.; Nag, N.K. and Ganguly, N.D.; "Kinetics of vapor-phase oxidation of methanol on reduced silver catalyst", *J. of Catalysis*, v.23, i.2, pp.158-167, 1971.
- Boggs, P.T. and Tolle, J.W.; "Sequential quadratic programming", *Acta Numerica*, pp. 1-52, 1996.
- Cao, E. and Gavriilidis, A.; "Oxidative dehydrogenation of methanol in a microstructured reactor", *Catalysis Today*, 110, pp.154-163, 2005.
- Carrol, D.L.; "Chemical laser modeling with genetic algorithm", *AIAA Journal*, v.34, no 2, pp.338-346, 1996a.
- Carrol, D.L.; "Genetic Algorithms and Optimizing Chemical Oxygen-Iodine Lasers", *Developments in Theoretical and Applied Mechanics*, v.XVIII, pp.411-424, 1996b.
- Costa, B.B.C and Maciel Filho, R.; "Evaluation of optimization techniques and control variable formulations for a batch cooling crystallization process", *Chemical Engineering Science*, 60, pp.5312-5322, 2005.
- Crank, J. and Nicholson, P.; *Proceedings of Cambridge Phil. Soc.*, v.43, p.50, 1947.
- Dai, W.L., Cao, Y, Ren, L.P., Yang, X.L., Xu, J.H., Li, H.X., He, H.Y. and Fan, K.N.; "Ag-SiO₂-Al₂O₃ composite as highly active catalyst for the formation of formaldehyde from the partial oxidation of methanol", *Journal of Catalysis*, 228, pp. 80-91, 2004.
- Davis, L.; "Handbook of Genetic Algorithms"; International Thomson Computer Press, Boston, 1991.
- Fogler, H.S.; "Elements of chemical reaction engineering", Prentice-Hall International, 2nd ed., New Jersey, p.71, 1992.
- Garrard, A. and Fraga, E.S.; "Mass exchange network synthesis using genetic algorithms", *Computers Chem. Engng.*, v.22, n.12, pp.1837-1850, 1998.
- Goldberg, D.E.; "Genetic Algorithms in Search, Optimization, and Machine Learning", Ed. Addison-Wesley Publishing Company, Inc., New York, 1989.
- Goldberg, D.E; Deb, K. and Clark, J.H.; "Genetic Algorithms, Noise and the Sizing of Populations", *Complex Systems*, 6, pp. 333-362, 1992.
- Gravilin, V.N. and Popov, B.I; *Kinet. Catal.*, 6, p.799, 1965.
- Holland, J.H.; "Adaptation", *Progress in theoretical biology*, 4, pp.263-293, 1976.
- Lefferts, L.; Ommen, J.G. and Ross, J.R.H.; "The oxidative dehydrogenation of methanol to formaldehyde over silver catalysts in relation to the oxygen-silver interaction", *Appl. Catal.*, 23, p.385, 1986.
- Lennox, B.; Montague, G.A.; Frith, A.M.; Gent, C. and Bevan, V.; "Industrial application of neural networks – an investigation", *Journal of Process Control*, v.11, pp.497-507, 2001.
- Nagy, A.; Mestl, G.; Ruhle, T.; Weinberg, G. and Schlogl, R.; "The dynamic restructuring of electrolytic silver during the formaldehyde synthesis reaction", *J. of Catalysis*, 179, pp.548-559, 1998.
- Nagy, A. and Mestl, G.; "High temperature partial oxidation reactions over silver catalysts", *Applied Catalysis A: General*, 188, pp.337-353, 1999.

- Papes Filho, A.C.; "Simulation and optimization of a silver formaldehyde reactor, using artificial intelligence techniques", PhD thesis (in English), UNICAMP – University of Campinas, Brazil, 2007.
- Papes Filho, A.C. and Cremasco, M.A.; "Correlation for estimation of diffusion coefficient for gases", Proceedings of the 1st Brazilian Congress of Chemical Engineering – Scientific Initiation, UFSCar Ed., www.ufscar.br, 1995.
- Papes Filho A.C. and Maciel Filho R.; "Concurrent Engineering Reactor Design", Computer Aided Chemical Engineering, v.20 A, Edited by Luis Puijagner and Antonio Espuña, Elsevier B.V., ISSN 1570-7946, pp.559-564, 2005.
- Papes Filho, A.C. and Maciel Filho, R.; "Novel Approach for Acquiring Rate of Reaction Data from Process Information for Neural Network Training: Application to an Industrial Reactor for Methanol Oxidation to Formaldehyde over Silver Catalyst Process", to be published, 2007a.
- Papes Filho, A.C. and Maciel Filho, R.; "Hybrid Training Method for Artificial Neural Networks using Genetic Algorithms for Rate of Reaction Estimation: Application to Industrial Methanol Oxidation to Formaldehyde over Silver Catalyst", to be published, 2007b.
- Papes Filho, A.C. and Maciel Filho, R.; "A Built-in Training Method for Universal Kinetic Models Through Neural Networks and Genetic Algorithms: Application to Industrial Methanol Oxidation to Formaldehyde over Silver Catalyst", to be published, 2007c.
- Papes Filho, A.C. and Maciel Filho, R.; "Hybrid Simulation of a Fixed-bed Formaldehyde Silver-catalyzed Reactor using Artificial Neural Networks", to be published, 2007d.
- Pham, D.T. and Pham, P.T.; "Artificial intelligence in engineering", International Journal of Machine Tools & Manufacture, v.39, pp. 937-949, 1999.
- Piccoli, R.L.; "Kinetic study of methanol selective oxidation to formaldehyde on iron molybdate catalyst", Master dissertation, Rijksuniversiteit Gent, Belgium, 1992.
- Pilato, L.A., Knop, A. and Gardziella, A.; "Phenolic resins", Springer, 2nd ed., New York, 2000.
- Pizzi, A.; "Advanced wood adhesives technology", Marcel Dekker Inc., 1st ed., New York, 1994.
- Press, W.H., Flannery, B.P., Teukolsky, S.A. and Vetterling, W.T.; "Numerical Recipes", Press Syndicate of the University of Cambridge, 1st ed., 1992.
- Psichogios, D.C. and Ungar, L.H.; "A hybrid neural network-first principles approach to process modeling", AIChE Journal, 38, 10, pp. 1499-1511, 1992.
- Qian, M.; Liauw, M.A. and Emig, G.; "Formaldehyde synthesis from methanol over silver catalysts", Applied Catalysis A: General, 238, pp.211-222, 2003.
- Reid, R.C; Prausnitz, J.M and Poling, B.E.; "The properties of gases and liquids", McGraw-Hill Book Company, 4th ed., New York, 1987.
- Rumelhart, D.E; Hinton, G.E. and Williams, R.J.; "Learning internal representations by error propagation" in Parallel distributed processing, v.1, pp.318-362, 1986.
- Sandler, S.I.; "Chemical and engineering thermodynamics", John Wiley & Sons, New York, 1989.
- Santacesaria, E. and Morbidelli, M.; "Kinetics of the catalytic oxidation of methanol to formaldehyde", Chem. Engng. Sci., v.36, pp.909-918, 1981.
- Sauer, J and Emig, G.; "The catalyzed dehydrogenation of methanol to formaldehyde at high temperatures", Chemical Engineering Technology, 18, pp. 284-291, 1995.
- Schubert, H; Tegtmeier, U. and Schlogl, R.; "On the mechanism of the selective oxidation of methanol over elemental silver", Catalysis Letters, 28, pp.383-395, 1994.
- SRI International; "Formaldehyde", Report n^o 23A, Menlo Park, California, 1978.
- Syswerda, G.; "Uniform crossover in genetic algorithms", Proceedings of the third international conference on genetic algorithms, San Mateo, California, Morgan Kaufmann publishers, 1989.
- Ullmann's Encyclopedia of Industrial Chemistry, v.A11, 5th ed., VHC Publishers, New York, 1988.
- Van Veen, A.C, Hinrichsen, O. and Muhler, M.; "Mechanistic studies on the oxidative dehydrogenation of methanol over polycrystalline silver using the temporal-analysis-of-products approach", J. of Catalysis, 210, pp. 53-56. 2002.
- Wachs, I.E. and Madix, R.; "The oxidation of methanol on a silver (110) catalyst", Surface Science, 76, pp. 531-558, 1978.
- Walker, J.F; "Formaldehyde"; Robert E. Krieger Publishing Company, 3rd Ed., New York, 1975.
- Wang, Q.J.; "Using Genetic Algorithms to Optimise Model Parameters", Environmental Modelling & Software, v.12, n.1, pp 27-34, 1997.
- Wasserman, P.D.; "Neural Computing: Theory and Practice", van Nostrand Reinhold Ed, 1st ed., New York, 1989.
- Waterhouse, G., Bowmaker, G. and Metson, J.; "Mechanism and active sites for the partial oxidation of methanol to formaldehyde over an electrolytic silver catalyst", Applied Catalysis A, 265, pp.85-101; 2004(a).

Waterhouse, G., Bowmaker, G. and Metson, J.; "Influence of catalyst morphology on performance of electrolytic silver catalysts for the partial oxidation of methanol to formaldehyde", Applied Catalysis A, 266, pp.257-273, 2004(b).

Welty, J.R.; Wicks, C.E. and Wilson, R.E.; "Fundamentals of momentum, heat and mass transfer", John Wiley & Sons editor, 3rd ed., New York, 1984.

7.3. Conclusões

Nesse Capítulo, apresentou-se a otimização matemática do reator de formaldeído-Prata. O simulador usado nos trabalhos de otimização foi descrito em detalhe nos Capítulos anteriores.

Um programa de otimização foi desenvolvido nessa tese, baseado em Algoritmo Genético. A função objetivo considerada nas otimizações foi o próprio simulador do reator e o consumo específico de metanol foi escolhido como o parâmetro a ser minimizado, sujeito a uma restrição de mínima conversão. Um menor consumo específico significa menos metanol gasto na fabricação e, conseqüentemente, menor custo de produção. Os parâmetros manipulados foram: a temperatura do leite e as vazões de ar, metanol e água.

Os resultados da otimização com AG foram comparados com os resultados obtidos com um programa baseado em SQP, usando o mesmo simulador para o reator. Os dois métodos apresentaram praticamente os mesmos resultados, com desvios insignificantes, desde que uma boa estimativa inicial tenha sido considerada para a otimização com o SQP.

O SQP mostrou-se um método de otimização bastante estável, robusto e rápido (menos de 1 minuto), mas seu desempenho depende fortemente da estimativa inicial, uma vez que para alguns casos, o resultado encontrado claramente foi diferente do ótimo global. O AG provou ser muito estável e sempre chegou ao resultado que se acredita ser o ótimo global (o método não depende de estimativa inicial), porém com um grande esforço computacional (3 horas). A melhor abordagem aparenta ser uma associação dos dois métodos, executando o AG por aproximadamente 20 iterações (ou gerações) e utilizando a melhor estimativa como o “chute inicial” para o SQP, que é executado mais rapidamente e converge para a solução com precisão desejada. Após 20 gerações, observou-se que o melhor indivíduo na otimização com AG encontrava-se muito próximo do ponto ótimo, identificado como o ótimo global.

Vários casos foram estudados, com diferentes restrições e objetivos, de modo a reportar condições ótimas de trabalho para uma série de circunstâncias encontradas na operação industrial desse processo. As condições otimizadas apresentadas nesse capítulo foram analisadas de acordo com as relações entre condições operacionais e desempenho do reator, detalhadas nos Capítulos anteriores, com resultados muito consistentes.

Altas conversões foram associadas com baixa seletividade para formaldeído. A razão molar metanol/oxigênio mostrou-se como a variável mais importante a ser otimizada. A vazão ótima de ar esteve geralmente no limite máximo definido, de modo a obter o mínimo tempo de residência, enquanto que a vazão de metanol foi ajustada convenientemente para manter a relação MeOH/O₂ em níveis altos. A vazão de água atingiu máximos valores possíveis, limitada pela relação MeOH/O₂ e pela conversão mínima (a água tem um efeito inibidor na conversão de metanol e um efeito positivo na seletividade para formaldeído). Baixas conversões provocadas por alto teor de água e altas razões MeOH/O₂ foram compensadas com maior temperatura do leito.

Uma análise de sensibilidade foi realizada em um dos pontos ótimos de operação identificados, de modo a verificar se esse ponto operacional é estável para uma planta industrial. Diferentes desvios foram simulados na temperatura e nas vazões de reagentes, mostrando que as condições otimizadas são industrialmente viáveis. Entretanto, ficou claro que um bom controle das variáveis é essencial para manter a planta na condição ótima de operação e extrair maior valor da melhoria no consumo específico de metanol.

O AG mostrou ser uma ferramenta eficiente para otimização de sistemas complexos, como o reator de formaldeído-Prata. Sua associação com o SQP melhorou o tempo de resposta sem perda da eficiência na busca do ótimo global. Existe grande demanda por ferramentas de otimização para reatores de leito fixo em diferentes áreas, incluindo o reator de formaldeído-Prata, com objetivo de melhorar a viabilidade econômica dos processos e minimizar geração de poluentes; nesse sentido, ferramentas como a desenvolvida nesse trabalho são extremamente desejadas por engenheiros e operadores. Algumas das informações apresentadas nesse Capítulo já foram implementadas em uma planta industrial com resultados significativos.

Comparações entre a condição de operação padrão industrial e as condições otimizadas apresentadas nesse capítulo demonstraram ganhos econômicos e ambientais. No campo econômico, o benefício traduz-se em uma redução no custo de fabricação da ordem de US\$ 700.000 por ano, em uma planta de médio porte, devido à diminuição no consumo específico de metanol. No campo ambiental, a melhoria da eficiência da planta representa 2.500 ton/ano a menos de emissões de CO₂ e CO para a atmosfera, contribuindo para os esforços globais contra o aquecimento do planeta.

CAPÍTULO 8

CONCLUSÕES E SUGESTÕES PARA TRABALHOS FUTUROS

8.1. Conclusões

Essa tese compreendeu o desenvolvimento de novas metodologias para a modelagem da cinética de reação, utilizando técnicas de inteligência artificial, aplicadas com sucesso a um reator de oxidação de metanol a formaldeído com catalisador de prata. O desenvolvimento de um simulador para o processo citado também foi objeto dessa tese, compreendendo uma modelagem híbrida com o uso de equações determinísticas e redes neurais artificiais. Finalmente, estudou-se a otimização matemática do sistema, empregando o simulador desenvolvido, através de uma abordagem envolvendo a combinação de Algoritmos Genéticos (AG) e Programação Quadrática Sucessiva (SQP).

Inicialmente, foi apresentada uma nova abordagem para obtenção de taxas de reação em sistemas onde apenas informações de processo encontram-se disponíveis (conversão e seletividades, no caso de um reator). De posse de um conjunto de dados contendo apenas informações de processo (temperatura, vazões de reagentes, conversão e seletividades), empregou-se uma equação cinética determinística simplificada em conjunto com o simulador do reator desenvolvido nesse trabalho para ajustar cada dado experimental individualmente. Uma vez que cada dado foi ajustado, obteve-se o perfil de taxas de reação ao longo do reator, associado ao perfil de pressões parciais de cada um dos componentes, como resultado da execução do simulador. Ao reproduzir o procedimento para todos os dados experimentais separadamente, obteve-se um grande conjunto de dados correlacionando taxas de reação às condições locais. Este novo conjunto de dados foi então utilizado para o treinamento da RNA através do algoritmo clássico da retro-propagação (RP). A vantagem dessa abordagem reside na obtenção de dados cinéticos a partir de dados de processo, não requerendo a realização de experimentos dispendiosos e complexos, embora necessite de um modelo teórico como estrutura básica para ajuste, o qual pôde ser obtido da literatura neste caso.

Visando ao aprimoramento do método de treinamento da rede neural, empregou-se uma associação de AG e RP: o AG realiza a parte inicial do treinamento, partindo de uma população de conjunto de pesos aleatórios até atingir um conjunto próximo do ótimo global; a RP utiliza essa solução do AG como estimativa inicial para refiná-la até convergir para o ótimo global. Os dados utilizados para o treinamento pela abordagem híbrida (AG +

RP) foram os mesmos dados de taxa de reação extraídos das informações de processo conforme o procedimento descrito. A associação do AG com a RP minimiza a possibilidade de convergência para um ótimo local, o que é comum em métodos baseados em uma estimativa inicial, como é o caso da RP. A função objetivo otimizada nesse caso foi o erro da rede, definido como a diferença entre as taxas de reação calculadas pela RNA e as taxas extraídas dos dados experimentais.

Em uma terceira abordagem, a RNA foi treinada como um modelo “acoplado” ao simulador do reator. Com o uso de AG, os pesos da rede foram ajustados de modo que o simulador fosse capaz de calcular corretamente a conversão e seletividades do reator. O algoritmo parte de uma população aleatória de pesos, usando os operadores genéticos para encontrar o conjunto ótimo que permite ao simulador modelar adequadamente o reator. A função objetivo nesse caso foi o erro do simulador, definido como a diferença entre a conversão e seletividades calculadas e os valores experimentais para um determinado conjunto de dados. As taxas calculadas pela rede no processo de treinamento não são visíveis ao usuário e, uma vez que o simulador consiga prever corretamente o desempenho do reator, acredita-se que a RNA esteja calculando corretamente as taxas de reação, com base nos pesos treinados. A vantagem dessa abordagem está na simplicidade de usar diretamente os dados de processo, ao invés de extrair os dados de taxa de reação pela abordagem citada anteriormente. A desvantagem encontra-se no grande tempo computacional, como um resultado líquido ainda vantajoso para essa abordagem, uma vez que capacidade computacional encontra-se mais disponível no meio industrial em comparação com recursos humanos.

Após o treinamento da RNA através de uma das três abordagens descritas, o simulador encontrou-se apto a calcular corretamente o desempenho do reator para diferentes condições operacionais. O simulador consiste em um modelo híbrido, baseado em equações determinísticas para o balanço de massa e a RNA para cálculo da taxa de reação. A solução numérica das equações diferenciais foi realizada pelo método de Crank-Nicholson, um algoritmo semi-implícito, intrinsecamente estável e muito apropriado para uso em simuladores de reatores complexos.

O simulador para o reator de formaldeído-Prata desenvolvido nessa tese representa um avanço em relação aos análogos encontrados na literatura, uma vez que considera a

decomposição do formaldeído na fase gasosa e exprime de forma mais precisa a influência da água na conversão e seletividade do reator Prata.

Como resultado de uma série de simulações, as influências de importantes variáveis operacionais no desempenho do reator foram determinadas e apresentadas na forma gráfica. As variáveis operacionais foram a temperatura e as vazões de ar, metanol e água. O desempenho do reator foi avaliado em termos da conversão e seletividades para formaldeído, dióxido de carbono e monóxido de carbono.

As variáveis operacionais apresentam grande inter-relação entre elas, sendo mais apropriadamente escritas, além da temperatura, como a razão molar metanol-oxigênio, razão molar água-metanol e o tempo de residência (função da vazão total). Esses parâmetros afetam diretamente o desempenho do reator, sendo de suma importância a sua compreensão. Comparações com dados de literatura e dados industriais corroboraram o sucesso do treinamento da RNA e a modelagem adequada do reator.

Utilizando o simulador validado, o reator foi otimizado através de uma associação de AG e SQP (Programação Quadrática Sucessiva). Os parâmetros otimizados foram as variáveis operacionais descritas anteriormente e o objetivo foi a minimização do consumo específico do metanol, refletindo a maximização da seletividade para formaldeído e a minimização do custo de fabricação.

O SQP mostrou-se um método de otimização bastante estável, robusto e rápido (menos de 1 minuto), mas seu desempenho depende fortemente da estimativa inicial, uma vez que, para alguns casos, o resultado encontrado claramente foi diferente do ótimo global. O AG provou ser muito estável e sempre chegou ao resultado que se acredita ser o ótimo global (o método não depende de estimativa inicial), empregando um grande esforço computacional (3 horas). A melhor abordagem aparenta ser uma associação dos dois métodos, executando o AG por aproximadamente 20 iterações (ou gerações) e utilizando a melhor estimativa como o “chute inicial” para o SQP, que é executado mais rapidamente e converge para a solução com precisão desejada. Após 20 gerações, observou-se que o melhor indivíduo na otimização com AG encontrava-se muito próximo do ponto ótimo, identificado como o ótimo global.

Vários casos foram estudados, com diferentes restrições e objetivos, de modo a reportar condições ótimas de trabalho para uma série de circunstâncias encontradas na

operação industrial desse processo. As condições otimizadas apresentadas nesse capítulo foram analisadas de acordo com as relações entre condições operacionais e desempenho do reator, detalhadas nos Capítulos anteriores, com resultados muito consistentes.

Altas conversões foram associadas com baixa seletividade para formaldeído. A razão molar metanol/oxigênio mostrou-se como a variável mais importante a ser otimizada. A vazão ótima de ar esteve geralmente no limite máximo definido, de modo a obter o mínimo tempo de residência, enquanto que a vazão de metanol foi ajustada convenientemente para manter a relação MeOH/O_2 em níveis altos. A vazão de água atingiu máximos valores possíveis, limitada pela relação MeOH/O_2 e pela conversão mínima (a água tem um efeito inibidor na conversão de metanol e um efeito positivo na seletividade para formaldeído). Baixas conversões provocadas por alto teor de água e altas razões MeOH/O_2 foram compensadas com maior temperatura do leito.

Uma análise de sensibilidade foi realizada em um dos pontos ótimos de operação identificados, de modo a verificar se esse ponto operacional é estável para uma planta industrial. Diferentes desvios foram simulados na temperatura e nas vazões de reagentes, mostrando que as condições otimizadas são industrialmente viáveis. Entretanto, ficou claro que um bom controle das variáveis é essencial para manter a planta na condição ótima de operação e extrair maior valor da melhoria no consumo específico de metanol. Algumas das informações apresentadas nessa tese já foram implementadas em uma planta industrial com excelentes resultados.

Comparações entre a condição de operação padrão industrial e as condições otimizadas apresentadas nesse trabalho demonstraram ganhos econômicos e ambientais. No campo econômico, o benefício traduz-se em uma redução no custo de fabricação da ordem de US\$ 700.000 por ano, em uma planta de médio porte, devido à diminuição no consumo de metanol. No campo ambiental, a melhoria da eficiência da planta representa 2.500 ton por ano a menos de emissões de CO_2 e CO para a atmosfera, contribuindo para os esforços globais contra o aquecimento do planeta.

O simulador híbrido desenvolvido nessa tese e a ferramenta de otimização baseada em AG mostraram-se eficazes na modelagem do processo Prata em condições industriais, bem como em condições reportadas na literatura, apresentando-se como uma evolução dos trabalhos publicados. As ferramentas e os resultados apresentados são de extrema

relevância para auxiliar operadores e engenheiros de plantas Prata na definição de políticas operacionais para redução de custo, maior segurança e menores emissões atmosféricas

Os procedimentos, metodologias, algoritmos e “softwares” apresentados nessa tese foram empregados no reator de formaldeído-Prata, porém são aplicáveis aos sistemas mais variados com mínimas adaptações.

8.2. Sugestões para trabalhos futuros

Ao longo do desenvolvimento desse trabalho, várias possibilidades de extensão do tema foram levantadas e ficam aqui registradas como sugestões para trabalhos futuros:

- a) Modelagem do sistema de separação da planta Prata, envolvendo uma coluna de absorção do formaldeído em água, uma coluna de absorção reativa do formaldeído com solução de uréia, uma coluna de destilação do formaldeído para reciclo de metanol e uma coluna de lavagem de gases. A eficiência do sistema de separação afeta fortemente o desempenho da planta, devido à perda de formaldeído para a atmosfera e ao reciclo de metanol;
- b) Comparação de simulações de desempenho entre o processo Prata e o processo Formox, buscando oportunidades de melhoria no primeiro;
- c) Levantamento de dados de flamabilidade para o sistema metanol-formaldeído-água-ar-nitrogênio-CO-CO₂, para definição dos limites seguros de operação e identificação de riscos.
- d) Inclusão da perda de atividade do catalisador de prata no desempenho do reator, considerando a formação do ácido fórmico no modelo;
- e) Comparar desempenho do reator com diferentes lotes de catalisador regenerado, buscando verificar o impacto do processo de regeneração na conversão e seletividade do processo, bem como identificar oportunidades de melhoria.
- f) Simular a injeção do efluente gasoso da planta (basicamente N₂, H₂, CO, CO₂ e água) na alimentação do reator para avaliar o efeito benéfico na diluição da corrente de entrada com inertes para reduzir a concentração de oxigênio e obter melhor seletividade para formaldeído (SRI, 1978).

APÊNDICE A

REVISÃO SOBRE ALGORITMO GENÉTICO

1. Introdução

O Apêndice A comenta as vantagens e desvantagens do Algoritmo Genético (AG) sobre outros métodos de busca. Os operadores do AG são descritos e um exemplo passo-a-passo é apresentado para clarificar a aplicação do método.

2. Desenvolvimento.

O desenvolvimento desse Apêndice é descrito no artigo intitulado “Overview on Genetic Algorithms”, apresentado a seguir, a ser posteriormente transformado em um artigo para submissão à publicação em revista indexada internacional.

3. Conclusão

No apêndice A, apresentou-se uma descrição dos operadores do AG, bem como um exemplo passo-a-passo, representando uma importante contribuição educacional nesse assunto, uma vez que existem poucos exemplos detalhados na literatura para facilitar a compreensão sobre a implementação do método.

Overview on Genetic Algorithms

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1. Introduction

The current literature identifies three main types of search methods: calculus-based, enumerative and random (Goldberg, 1989).

Calculus-based methods are local in scope, searching for optima in the neighborhood of current point and they depend on the existence of derivatives: the functions must be well-defined, including the determination of slope values. Methods that depend on restrictive requirements of continuity and derivative existence are suitable only for a very limited problem domain.

Enumerative methods evaluate the objective function at every point in the search space, one at a time. They are not efficient once they are too slow and complex (Carrol, 1996a).

Random search algorithms' popularity has increased among the researchers, recognizing the shortcomings of calculus-based and enumerative schemes. The genetic algorithm is an example of a search method that uses random choices as a tool to guide a highly exploratory search through the domain.

Genetic algorithm (GA), firstly published in Holland's monograph (1975), is a mathematical method to solve problems, based on the mechanics of natural selection and natural genetics, combining an artificial survival of the fittest with genetic operators abstracted from nature (Holland, 1976; Wang, 1997). Its advantages are (Goldberg, 1989; Garrard and Fraga, 1998):

- They perform a global search and are less likely to converge to a local optima;
- They search from a population of points and not from a single point;
- No need to calculate derivatives;
- The objective function may be a black box and no derivative information is required;
- Every iteration presents a better estimative of the solution and multiple solutions may be found;
- They are theoretically and empirically proven to provide a robust search in complex spaces;

1.1. Genetics and Genetic Algorithm

In nature, any population of any specie has individuals with small differences one to each other, due to the genetic mixture on the reproductive process. This genetic mixture takes place randomly, as crossing-over modifications on chromosomes happens during gamete formation.

Small differences among the individuals will make each one more or less able to survive in his habitat, or being chosen by the partner to procreate. In this sense, the genetic material more compatible with the habitat will be always encouraged to be maintained, while the less compatible will be extinct.

However, evolution can only happen if the population always maintains variability of genetic material, otherwise the evolutionary process would only converge to one genetic material that would be copied generation after generation without any change (or without any further improvement). In other words, if genetic variability is not maintained through the generations, the future of any specie would be a population of identical individuals.

Nature found ways to always maintain the genetic variability of a population: reproduction, cross-over and mutations, which are the three basic operators of Genetic Algorithm.

Reproduction is a process in which the chromosomes of the fittest are copied to the next generation according to their objective function value, or "fitness" to the environment. This operator is an artificial version of natural selection, a Darwinian survival of the fittest.

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During gamete formation, there are mixtures between genes in each pair of chromosomes that regulates the same characteristics: this process is named “cross-over”. This mixture takes place in different points of the chromosomes, with a wide range of combinations. This means that a particular chromosome chain that is passed from an individual to his child is not identical to the ones that he inherited from his parents.

Mutations are modifications on the genetic code, due to an imperfect copy of the chromosome during cell division. This may be caused naturally or due to external factors as radiation and exposure to chemicals. Mutations may originate a new characteristic on the individual, which could be completely different from the other individuals of its specie. This can represent an evolution jump (when mutation generates a more adapted individual) or quick gene extinction (when mutation generates a less adapted individual).

Genetic algorithm (GA) simulates the evolutionary process and has demonstrated ability to solve complex problems (Goldberg, 1989) that other classical numerical methods were not able to handle. This is an iterative methodology, where the starting point is a set of random solutions (initial population or first generation). All of the solutions are evaluated and ranked according to specified criteria (objective or target function). The best solutions will be kept for reproduction and the worse solutions will be deleted (extinction).

The second generation (children) is formed by mating the best solutions of the first generation (parents – mores adapted ones). The one or two best solutions of the first generation will be kept unchanged to prevent the algorithm to step back, but most of the new solutions (next generation) will be slight different from the best solutions of the preceding generation. Mutation is also simulated by randomly changing part of one solution to be tested on the next generation.

In such way, a second generation is created by keeping best individuals, mixing best solutions and adding new solutions by mutation. This procedure keeps variability of solutions and guarantees that the algorithm does not get trapped into a non-optimal solution.

All of the individuals of the new generation are evaluated and ranked, repeating this cycle for a defined number of times.

The GA uses a random method to guide the wide exploratory search through the studied range of variables. Using a random strategy as a search tool may seem strange at first sight but it is important to emphasize that the algorithm is not a search without direction; they efficiently exploit historical information to direct the search on new points with expected improved performance.

Table 1: Genetic Algorithm x Analytical Methods

	Analytical Methods	Genetic Algorithm
Speed	Depends on the problem, usually quick.	Average to slow.
Performance	Depends on the problems	Excellent
Problem comprehension	Necessary	Unnecessary
Human resources	Minutes to years, depending on the problem	Some days
Applicability	Low. It is specific.	General.
Intermediate steps	Solution is only valid after the end of computing run.	Intermediate solutions (each generation) are better and better estimations of the correct solution.

The mathematical operations to simulate crossing-over, reproduction, mutation and selection, as will be detailed below, favor the origin of better and better solutions. Encouraging the best solution and deleting the worse, the initial random population will be continually improved, as a whole. This is known as “selective pressure”.

The solutions for the problem are not calculated, but the best solutions are merely selected and encouraged, after certain random operations. When there is no known solution for a problem, this algorithm is extremely useful and all one need to do is define the “goal function”. GA may be used for solving the root of an equation or optimization of any problem, provided that it is possible to evaluate if the solutions are close or not to the target.

Table 1 shows a comparison between GA and conventional analytical methods for problem solving.

2. Methodology

2.1. Theory – Basic Genetic Algorithm operations

The basic principles of GA are summarized below. Some researchers use variations of these principles, with specific objectives, but still there is no much available literature that describes the algorithm detailed enough for simple implementation.

2.1.1. The chromosomes

GA represents the chromosomes as a vector containing the searched solutions. For example, if a particular problem has 5 variables to be optimized (a,b,c,d,e), the chromosome will be a vector with 5 positions “abcde”. The individual values of the chromosome (“a”,“b”,“c”,“d”,“e”) are the genes (in this example, the chromosome has 5 genes).

The chromosomes may be represented in 2 ways:

- *Real code (Floating Point Code)*

The values stored in each gene are a real number that corresponds to the searched solution. See below an example of a chromosome with 5 genes and real code:

2.0	2.4	1.2	0.6	1.8
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- *Binary Code*

The parameters are represented in “N” discrete possibilities where each one is characterized by a chain of “0” and “1”, using binary language. Two examples are given in Table 2.

Table 2: Example of binary numbers and their equivalent decimal

Binary number	Calculation	Equivalent decimal #
1010	$1 \cdot 2^3 + 0 \cdot 2^2 + 1 \cdot 2^1 + 0 \cdot 2^0$	10
01001	$1 \cdot 2^4 + 1 \cdot 2^3 + 0 \cdot 2^2 + 0 \cdot 2^1 + 1 \cdot 2^0$	25

As an example, suppose that a particular parameter could vary in the range 0 e 3.0 and we would like to represent this range with 16 discrete possibilities, presented on Table 3. In this case, the precision of the discrete values would be 0.2.

If the same chromosome used as an example for the real code representation would be converted to Binary Code, each of the 5 genes would represent a parameter whose values might vary between 0.0 and 3.0. Considering that the precision of 0.2 is acceptable for this example, each gene can be formed by 4 binary bases, according to Table 3. The binary representation for this case is written on Table 4 and the binary chromosome would be :

1010	1100	0110	0011	1001
------	------	------	------	------

Or simply:

10101100011000111001

- *Real or Binary code?*

The advantage of the Real Code is the possibility of working with a continuous range and using the true value of the parameters without converting binary to real representation.

The advantage of the Binary Code is that any parameter may be represented by many digits. If the problem has small number of parameters, the cross-over operation may not be so significant to improve variability if Real Code is used, but converting the problem to Binary Code, the chromosome has more genes, making GA operations relevant. With Binary Code, the cross-over point may be located in the middle of a gene, and not only between two genes (see “children”), bringing more genetic variability.

As a rule of thumb, the Real Code should be used first and if GA’s performance is poor, the problem should be converted to Binary Code.

Table 3: Binary code representation

Possibility #	Binary representation of the possibility	Real value (discrete)
0	0000	0.0
1	0001	0.2
2	0010	0.4
3	0011	0.6
4	0100	0.8
5	0101	1.0
6	0110	1.2
7	0111	1.4
8	1000	1.6
9	1001	1.8
10	1010	2.0
11	1011	2.2
12	1100	2.4
13	1101	2.6
14	1110	2.8
15	1111	3.0

Table 4: Binary representation

Gene	Real value	Possibility # (Table 3)	Binary Representation
A	2.0	10	1010
B	2.4	12	1100
C	1.2	6	0110
D	0.6	3	0011
E	1.8	9	1001

2.1.2. Individuals

An individual is a representation of a possible solution. In the example given above, each individual is represented by a chromosome “abcde”, however, for some problems, the individual may be represented by two or more chromosomes.

If one were to solve two equations simultaneously:

$$z_1 = a_1 \cdot x + a_2 \cdot y^2 + a_3 \cdot \ln(w)$$

$$z_2 = a_4 \cdot x^{a_5} - a_6 \cdot v^{0.5} + a_7 \cdot u$$

where $a_1 - a_7$ are the parameters to be solved, each individual could be represented by 2 chromosomes: $[a_1, a_2, a_3]$ and $[a_4, a_5, a_6, a_7]$.

2.1.3. Population

Population is a set of all individuals in a generation. Normally population size is constant (n) throughout generations (see example below), differently than nature. There is no particular reason to keep the population size constant, just simplicity.

Population size must be optimized, keeping the balance between precision and computing time. In large populations, the probability of finding a better individual in small number of generations is higher, but computing time will be larger.

Some authors report methodologies for population size calculations (Goldberg, 1992; Carrol, 1996ab), but in practice it is set as large as computing time allows.

2.1.4. Generation

Generation is the set of individuals that will compete to survive. The fittest will survive and will be the “parents” of the next generation. In computing words, a “generation” means an iteration.

2.1.5. Selection of parents for the next generation

The next generation of individuals is composed by children of the individuals from the previous generation. The parents (best solution of a generation) may or may not be maintained in the new generation. Usually, they are maintained for prevent losing them in case of the children are less able than the parents (this procedure is named “elitism”).

There are two ways to select the parents:

- *Selection of best individuals*

In this case, the best individuals of a generation are selected to be the parents of the new generation. The best individuals are the ones with better fitness function value.

The number of parents in each generation may be fixed by user (generally the number of parents is adjusted to obtain better GA performance) or a limit may be defined by user (the selected parents are the ones with fitness value above certain limit). The selected individuals are grouped in pairs to generate children.

The pairing method may vary: priority to the best individuals or random pairing. In the first case, the children are formed preferably by the best individuals, in the fitting order. In the second, any pair of parents is possible among the ones selected.

- *Tournament*

Two pairs are randomly chosen. The best individual of each pair is selected and the pair of selected individuals generates a child. Two new pairs are chosen and the process repeated until the new generation is completed.

2.1.6. Children

Children are created from the mixture of the parents’ chromosomes. Initially the pair of parents is selected and then the child chromosome is created by the following ways:

- *Single-point crossover*

The chromosome from one of the parents is copied to the child (e.g.: “abcde”). If the chromosome of the second parent is “ABCDE”, a random point of it is selected as cross-over point, let’s say, between genes “C” and “D”. Then, part of the second parent’s chromosome is copied over the chromosome of the child and the result is “abcDE”.

- *Uniform crossover (Syswerda, 1989)*

A combination of any order with the parents’ chromosomes, as: “aBcDe” or “AbcdE” or “abCDe”.

- *Single or Uniform crossover?*

Researchers give probabilities for each case (uniform or single), distributing children formation through the 2 methods. Carrol (1996a) defined equal probabilities for the two methods.

The number of children per pair is a relatively new question on GA community. Generally, researchers use one child per parents' pair. Some papers (Carrol, 1996a; Costa and Maciel Filho, 2005) point out better results with 2 children per pair.

One important feature of single crossover is that it can produce children that are radically different from its parents. Another important feature is that it will not introduce differences for a gene in a position where both parents have the same value for the gene.

Crossover is an extremely important component of a genetic algorithm. Many researchers believe that if we exclude the crossover operator from a GA the result is no longer a GA and performance is degraded on a variety of problems. This claim has not been made for mutation operators (Davis, 1991).

2.1.7. Mutation

As in nature, a mutation on a gene of some children is simulated in two ways. See examples below.

- *Creep Mutation*

One gene (parameters) of an individual "just-born" may be slightly changed. In other words, a child with a chromosome "abCdE" may mutate to a chromosome "abCdF", where "F" is not as gene from any of the two parents, but is similar.

- *Jump mutation*

The same case, but mutation is bigger. An individual with a chromosome "abCdE" may mutate to "abCdP", where "P" is a gene very different from the parents'.

- *Jump or Creep mutation?*

The probability for each type of mutation is defined by user. Usually, the probability for Creep mutation is "1/n" and the probability for Jump mutation is "2/n", where "n" is population size (Carrol, 1996a).

Mutation may occur in one or more genes of the individual. The probability of mutation for each gene is the same.

Holland (1975) considered a third operator, besides crossover and mutation: the inversion. Inversion operates a single chromosome, inverting the order of the genes between two randomly chosen points. Even being inspired in a biological process, this operator has not been found to be useful in practice and it is rarely used at present.

3. Discussion - a simulation by hand

The simple example stated below demonstrates the basics of GA.

Suppose an experimental data set as presented on Table 5, where variable "z" is a function of "x" and "y" and the following model should be used to fit this experimental data.

$$z = a \cdot x^2 + b \cdot y^2 + c$$

Table 5: Experimental data for an exploratory example

Data #	x	Y	z
1	0	0	0.41
2	1	1	3.45
3	1	2	9.45
4	2	1	6.40
5	2	2	12.49

1st Step: Define the goal

The goal of the problem is to define “a”, “b” and “c” in order to fit the experimental data with the proposed model. Thus, “a”, “b” and “c” are the searched solutions for the problem.

2nd Step: Define objective function

We must be able to evaluate if a solution is good or not. In this case, the sum of squares could be used (Eq 1).

$$E = \sum_{i=1}^5 (\hat{z}_i - z_i)^2 \quad (1)$$

Where “E” is the fitness error; “ \hat{z}_i ” is the estimated function value and “ z_i ” is the experimental value. The lower the E value, the better is the solution (a-b-c).

3rd Step: Create a starting population

The first generation of random individuals is created. Let us suppose a population with 10 individuals (10 solutions candidates), each one with 1 chromosome containing 3 genes, a-b-c.

Table 6 shows 10 random individuals and the corresponding objective function value (E). Each value “E” was calculated based on the sum of squares (Eq 1), comparing the experimental “z” from Table 5 with the “z” calculated using the parameters a-b-c of the row on Table 6.

Table 6: First generation

Individual (solution)	a	B	c	E
1	4.9	4.0	3.4	1435
2	3.2	0.1	4.7	195
3	4.8	0.7	1.0	331
4	4.0	2.1	2.3	453
5	2.0	2.4	1.8	106
6	1.2	4.0	3.6	345
7	4.4	1.8	4.3	681
8	3.7	3.8	4.8	1087
9	4.2	2.4	0.8	443
10	4.1	2.0	1.4	391

If we define that only 2 individuals will survive and generate children, the individuals #5 and #2 are the one with lowest E value on Table 6 and could fit better experimental data. The other individuals will be deleted.

4th Step: Second generation

Second generation will be formed by individuals #5 and #2 (maintained) and by their children: combinations of “a”, “b” and “c” values from maintained individuals, mimicking crossing-over process. Table 7 shows the new population.

Table 7: Second generation

Individual	a	b	C	E	Note
1	2.0	2.4	1.8	106	Individual #5 from 1st gen.
2	3.2	0.1	4.7	195	Individual #2 from 1st gen.
3	2.0	0.1	4.7	76	Child from 1 + 2
4	2.0	2.4	4.7	269	Child from 1 + 2
5	3.2	0.1	1.8	96	Child from 1 + 2
6	3.2	2.4	1.8	293	Child from 1 + 2
7	1.9	2.4	4.7	100	Child 1 + 2 + creep mutation
8	3.2	0.1	1.9	119	Child 1 + 2 + creep mutation
9	2.0	3.0	4.7	339	Child 1 + 2 + jump mutation
10	3.8	3.3	1.9	635	New random individual

The new individuals #1 and #2 are the two best individuals from last generation. They were kept to preserve the genetic material. The individuals #3, #4, #5 and #6 are children from #1 and #2, formed by cross-over. Individuals #7 and #8 are children from #1 and #2, but they had a creep mutation on gene “a” and “c” respectively. Child #9 had a jump mutation on gene “b”. Child #10 had a big mutation (is a completely random new individual).

5th Step: Third generation

The same procedure is repeated.

Table 8: Third generation

Individual	a	b	c	E	Note
1	2.0	0.1	4.7	76	Individual #3 from 2nd gen.
2	3.2	0.1	1.8	96	Individual #5 from 2nd gen.
3	2.0	0.1	1.8	47	Child from 1 + 2
4	2.0	0.1	1.8	47	Child from 1 + 2
5	3.2	0.1	4.7	195	Child from 1 + 2
6	3.2	0.1	4.7	195	Child from 1 + 2
7	2.0	0.2	1.8	98	Child 1 + 2 + creep mutation
8	2.0	0.1	1.7	75	Child 1 + 2 + creep mutation
9	1.0	0.1	4.7	109	Child 1 + 2 + jump mutation
10	0.8	0.3	0.0	135	New random individual

This procedure is repeated through a defined number of generations. Table 9 shows a summary of next generations, with the best individual (lowest “E”) of each. Note that in some generations (#13 and #14) there is no better individual and the best one is still the parent kept from preceding generation.

Most of the times, the fittest is a child, with “E” value a little bit better than his parents’. Big changes on “E” come with individuals mutated (as in nature).

Table 9: Next generations

Generation	a	b	c	E
3	2.0	0.1	1.8	47
4	1.9	0.1	1.8	46
5	2.0	0.1	1.9	46
10	2.0	0.2	1.8	44
11	1.8	0.2	2.0	43
12	0.5	1.4	2.6	11
13	0.5	1.4	2.6	11
14	0.5	1.4	2.6	11
20	0.5	1.6	2.3	7.0
25	0.5	1.8	2.1	5.0
30	1.0	1.7	1.6	3.0
35	0.9	1.7	1.6	2.3
50	0.9	1.8	1.1	0.83
70	0.9	1.9	0.9	0.46
100	1.0	1.9	0.8	0.26
120	1.0	2.0	0.7	0.11
150	1.0	2.0	0.5	0.04

Algorithm end

The algorithm normally stops after a defined number of generations and the final solution is the fittest of this last generation. The algorithm may also be programmed to stop when the fittest solution of a generation is below some defined limit, despite the number of generations.

4. Concluding remarks

An overview of the Genetic Algorithm was summarized, highlighting its advantages and disadvantages. The main operators were described and a simulation by hand was presented for educational ends.

References

- Carrol, D.; "Genetic Algorithms and Optimizing Chemical Oxygen-Iodine Lasers", *Developments in Theoretical and Applied Mechanics*, v.XVIII, pp.411-424, 1996b.
- Carrol, D.L., "Chemical laser modeling with genetic algorithm", *AIAA Journal*, v.34, no 2, pp.338-346, 1996a.
- Costa, B.B.C and Maciel Filho, R.; "Evaluation of optimization techniques and control variable formulations for a batch cooling crystallization process", *Chemical Engineering Science*, 60, pp.5312-5322, 2005.
- Davis, L.; "Handbook of Genetic Algorithms", International Thomson Computer Press, Boston, 1991.
- Garrard, A. and Fraga, E.S.; "Mass exchange network synthesis using genetic algorithms", *Computers Chem. Engng.*, v.22, n.12, pp.1837-1850, 1998.
- Goldberg, D.E.; "Genetic Algorithms in Search, Optimization, and Machine Learning", Ed. Addison-Wesley Publishing Company, Inc, New York, 1989.
- Goldberg, D.E; Deb, K. and Clark, J.H.; "Genetic Algorithms, Noise and the Sizing of Populations", *Complex Systems*, 6, pp. 333-362, 1992.
- Holland, J.H.; "Adaptation in natural and artificial systems", Ann Arbor: The University of Michigan Press, 1975.
- Holland, J.H.; "Adaptation", *Progress in theoretical biology*, 4, pp.263-293, 1976.
- Syswerda, G.; "Uniform crossover in genetic algorithms", *Proceedings of the third international conference on genetic algorithms*. San Mateo, California, Morgan Kaufmann publishers, 1989.
- Wang, Q.J.; "Using Genetic Algorithms to Optimise Model Parameters", *Environmental Modelling & Software*, v.12, n.1, pp 27-34, 1997.

APÊNDICE B

REVISÃO SOBRE O MÉTODO NUMÉRICO DE CRANK-NICHOLSON

1. Introdução

O Apêndice B descreve o método numérico de Crank-Nicholson, aplicado sobre as equações diferenciais de balanço de massa e energia para um reator de leito fixo. O desenvolvimento das equações é realizado em etapas para facilitar a compreensão sobre a aplicação do método.

2. Desenvolvimento.

O desenvolvimento desse Apêndice é descrito no artigo intitulado “Método Numérico Crank-Nicholson aplicado a solução de equações de balanço de massa e energia na simulação de reatores de leito fixo”, apresentado a seguir, que será posteriormente transformado em um artigo para submissão a publicação em revista indexada.

3. Conclusão

No Apêndice B, apresentou-se uma descrição do método numérico de Crank-Nicholson, aplicado às equações diferenciais de balanço de massa e energia para um reator de leito fixo.

Método Numérico Crank-Nicholson aplicado à solução de equações de balanço de massa e energia na simulação de reatores de leito fixo

Antonio Carlos Papes Filho^{1*} e Rubens Maciel Filho¹

1. Introdução

A criação de simuladores para reatores de leito fixo passa obrigatoriamente pela solução simultânea das equações de balanço de massa, energia e momento. Uma vez que as mesmas envolvem derivadas parciais em mais de uma direção do espaço ou tempo, torna-se necessária a aplicação de métodos numéricos para a solução dessas equações.

Métodos clássicos empregados amplamente em problemas de engenharia são o Runge-Kutta e a colocação ortogonal, devido a sua simplicidade, grande precisão e baixa necessidade de recursos computacionais.

O método de Crank-Nicholson foi apresentado em 1947 (Crank e Nicholson, 1947), consistindo em um algoritmo semi-implícito conhecido pela sua estabilidade incondicional, diferentemente dos métodos explícitos. A desvantagem desse método é a necessidade de solução de uma grande matriz tridiagonal, utilizando vasto poder computacional.

Por muito tempo esse método teve baixa aceitação por não haver capacidade computacional disponível. Com o rápido avanço dos computadores pessoais, hoje, praticamente qualquer máquina pode realizar as operações do método Crank-Nicholson em um tempo razoável. Isso torna esse método uma excelente opção para os cálculos de engenharia, principalmente para a simulação de reatores, onde a estabilidade do método é uma característica bastante desejada.

Nesse trabalho, o método Crank-Nicholson será apresentado, aplicado à solução das equações diferenciais de balanço de massa e energia para o estado estacionário.

2. Apresentação do método

2.1. Equações diferenciais

As equações diferenciais que serão tratadas nesse estudo são do tipo das equações de balanço aplicadas a coordenadas cilíndricas, mais comuns em reatores de leito fixo. Esse tipo de equação pode ser escrito genericamente como a equação (1).

$$a \cdot \frac{\partial^2 Y}{\partial z^2} + b \cdot \left(\frac{\partial^2 Y}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial Y}{\partial r} \right) - d \cdot \frac{\partial Y}{\partial z} + e \cdot f(Y, r, z) = 0 \quad (1)$$

representando as equações diferenciais de balanço de massa (Eq.2) e energia (Eq.3).

$$D_L \cdot \frac{\partial^2 C}{\partial z^2} + D_R \cdot \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial C}{\partial r} \right) - V_Z \cdot \frac{\partial C}{\partial z} + v_A \cdot r_V = 0 \quad (2)$$

$$k_L \cdot \frac{\partial^2 T}{\partial z^2} + k_R \cdot \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial T}{\partial r} \right) - \rho \cdot C_p \cdot V_Z \cdot \frac{\partial T}{\partial z} - \Delta H_R \cdot r_V = 0 \quad (3)$$

Onde:

Y: função genérica de “r” e “z”

C: concentração da substância “A”, kg/m³

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T:	temperatura, K
z:	distância axial a partir da entrada do reator (coordenadas cilíndricas), m
r:	distância radial a partir da linha de centro do reator (coordenadas cilíndricas), m
D_L :	coeficiente de difusão axial, m^2/s
D_R :	coeficiente de difusão radial, m^2/s
k_L :	condutividade térmica axial, W/m.K
k_R :	condutividade térmica radial, W/m.K
V_z :	velocidade axial, m/s
ν_A :	coeficiente estequiométrico da substância "A"
ρ :	densidade da mistura, kg/m^3
C_p :	capacidade calorífica da mistura, J/kg.K
ΔH_R :	calor de reação, J/mol
r_v :	taxa de reação por volume, $kg/m^3.s$

2.2. Adimensionalização

Antes de aplicar um método numérico sobre equações diferenciais, é necessário adimensionalizá-las para evitar que diferenças na grandeza das variáveis afetem a precisão do resultado ou que ocorram erros de "overflow" na solução computacional por operação de divisão com denominador muito menor que o numerador.

As equações adimensionalizadas são:

$$\frac{D_L}{L.V_z} \cdot \frac{\partial^2 X}{\partial (z^*)^2} + \frac{D_R.L}{V_z.R^2} \cdot \left(\frac{\partial^2 X}{\partial (r^*)^2} + \frac{1}{(r^*)} \cdot \frac{\partial X}{\partial r^*} \right) - \frac{\partial X}{\partial z^*} + \frac{\nu_A.L}{C_o.V_z} \cdot r_v = 0 \quad (4)$$

$$\frac{k_L}{\rho.C_p.V_z.L} \cdot \frac{\partial^2 W}{\partial (z^*)^2} + \frac{k_R.L}{\rho.C_p.V_z.R^2} \cdot \left(\frac{\partial^2 W}{\partial (r^*)^2} + \frac{1}{(r^*)} \cdot \frac{\partial W}{\partial r^*} \right) - \frac{\partial W}{\partial z^*} - \frac{\Delta H_R.L}{\rho.C_p.V_z.T_o} \cdot r_v = 0 \quad (5)$$

Onde:

$X = C/C_o$, sendo C_o a concentração da substância na entrada do reator, ou a concentração de referência

$W = T/T_o$, sendo T_o a temperatura na entrada do reator ou a temperatura de referência

$z^* = z/L$, sendo L o comprimento do reator

$r^* = r/R$, sendo R o raio do reator

Nessa forma, as equações ainda apresentam uma deficiência por levarem a uma indeterminação quando $r = 0$. Portanto, uma nova mudança de variáveis é necessária:

$$\frac{D_L}{L.V_z} \cdot \frac{\partial^2 X}{\partial (z^*)^2} + \frac{4.D_R.L}{V_z.R^2} \cdot \left(u \cdot \frac{\partial^2 X}{\partial u^2} + \frac{\partial X}{\partial u} \right) - \frac{\partial X}{\partial z^*} + \frac{\nu_A.L}{C_o.V_z} \cdot r_v = 0 \quad (6)$$

$$\frac{k_L}{\rho.C_p.V_z.L} \cdot \frac{\partial^2 W}{\partial (z^*)^2} + \frac{4.k_R.L}{\rho.C_p.V_z.R^2} \cdot \left(u \cdot \frac{\partial^2 W}{\partial u^2} + \frac{\partial W}{\partial u} \right) - \frac{\partial W}{\partial z^*} - \frac{\Delta H_R.L}{\rho.C_p.V_z.T_o} \cdot r_v = 0 \quad (7)$$

Onde $u = (r^*)^2$

Observe que as equações (6) e (7) são semelhantes e poderiam ser representadas por uma mesma equação:

$$\alpha \cdot \frac{\partial^2 Q}{\partial (z^*)^2} + \beta \cdot \left(u \cdot \frac{\partial^2 Q}{\partial u^2} + \frac{\partial Q}{\partial u} \right) - \frac{\partial Q}{\partial z^*} + \gamma \cdot r_v = 0 \quad (8)$$

Sendo que para o balanço de massa:

$$Q = X \quad \alpha = \frac{D_L}{L.V_Z} \quad \beta = \frac{4.D_R.L}{V_Z.R^2} \quad \gamma = \frac{v_A.L}{C_O.V_Z} \quad (9)$$

e para o balanço de energia:

$$Q = W \quad \alpha = \frac{k_L}{\rho.C_p.V_Z.L} \quad \beta = \frac{4.k_R.L}{\rho.C_p.V_Z.R^2} \quad \gamma = \frac{\Delta H_R.L}{\rho.C_p.V_Z.T_O} \quad (10)$$

2.3. Aplicação do método numérico sobre as equações

O desenvolvimento do método pode ser encontrado na literatura, observando-se que ele é estável para qualquer tamanho de passo na direção axial ou radial.

Para implementação do método, é necessário definir o universo de trabalho. Para tal, será considerado que tanto o perfil de temperatura quanto o perfil de concentração apresentam uma distribuição simétrica em relação ao eixo do tubo (simetria radial), de modo que possamos trabalhar dentro do espaço “R x L”, que, em termos adimensionais, será um quadrado de 1 x 1.

Esse espaço deve ser dividido em pequenas partes, fracionando cada dimensão em vários passos: “N_Z” divisões na dimensão “z” e “N_u” divisões na dimensão “u”, produzindo dentro do espaço “R x L” uma malha de retângulos com dimensões Δz* por Δu, sendo:

$$\Delta z^* = 1/N_Z \quad \text{e} \quad \Delta u = 1/N_u$$

Lembrando que “u” guarda uma relação não linear com “r”, deve-se observar que o intervalo Δr entre dois passos não será sempre o mesmo:

$$\Delta r = \frac{\Delta u.R^2}{2.r}, \text{ sendo } \Delta u \text{ constante}$$

Na demonstração a seguir, as partições em “z*” serão representadas pela letra “n”, variando desde 1 (primeiro passo, em z = 0) até “N_Z + 1” (último passo, em z = L). Igualmente, a letra “j” representará as divisões em “u”, variando de 1 (primeiro passo, em r = 0) até “N_u + 1” (último passo, em r = R).

O espaço de trabalho está identificado nas Figuras 1 e 2.

A concentração e a temperatura adimensionais em um ponto qualquer da malha dentro do espaço de trabalho serão representados respectivamente por X_j^n e W_j^n .

As derivadas de primeira ordem em z* serão avaliadas entre os pontos (j; n+1) e (j;n) e, para que o erro associado a essa aproximação seja minimizado, deve-se atribuir o valor numérico correspondente ao ponto médio desse intervalo, ou seja, ao ponto (j; n+½):

$$\frac{\partial Q}{\partial z^*} = \frac{Q_j^{n+1} - Q_j^n}{\Delta z^*} \quad (11)$$

Por coerência, como o valor da derivada anterior foi convenientemente atribuído ao ponto (j; n+½), a derivada numérica de primeira ordem em “u” deve também estar centrada nesse ponto. Para tanto, é necessário tomar o valor médio entre a derivada calculada entre os pontos (j-1; n+1) e (j+1; n+1) e aquela calculada entre os pontos (j-1; n) e (j+1; n):

$$\frac{\partial Q}{\partial u} = \frac{1}{2} \left(\frac{Q_{j+1}^{n+1} - Q_{j-1}^{n+1}}{2.\Delta u} + \frac{Q_{j+1}^n - Q_{j-1}^n}{2.\Delta u} \right) \quad (12)$$

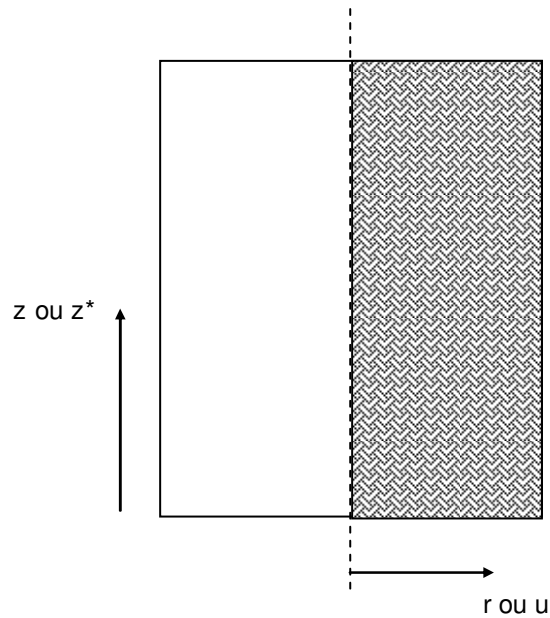


Figura 1: Identificação do espaço de trabalho R x L no reator tubular de leito fixo

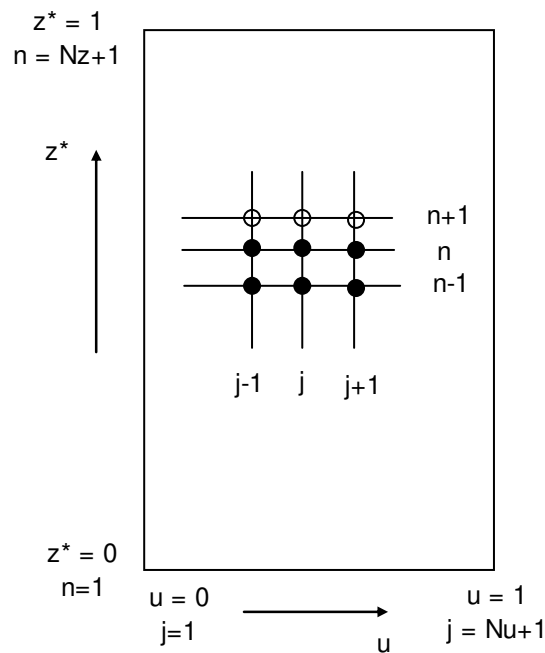


Figura 2: Identificação dos passos no espaço de trabalho, formando a malha

O mesmo procedimento deve ser adotado para a derivada de segunda ordem em “u”:

$$\frac{\partial^2 Q}{\partial u^2} = \frac{1}{2} \left(\frac{Q_{j+1}^{n+1} - 2 \cdot Q_j^{n+1} + Q_{j-1}^{n+1}}{(\Delta u)^2} + \frac{Q_{j+1}^n - 2 \cdot Q_j^n + Q_{j-1}^n}{(\Delta u)^2} \right) \quad (13)$$

Esse raciocínio não pode ser aplicado para a derivada de segunda ordem em z^* uma vez que essa é avaliada entre os pontos $(j; n-1)$, $(j; n)$ e $(j; n+1)$, estando necessariamente associada ao ponto $(j; n)$. Dessa forma, todas as derivadas estarão centradas no ponto $(j; n+1/2)$, exceto a derivada de segunda ordem em z^* . Por um lado,

esse fato introduzirá um erro de aproximação nos cálculos, o qual pode ser minimizado com um grande número de divisões na direção z^* (malha mais fina). Por outro lado, se todas as derivadas ficarem centradas no ponto $(j; n)$, o algoritmo será simplificado, resultando em um algoritmo diferente do proposto por Crank e Nicholson. A derivada de segunda ordem na direção z^* será:

$$\frac{\partial^2 Q}{\partial (z^*)^2} = \frac{Q_j^{n+1} - 2 \cdot Q_j^n + Q_j^{n-1}}{(\Delta z^*)^2} \quad (14)$$

A função “ r_v ” também deveria ser avaliada em $(j; n+1/2)$, porém seu valor só é conhecido no ponto $(j; n)$ e haveria a necessidade de se tomar a sua média com o valor avaliado em $(j; n+1)$, que não é conhecido. A solução é avaliar a função apenas em $(j; n)$ da mesma forma que o exposto acima.

Substituindo as representações numéricas das derivadas na equação diferencial geral (8) e arranjando os termos, pode-se obter a seguinte expressão:

$$A_1 \cdot Q_{j-1}^{n+1} - A_2 \cdot Q_j^{n+1} + A_3 \cdot Q_{j+1}^{n+1} = -A_1 \cdot Q_{j-1}^n + A_4 \cdot Q_j^n - A_3 \cdot Q_{j+1}^n - A_5 \cdot Q_j^{n-1} - \gamma \cdot r_v \quad (15)$$

onde

$$A_1 = \frac{\beta}{4 \cdot (\Delta u)^2} \cdot (2 \cdot u - \Delta u) \quad (16)$$

$$A_2 = \frac{\beta \cdot u}{(\Delta u)^2} + \frac{1}{\Delta z^*} - \frac{\alpha}{(\Delta z^*)^2} \quad (17)$$

$$A_3 = \frac{\beta}{4 \cdot (\Delta u)^2} \cdot (2 \cdot u + \Delta u) \quad (18)$$

$$A_4 = \frac{\beta \cdot u}{(\Delta u)^2} - \frac{1}{\Delta z^*} + \frac{2 \cdot \alpha}{(\Delta z^*)^2} \quad (19)$$

$$A_5 = \frac{\alpha}{(\Delta z^*)^2} \quad (20)$$

$$u = (j - 1) \cdot \Delta u \quad (21)$$

Sendo as variáveis completamente conhecidas nos passos “ $n-1$ ” e “ n ” (pontos cheios na Figura 2), o lado direito da equação acima é plenamente determinado, restando incógnitas as três variáveis “ Q ” no passo “ $n+1$ ”, no lado esquerdo da equação (pontos vazios na Figura 2). Os coeficientes “ A_i ” da equação dependem apenas das propriedades físicas do sistema e do tamanho dos passos, sendo facilmente calculados. Os valores de α , β , γ e Q devem ser corretamente empregados, de acordo com o tipo de balanço (massa ou energia).

Em um determinado passo $n > 1$, tomando como exemplo uma malha de 5 passos em “ u ” (6 pontos em u), teremos um conjunto de 4 equações lineares centradas no pontos $1 < j < 6$, envolvendo as seguintes variáveis: $Q_1^{n+1}, Q_2^{n+1}, Q_3^{n+1}, Q_4^{n+1}, Q_5^{n+1}, Q_6^{n+1}$. As variáveis avaliadas nos passos “ n ” e “ $n-1$ ” são conhecidas. Dessa forma, temos 4 equações lineares para 6 incógnitas e faz-se necessário incluir mais duas equações, correspondendo às condições de contorno, uma vez que as equações apresentadas não podem ser aplicadas nos pontos $j = 1$ e $j = 6$.

2.4. Condições de contorno

2.4.1. Para o centro do reator

Assumindo-se simetria radial nos perfis de concentração e temperatura em qualquer secção “ z ” do tubo, na posição $r = 0$; $r^* = 0$; $u = 0$ ou $j = 1$, teremos:

$$\frac{\partial C}{\partial r} = 0 \quad \text{e} \quad \frac{\partial T}{\partial r} = 0 \quad \text{ou} \quad \frac{\partial Q}{\partial u} = 0 \quad (22)$$

Aplicando-se a derivada numérica nessa equação:

$$Q_1^{n+1} - Q_2^{n+1} = 0 \quad (23)$$

2.4.2. Para a parede interna do tubo no balanço de massa

Assumindo-se que não há transferência de massa pelas paredes do tubo, na posição $r = R$, $r^* = 1$, $u = 1$ ou $j = J$, teremos:

$$\frac{\partial C}{\partial r} = 0 \quad \text{ou} \quad \frac{\partial X}{\partial u} = 0 \quad (24)$$

Aplicando-se a derivada numérica:

$$X_{J-1}^{n+1} - X_J^{n+1} = 0 \quad (25)$$

2.4.3. Para a parede interna do tubo no balanço de energia

Deve haver continuidade entre o calor transferido do fluido para o tubo e o calor conduzido pelo tubo:

$$-K_R \cdot \frac{\partial T}{\partial r} = h_{WI} \cdot (T_R - T_W) \quad (26)$$

sendo:

K_R a condutividade térmica efetiva radial do fluido, W/m.K

h_{WI} o coeficiente convectivo na parede interna, W/m².K

T_R a temperatura do fluido próxima à parede ($j = J$) no passo “n+1”, K

T_W a temperatura da parede do tubo na secção “n+1”, K

Adimensionalizando-se essa equação, usando “ T_0 ” e “ R ”, e aplicando a derivada numérica:

$$2.K_R \cdot \frac{W_J^{n+1} - W_{J-1}^{n+1}}{\Delta u} = h_{WI} \cdot R \cdot (W_{wall}^{n+1} - W_J^{n+1}) \quad (27)$$

que pode ser escrita da forma rearranjada abaixo:

$$-2.K_R \cdot W_{J-1}^{n+1} + (2.K_R + \eta) \cdot W_J^{n+1} - \eta \cdot W_{wall}^{n+1} = 0 \quad (28)$$

sendo $\eta = h_{WI} \cdot R \cdot \Delta u$

Com a equação acima, mais uma variável foi adicionada ao sistema (W_{wall}) e uma nova equação linear precisará ser considerada: a condução de calor pela parede do tubo:

$$h_{WI} \cdot W_J^{n+1} - (h_{WI} + h_{WE} \cdot G) \cdot W_{wall}^{n+1} = -h_{WE} \cdot G \cdot W_F^{n+1} \quad (29)$$

$$G = \frac{R + E}{R} \quad (30)$$

Onde:

h_{WE} é o coeficiente convectivo na parede externa, $W/m^2.K$

E é a espessura da parede do tubo, m

R é o raio do tubo, m

W_F é a temperatura do fluido refrigerante, adimensionalizada

Se a temperatura do fluido refrigerante for considerada constante, o lado direito da equação 29 é determinado facilmente. Se considerada variável, W_F pode ser determinada pelo balanço energético para o fluido refrigerante:

$$\frac{dT_F}{dz} = \frac{2.R.U_C.\pi}{m_F.C_{PF}}.(T_R - T_F) \quad (31)$$

onde

T_F é a temperatura do fluido refrigerante, K

U_C é o coeficiente global de transferência de calor, $W/m^2.K$

C_{PF} é a capacidade calorífica do fluido refrigerante, $J/kg.K$

m_F é a vazão mássica do fluido refrigerante, kg/s

As variáveis " T_F ", " T_R " e " z " foram adimensionalizadas, dividindo-as por " T_O " e " L " respectivamente, transformando-as em W_F , W_J e z^* . Aplicando-se a diferencial numérica:

$$W_F^{n+1} = \xi.W_J^n + (1 - \xi).W_F^n \quad (32)$$

onde

$$\xi = \frac{2.U_C.\pi.L.R.\Delta z^*}{m_F.C_{PF}} \quad (33)$$

Essa equação permite o cálculo de W_F na posição " $n+1$ " usando apenas valores conhecidos no passo " n ", não introduzindo novas variáveis ao sistema.

Com essas condições de contorno, é possível adicionar as duas equações faltantes para a solução do sistema. Escrevendo o problema na forma matricial, tem-se:

$$[MT].[VAR] = [TI]$$

Sendo

"MT" uma matriz tridiagonal de dimensões $J \times J$ contendo os coeficientes do lado esquerdo da equação 15, e os coeficientes das condições de contorno (equações 23 e 25). As linhas 2 a 5 da matriz exemplo referem-se aos pontos típicos da malha. A primeira e a última linhas referem-se aos termos das condições de contorno no centro do tubo e na parede.

"VAR" um vetor de dimensão " J " contendo as variáveis, ou seja, o perfil radial de concentrações ou temperaturas no passo " $n+1$ ".

"TI" é um vetor de dimensão " J " contendo os termos independentes correspondentes ao valor numérico calculado para a parte direita da equação 15 (I_2 a I_5 , no exemplo) e aqueles correspondentes aos termos independentes das condições de contorno nas equações 23, 25, 28 e 29 (I_1 e I_6 , no exemplo). Esses valores dependem dos perfis conhecidos no passo " n " e no passo " $n-1$ ".

Para o balanço de massa, o sistema pode ser escrito na forma matricial, como no exemplo a seguir, com $J = 6$. Os coeficientes A_1 , A_2 e A_3 devem ser calculados pelas equações 16, 17 e 18, utilizando os termos α , β e γ referentes às equações do balanço de massa (equações 9). Os termos independentes I_2 a I_5 são calculados conforme o lado direito da equação 15, cujos coeficientes A_1 , A_3 , A_4 e A_5 devem ser expressos pelas equações 16, 18, 19 e 20, utilizando os termos α , β e γ referentes às equações do balanço de massa (equações 9). Os termos independentes I_1 e I_6 são nulos (lado direito das equações 23 e 25).

$$\begin{bmatrix}
1 & -1 & 0 & 0 & 0 & 0 \\
A_{1,j=2} & -A_{2,j=2} & A_{3,j=2} & 0 & 0 & 0 \\
0 & A_{1,j=3} & -A_{2,j=3} & A_{3,j=3} & 0 & 0 \\
0 & 0 & A_{1,j=4} & -A_{2,j=4} & A_{3,j=4} & 0 \\
0 & 0 & 0 & A_{1,j=5} & -A_{2,j=5} & A_{3,j=5} \\
0 & 0 & 0 & 0 & 1 & -1
\end{bmatrix}
\times
\begin{bmatrix}
X_1^{n+1} \\
X_2^{n+1} \\
X_3^{n+1} \\
X_4^{n+1} \\
X_5^{n+1} \\
X_6^{n+1}
\end{bmatrix}
=
\begin{bmatrix}
I_1^M \\
I_2^M \\
I_3^M \\
I_4^M \\
I_5^M \\
I_6^M
\end{bmatrix}
\quad
\begin{matrix}
j = 1 \\
j = 2 \\
j = 3 \\
j = 4 \\
j = 5 \\
j = 6
\end{matrix}$$

Para o balanço de energia, a descrição matricial é um pouco mais complicada, pois compreende uma linha extra para englobar a variável “temperatura da parede” (W_{wall}). Os coeficientes A_1 , A_2 e A_3 devem ser calculados pelas equações 16, 17 e 18, utilizando os termos α , β e γ referentes às equações do balanço de massa (equações 10). Os termos independentes I_2 a I_5 são calculados conforme o lado direito da equação 15, cujos coeficientes A_1 , A_3 , A_4 e A_5 devem ser expressos pelas equações 16, 18, 19 e 20, utilizando os termos α , β e γ referentes às equações do balanço de massa (equações 10). Os termos independentes I_1 e I_6 são nulos (lado direito das equações 23 e 28). O termo independente I_{wall} refere-se ao lado direito da equação 29, calculado com o apoio das equações 32 e 33.

$$\begin{bmatrix}
1 & -1 & 0 & 0 & 0 & 0 & 0 \\
A_{1,j=2} & -A_{2,j=2} & A_{3,j=2} & 0 & 0 & 0 & 0 \\
0 & A_{1,j=3} & -A_{2,j=3} & A_{3,j=3} & 0 & 0 & 0 \\
0 & 0 & A_{1,j=4} & -A_{2,j=4} & A_{3,j=4} & 0 & 0 \\
0 & 0 & 0 & A_{1,j=5} & -A_{2,j=5} & A_{3,j=5} & 0 \\
0 & 0 & 0 & 0 & -2.K_R & (2.K_R + \eta) & -\eta \\
0 & 0 & 0 & 0 & 0 & \alpha_{WI} & -(\alpha_{WI} + \alpha_{WE}.G)
\end{bmatrix}
\times
\begin{bmatrix}
W_1^{n+1} \\
W_2^{n+1} \\
W_3^{n+1} \\
W_4^{n+1} \\
W_5^{n+1} \\
W_6^{n+1} \\
W_{wall}^{n+1}
\end{bmatrix}
=
\begin{bmatrix}
I_1^E \\
I_2^E \\
I_3^E \\
I_4^E \\
I_5^E \\
I_6^E \\
I_{wall}^E
\end{bmatrix}$$

2.5. Condição inicial

Na entrada do reator, em $n = 1$, é necessário definir os perfis radiais de temperatura e concentração. Essa condição pode ser dada por um perfil uniforme, onde:

$$C_j^1 = C_o \quad \text{ou} \quad X_j^1 = 1; \quad T_j^1 = T_o \quad \text{ou} \quad W_j^1 = 1; \quad \text{ou ainda} \quad Q_j^1 = 1, \quad \text{qualquer que seja "j"}.$$

ou ainda pode ser considerado um perfil qualquer, atribuindo-se um valor conhecido para cada ponto Q_j^1 .

Também é necessário definir o perfil para o passo “n-1”, que seria o passo “0”, imediatamente antes da entrada do reator, o que é fisicamente inconsistente, uma vez que essa secção ainda não pertence ao reator. Porém, pode-se considerar que a secção “0” é tão próxima de “n=1”, de tal modo que $Q_j^1 = Q_j^0$, qualquer que seja “j”. O erro associado a essa aproximação é tanto menor quanto maior o número de passos na direção “z”.

2.6. Desenvolvimento do método

Os cálculos são realizados iterativamente, de acordo com cada passo “n” na direção “z”. O algoritmo inicia-se em $n = 1$, gerando o sistema matricial para encontrar os valores de “Q” em $n = 2$.

Em cada iteração, a solução do sistema matricial fornece de uma só vez o perfil radial completo de concentração e de temperatura para o passo “n+1”, usando os valores conhecidos das variáveis nos passos “n” e “n-1”.

O algoritmo prossegue com os cálculos até que o passo $n = N_z + 1$ seja calculado, definindo-se o perfil radial de concentração e temperatura na saída do reator, que permite o cálculo da concentração e temperaturas médias na corrente de saída.

Se houver mais de uma reação química no processo estudado, pode-se estabelecer uma equação de balanço de massa para componentes representativos de cada reação, solucionando numericamente todas as equações diferenciais simultaneamente, aplicando o mesmo procedimento descrito acima.

2.7. Solução do sistema matricial

Os sistemas tridiagonais como o encontrado no algoritmo de Crank-Nicholson, podem ser solucionados pelo algoritmo de Thomas (Press et al., 1992), o qual requer menor número de operações que os sistemas tradicionais, como o método LU, por exemplo.

3. Conclusão

O método numérico de Crank-Nicholson foi utilizado nesse trabalho para solucionar numericamente as equações de balanço de massa e energia em um simulador criado para reator de leito fixo genérico.

Ao longo dos trabalhos desenvolvidos por Papes Filho (1999, 2001, 2007), foram executadas cerca de centenas de milhões de simulações, onde ficou comprovada a estabilidade do método numérico para uma grande variedade de problemas e verificou-se que a precisão do método é adequada, permitindo estimar com sucesso valores de conversão e seletividade.

Referências

- Crank, J. e Nicholson, P. ; Proc. Camb. Phil. Soc., v.43, p.50, 1947.
- Fogler, H.S.; "Elements of chemical reaction engineering", Prentice-Hall International, 2^a ed., New Jersey, p.71, 1992.
- Mihail, R. e Iordache, C.; Chem. Eng. Sci. V.31, p.83, 1976.
- Papes Filho, A.C.; "Projeto e operação de reatores auxiliados por computador". Campinas: Faculdade de Engenharia Química, Universidade Estadual de Campinas – UNICAMP, 1999. Dissertação de Mestrado.
- Papes Filho, A.C.; "Predição da resistência interna do papel utilizando redes neurais artificiais", O Papel, novembro 2001.
- Papes Filho, A.C.; "Projeto e operação de reatores auxiliados por computador". Campinas: Faculdade de Engenharia Química, Universidade Estadual de Campinas – UNICAMP, 2007. Tese de Doutorado.
- Press, W.H.; Flannery, B.P., Teukolsky, S.A. e Vetterling, W.T.; "Numerical Recipes", 1^a ed., Press Syndicate of the University of Cambridge, 1992.
- Villadesen, J. e Michelsen, M.; "Solution of differential equation models by polynomial approximation", Prentice-Hall, New York, 1978.
- Welty, J.R.; Wicks, C.E. e Wilson, R.E.; "Fundamentals of momentum, heat and mass transfer", John Wiley & Sons editor, 3rd ed., New York, 1984.

APÊNDICE C

PROJETO DE REATORES USANDO ENGENHARIA CO-CORRENTE

1. Introdução

O Apêndice C descreve uma aplicação do software de RNA desenvolvido nesse trabalho para a simulação de um reator de acetaldeído, por oxidação de etanol. Um sistema de softwares foi criado, interligando o simulador do reator com um “Sistema Inteligente” para guiar usuários menos experientes em ferramentas computacionais nas simulações (PAPES FILHO, 1999).

O sistema interligado de simulação baseia-se nos princípios da Engenharia Co-Corrente, área do conhecimento que estuda metodologias para realizar um conjunto de tarefas de forma integrada, de modo a atingir um determinado objetivo com máxima eficiência. Nesse tipo de atividade, há alta troca de informações entre os objetos das diferentes tarefas (quer sejam pessoas ou softwares), possibilitando a realização de atividades paralelas, obtendo-se o resultado desejado em menor tempo (MCGRAVY ET AL., 1996).

2. Desenvolvimento.

O desenvolvimento desse Apêndice é descrito no artigo intitulado “Concurrent Engineering Reactor Design”, apresentado a seguir, publicado no ESCAPE 15 (PAPES FILHO e MACIEL FILHO, 2005).

3. Conclusão

O Apêndice C apresenta o conceito de Engenharia Co-Corrente (Concurrent Engineering) aplicado a um reator de acetaldeído, também simulado com a aplicação de uma RNA para cálculo das taxas de reação. O conceito baseia-se na integração de diferentes “softwares” ou grupos de trabalho para que informações geradas por cada parte sejam agrupadas e harmonizadas, maximizando o desempenho do sistema e fornecendo resultados de forma ágil e prática. No caso apresentado, “softwares” de treinamento da RNA e simulador do reator de acetaldeído são integrados por um Sistema Especialista (Expert System) que coordena a entrada de dados do usuário, a simulação automática de diferentes casos e realiza cálculos termodinâmicos, apresentando resultados na forma de gráficos ou relatórios, facilmente compreensíveis pela equipe operacional da planta. O Sistema Especialista também emite alarmes e fornece sugestões de alterações nas condições

operacionais permitindo aos operadores agir rapidamente frente a situações inesperadas, mantendo a planta nas condições ideais de desempenho (conversão e seletividade) e segurança (limites de inflamabilidade). O conceito pode ser aplicado igualmente para uma planta de formaldeído, integrando-se os “softwares” desenvolvidos nessa tese (treinamento da RNA, simulação e otimização do reator de Prata) para auxiliar equipe operacional na sua utilização diária.

Concurrent Engineering Reactor Design

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Abstract

A system of softwares was developed in order to aid chemical reactor operation and design, as a tool to define operational policies and support process engineers. A C++ software, using artificial intelligence techniques, acts as an Expert System, guiding the user throughout reactor simulation and providing results in an easily comprehensible form. A Fortran software was used to simulate a reactor, including a neural network algorithm to estimate the rate of reaction. The C++ environment works together with the Fortran reactor simulator and a Fortran neural training software. This linked structure is considered part of the “concurrent engineering” study area. As a case study, the Expert System was applied to a fixed bed reactor for ethanol oxidation to acetaldehyde, over a Fe-Mo catalyst.

Keywords: Artificial intelligence, Concurrent engineering, Computer Aided Design, CAD, Neural networks.

1. Introduction

In modern chemical plants, process is controlled by a digital distributed system (DCS), under operator supervision. Recently, the role of these operators have shifted from direct responsibility for control to a supervision status, including identifying abnormal situations and determining the necessary actions to be taken when the process is not stable (like inevitable feedstock changes). For that, simulation tools are effective to help them modify rapidly and safely the process to the proper condition. Even when the system is normal (that is, operating at nominal conditions), a fail can occur, resulting in a shutdown or a risky situation. Early detection of such situations and quick diagnosis of faults require insight into the operational performance and anything that assists this task is clearly a competitive advantage and a useful tool.

Quantitative and qualitative techniques (such as property databases, optimisation procedures, steady state and dynamic simulation, operation training) have been available for some time. Recently, techniques from artificial intelligence field have been adapted to help in using these packages cooperatively and have been especially effective in speeding up the response time of operators (Wang et al., 1994).

This has encouraged the development of diagnostic expert systems for process evaluation: the computer acts as a specialist, analyzing data and showing conclusions about the simulation and the operation. This technique is part of the Artificial Intelligence field (Bugaeva et al., 1996).

A neural network was used in this work to predict the rate of reaction. It is an important tool for process simulation in cases where deterministic models are not available. The net must be trained for the first time, introducing it to a set of pairs [input, output]. An iterative adjustment of the *weights* occurs, trying to minimize the difference between calculated outputs and the actual outputs. Once the optimal weights were obtained, it is possible to predict outputs from new inputs (Bhagat, 1990; Wasserman, 1989).

2. Architecture of the Environment

The software tools developed for carrying out the simulation and its analysis include:

1. Neural network training software (Fortran);
2. Reactor simulator (Fortran);
3. Expert system (C++), responsible for the analysis of the simulation.

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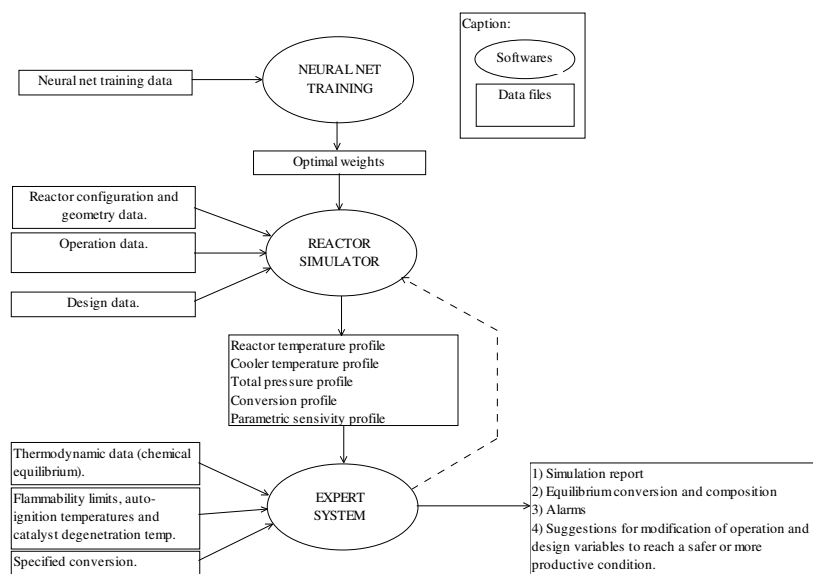


Figure 1. The environment structure

Figure 1 shows the linked system of softwares, and the information stream between them (the dashed line means that the expert system controls the reactor simulator). This crosslinked architecture allows an efficient execution of all softwares in order to simulate the system, including concepts of concurrent engineering. The techniques discussed on this paper can be applied to any system or equipment, but for computing ends, it was necessary to choose a case study to be implemented: the ethanol oxidation to acetaldehyde, under air stream, in a fixed-bed tubular reactor filled with Fe-Mo catalyst. The chemical equation is showed in Eq.1:



3. Reactor Simulator: the core of the system

The reactor simulator is based on mass, energy and momentum balance differential equations, solved simultaneously by fourth-order Runge-Kutta numerical method.

Input data involve operating and design parameters, like inlet feed temperature, inlet cooler temperature, inlet pressure, feed flow, cooler flow, air to ethanol molar ratio, reactor length, tube diameter, type of configuration (concurrent or countercurrent), catalyst particle diameter and catalyst density.

Inlet temperature, cooler temperature, feed flow and cooler flow were chosen as operation variables. Reactor length, tube diameter, particle diameter and inlet pressure were chosen as design variables. Simulation outputs are reactor temperature, coolant temperature, conversion, total pressure and parametric sensitivity profiles.

The parametric sensitivity, as defined by Rodrigues (1994), measures the variation of reactor temperature, as a response for a given variation in a selected inlet variable (coolant inlet temperature). This parameter gives an indication about the stability of the reactor, and allows the detection of unsafe conditions, helping to avoid system runaway.

Reaction rate is calculated by a neural network sub-routine, using the weights determined by the training software. The input variables to the net are: conversion, temperature, pressure and feed composition (air to ethanol molar ratio). The output of the net is the rate of reaction. The neural net approach was used to allow the software to be generic for cases when the operation data are available but the reaction rate is not. The net was trained with data used in previous work (Maciel Filho, 1985). Input data range from 0 to 1.0 for conversion, from 463 to 679 K for temperature and from 1.8 to 2.2 atm for pressure.

4. Expert System

The expert system is a C++ software developed to analyze reactor data simulation and eventually it calls the simulator itself. The reports emitted help the operator in making decisions and previewing dangerous situations.

This software is structured in modules, each one with a particular function:

Chemical equilibrium module: computes equilibrium conversion for the chemical reaction studied, using parameters given by the user: stoichiometric coefficients, enthalpy of formation of the species, Gibbs free energy of species, polynomial equation for heat capacity (Sandler, 1989). Other information is given by simulator, like mean reactor temperature and feed composition. The software calculates the equilibrium conversion and the equilibrium stream composition at the end of reactor. Finally, the system shows how far the reactor is from the maximum conversion.

Operational variables study: carries out a study of the influence of operational variables on process variables. The inlet feed temperature, feed flow and cooler flow were chosen as operational variables. The process variables were maximum reactor temperature (hot spot), mean reactor temperature, final conversion, pressure drop and maximum parametric sensitivity.

Alarms: deals with extreme or risky situations. Some information must be given by user, as specified conversion, catalyst degenerating temperature, flammable species, auto-ignition temperature of species, flammability limits, maximum pressure drop.

Once abnormal situation is detected, the expert system pops an alarm and it suggests a new condition to avoid the problem or risky situation.

Design variable study: performs a study about the influence of design variables on process variables, in order to help designing this type of equipment. The reactor length, tube inside diameter, catalyst particle diameter and inlet total pressure were chosen as design variables. The process variables are: maximum reactor temperature (hot spot), mean reactor temperature, final conversion, pressure drop and maximum parametric sensitivity.

Condition of non-degeneration of catalyst: calculates the values of operational variables to which the catalyst degenerating temperature is not overcome. In this case, the maximum temperature in reactor is below the catalyst degenerating temperature (281 °C). Process variables at this condition are also calculated.

5. Results and Discussion

The system of softwares was executed for an example condition in order to depict its features and potentialities. At first, the chemical equilibrium module is activated, computing data given in Table 1. Note that acetaldehyde production in the simulated case is very close to equilibrium condition. This is in fact a possible operation condition as shown experimentally by Maciel Filho (1985) and discussed in a scale up of the process studied by Domingues and Maciel Filho (1992).

The next step is to report process variables at simulated condition, showed in Table 2.

Table 1. Chemical equilibrium data

Parameter	Value	Unit
Equilibrium conversion	0.999992	
Specified conversion	0.99	
Simulated conversion	0.9994	
Acetaldehyde production: Equilibrium condition	2.559	moles/h
Simulated condition	2.533	moles/h

Table 2. Process variables

Parameter	Value	Unit
Mean temperature	228	°C
Maximum temperature	328	°C
Final conversion	0.9994	
Pressure drop	0.025	Atm
Maximum parametric sensitivity	52	

The alarm module is then executed, giving the following warnings:

Alarm 1: auto-ignition temperature of acetaldehyde (130 °C) was overcome, but there is no explosion risk, once its concentration is outside flammability limits (4,0 - 60,0 %);

Alarm 2: reactor temperature is too high, causing catalyst degeneration. Immediately, the expert system calls the “non-degeneration condition” module, and suggests to lower inlet feed temperature to 198 °C (maximum possible value), maintaining the original value of the other parameters. The module also advises that at this condition, the reactor temperature in any point will be smaller than catalyst degeneration temperature, but the final conversion will decrease to 0.92.

Pressure drop at simulated case is smaller than the limit value (0.2 atm), and final conversion is above the specified one (0.99). No alarms are emitted in these cases.

The “operational variables study” module generates 15 graphs, correlating maximum temperature, mean temperature, final conversion, pressure drop and maximum parametric sensitivity to inlet feed temperature, feed flow and cooler flow. Figure 2 shows some of these graphs related to feed flow study.

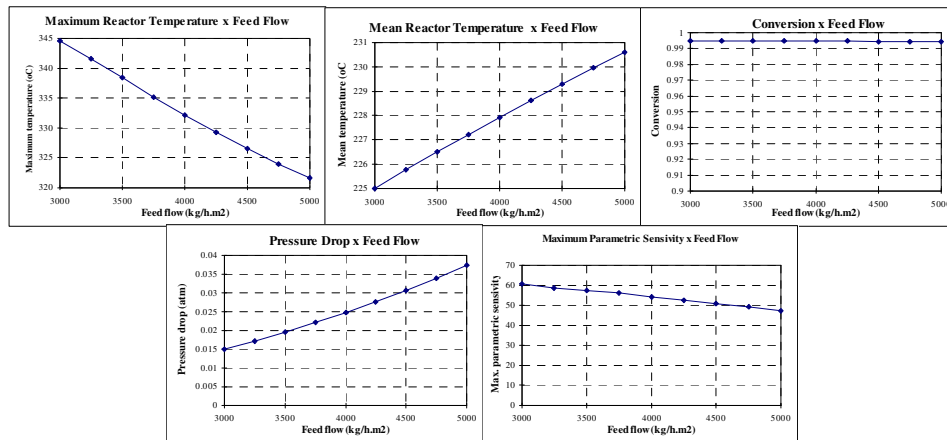


Figure 2. Operational variables study graphs.

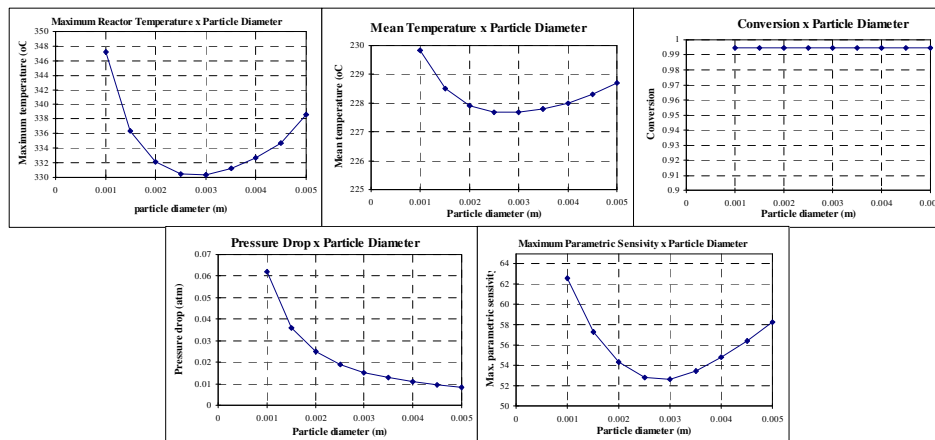


Figure 3. Design variables study graphs

Based on this study, the operator can foresee what is going to happen in case of some change in operational variables and take an action to maintain the process at an optimum condition or avoid an unsafe operation. In this case, the parametric sensitivity will raise from 54 to 60, indicating that reactor temperature will be less stable.

The “design variables study” module generates 17 graphs, correlating maximum temperature, mean temperature, final conversion, pressure drop and maximum parametric sensitivity to tube diameter, catalyst particle diameter, inlet total pressure, plus a reactor length graph and a partial pressure profile of all compounds in reactor. Figure 3 shows some of these graphs related to particle Diameter.

The goal of these graphs is to aid designing this type of equipment, looking for optimal operational conditions. For example, let us suppose that the task is to determine the best catalyst particle diameter to be used in the reactor. After having executed the simulation, studying particle size influence in the range from 1 mm to 5 mm, the graphs in figure 3 are available to take such decision. The maximum reactor temperature, mean reactor temperature and maximum parametric sensitivity graphs show that particle diameter from 2.5 to 3.0 leads to a highest heat transfer and gives the reactor more stability.

Having this information in hand, design engineer does not need to ask for experimental work or may reduce the number of experimental runs in order to decide which is the best particle size to be used.

6. Concluding Remarks

A system of softwares was presented, based on concurrent engineering principles, in order to perform an intelligent simulation of fixed-bed chemical reactors. A C++ environment was developed as a tool for aiding plant operators in making rapid decisions to determine new operating conditions when process is changed and also for supporting engineers to design more effective equipments and determine the best operational policy. Neural nets algorithms were included in a FORTRAN reactor simulator to estimate the rate of reaction, at given conversion, temperature and pressure. Comparison between neural nets and the rate model showed good agreement (Papes, 1994). The neural training process was carried out by a FORTRAN software also developed in this work.

As an example, the system of softwares was applied to the reaction of ethanol oxidation to acetaldehyde, over Fe-Mo catalyst, in a tubular reactor. Some of the graphs generated by the system were showed, illustrating the benefits of this tool in assisting operation and design of chemical reactors. Limitations of space have not permitted other examples to be given but they were equally successful (Papes, 1999, 2004).

References

- Bhagat, P., 1990, Chemical Engineering Progress. August, 55.
- Bugaeva, L.M., Y.A. Bezosik., G.A. Statjukha and A.A. Kvitka, 1996, Computers Chem. Engng. 20, S401-S406.
- Maciel Filho, R. and A. Domingues, 1992, Chem. Engng. Sci. 47, i.9, June, 2571.
- Maciel Filho, R., 1985, Internal report on the catalytic synthesis of acetaldehyde by oxidation of ethanol. State University of Campinas, Sao Paulo, Brazil.
- Papes Filho, A. C., 2004, Doctor Thesis. State University of Campinas, Sao Paulo, Brazil.
- Papes Filho, A. C., 1999, Computer aided operation and design, Master Thesis. State University of Campinas, Sao Paulo, Brazil.
- Rodrigues, V.F., 1994, Stability criteria for fixed bed reactors, Master Thesis. State University of Campinas, Sao Paulo, Brazil.
- Sandler, S.I., 1989, Chemical Engineering Thermodynamics. Wiley & Sons, 2nd. Ed.
- Wang, X.Z., M.L. Lu and C. McGravy, 1994, ICHIME Symposium series. 133, 33.
- Wasserman, P.D., 1989, Neural Computing: Theory and Practice. Van Nostrand Reinhold.

APÊNDICE D

EQUAÇÕES, PROPRIEDADES E DADOS DE BASE

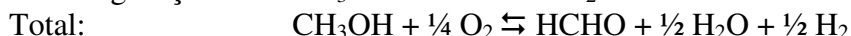
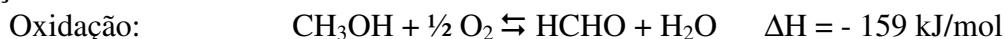
1. Introdução

O apêndice D reúne as principais equações utilizadas nessa tese, bem como as propriedades físicas e termodinâmicas e os dados de base mais relevantes.

2. Desenvolvimento.

2.1. Equações químicas para o processo prata

Formação do formaldeído:



Combustão do formaldeído:



Decomposição do formaldeído:



2.2. Equação diferencial do balanço de massa para o reator de Prata (leito-fix)

$$D_L \cdot \frac{\partial^2 C}{\partial z^2} + D_R \cdot \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial C}{\partial r} \right) - V_z \cdot \frac{\partial C}{\partial z} + v_A \cdot R_V = 0$$

“C”: concentração da substância (kg/m^3);

“r”: distância em ralação à linha central do reator (m);

“z”: distância da entrada do reator (m);

“ D_L ”: coeficiente de difusão axial (m^2/s);

“ D_R ”: coeficiente de difusão radial (m^2/s);

“ V_z ”: velocidade axial (m/s);

“ v_A ”: coeficiente estequiométrico para a substância estudada (adimensional);

“ R_V ”: taxa de reação por volume ($\text{kg/m}^3 \cdot \text{s}$).

2.3. Cálculo do número de moles de cada espécie ao longo do reator

Formaldeído: $n_1 = n_1^0 + \xi_{\text{HCHO}} - \xi_{\text{CO}_2} - \xi_{\text{CO}}$

Dióxido de carbono: $n_2 = n_2^0 + \xi_{\text{CO}_2}$

Monóxido de carbono: $n_3 = n_3^0 + \xi_{\text{CO}}$

Metanol: $n_4 = n_4^0 - \xi_{\text{HCHO}}$

Oxigênio: $n_5 = n_5^0 - 0.25 \cdot \xi_{\text{HCHO}} - \xi_{\text{CO}_2}$

Água: $n_6 = n_6^0 + 0.5 \cdot \xi_{\text{HCHO}} + \xi_{\text{CO}_2}$

Hidrogênio: $n_7 = n_7^0 + 0.5 \cdot \xi_{\text{HCHO}} + \xi_{\text{CO}}$

Nitrogênio: $n_8 = n_8^0$

- “ n_i ”:
 “ n_i^0 ”:
 “ ξ_{HCHO} ”:
 “ ξ_{CO_2} ”:
 “ ξ_{CO} ”
- número de moles da substância “ i ” em um certo ponto do reator;
 número de moles inicial para a substância “ i ”;
 grau de avanço da reação de formação do formaldeído (kmol/h);
 grau de avanço da reação de combustão do formaldeído (kmol/h);
 grau de avanço da reação de decomposição do formaldeído (kmol/h).

n_1^0 , n_2^0 , n_3^0 e n_7^0 geralmente são iguais a zero.

n_4^0 e n_6^0 equivalem à alimentação molar de metanol e água, respectivamente, no reator.

n_5^0 equivale à alimentação molar de ar no reator, multiplicado por 21%.

n_8^0 equivale à alimentação molar de ar no reator, multiplicado por 79%.

2.4. Cálculo do grau de avanço das reações

“ ξ_{HCHO} ” é calculado com base no número de moles de formaldeído formados desde a entrada até um determinado ponto do reator, fornecido a partir da solução numérica da equação de balanço de massa.

$$\xi_{HCHO} = X_{HCHO} \cdot C_o \cdot \frac{V_g}{\rho}$$

“ C_o ”:
 concentração de metanol na entrada do reator (kmol/m³) – fator de adimensionalização das concentrações.

“ X_{HCHO} ”:
 Concentração adimensional em certa posição do reator, dada pela solução do método numérico.

“ V_g/ρ ”:
 Vazão volumétrica total em certa posição do reator (m³/h).

“ ξ_{CO_2} ” e “ ξ_{CO} ” são calculados da mesma maneira, com base no número de moles de dióxido de carbono e monóxido de carbono, respectivamente, formados desde a entrada até um determinado ponto do reator.

$$\xi_{CO_2} = X_{CO_2} \cdot C_o \cdot \frac{V_g}{\rho}$$

$$\xi_{CO} = X_{CO} \cdot C_o \cdot \frac{V_g}{\rho}$$

2.5. Cálculo das pressões parciais

As pressões parciais dos componentes são calculadas com base nas frações molares (y_i) e na pressão total em um determinado ponto do reator (P_T).

Frações molares:

$$y_i = \frac{n_i}{\sum_{i=1}^8 n_i}$$

Pressões parciais:

$$P_i = y_i \cdot P_T$$

2.6. Cálculo da conversão e seletividades

Conversão de metanol:
$$\text{Conversão} = \frac{\xi_{HCHO}}{n_4^o}$$

Seletividade para formaldeído:
$$S_{HCHO} = \frac{\xi_{HCHO} - \xi_{CO_2} - \xi_{CO}}{\xi_{HCHO}}$$

Seletividade para CO₂:
$$S_{CO_2} = \frac{\xi_{CO_2}}{\xi_{HCHO}}$$

Seletividade para CO:
$$S_{CO} = \frac{\xi_{CO}}{\xi_{HCHO}}$$

Rendimento para formaldeído:
$$\text{Yield HCHO} = S_{HCHO} \times \text{Conversão}$$

Rendimento para CO₂:
$$\text{Yield CO}_2 = S_{CO_2} \times \text{Conversão}$$

Rendimento para CO:
$$\text{Yield CO} = S_{CO} \times \text{Conversão}$$

2.7. Propriedades físicas

2.7.1. Viscosidade

2.7.1.1. Viscosidade das substâncias puras

Substância	Equação	Faixa de validade
Metanol	$\mu = 3,0663E-7 * (T^{0,69655}) / (1 + 205/T)$	240 a 1000 K
Oxigênio	$\mu = 1,101E-6 * T^{0,5634} / (1 + 96,3/T)$	54,35 a 1500 K
Água	$\mu = 1,7851E-7 * T^{0,813} / (1 + 304,72/T)$	371,3 a 1073 K
Nitrogênio	$\mu = 6,5592E-7 * T^{0,6081} / (1 + 54,714/T)$	63,15 a 1970 K
Formaldeído	$\mu = 4,758E-7 * (T^{0,6405}) / (1 + 161,7/T)$	181,1 a 1000 K
Hidrogênio	$\mu = 1,8704E-7 * (T^{0,67896}) / (1 + 1,35/T + 113,24/T^2)$	20,27 to 1800 K
CO ₂	$\mu = 2,148E-6 * (T^{0,46}) / (1 + 290/T)$	194,7 a 1500 K
CO ⁽¹⁾	$\mu = 6,161E-7 * (T^{0,614155}) / (1 + 37/T)$	273 a 1173 K

Notas:

Valores de "T" em K e "μ" em Pa.s.

(1) Correlação sobre valores extraídos Da Fig.3.44 de PERRY E CHILTON (1980).

2.7.1.2. Viscosidade da mistura

Método de Wilke (REID ET AL., 1987)

$$\mu_{MIX} = \frac{\sum_{i=1}^N y_i \cdot \mu_i}{\sum_{j=1}^N y_j \cdot \phi_{ij}}$$

$$\phi_{ij} = \frac{[1 + (\mu_i / \mu_j)^{1/2} \cdot (M_j \cdot M_i)^{1/4}]^2}{[8 \cdot (1 + M_i / M_j)]^{1/2}}$$

μ_{MIX} : viscosidade da mistura;
 μ_i : viscosidade do componente “i”;
 y_i : fração molar do componente “i”;
 M_i : peso molecular do componente “i”.

2.7.2. Condutividade térmica

2.7.2.1. Condutividade térmica das substâncias puras

Substância	Equação	Faixa validade
Metanol	$k = -7,797E-3 + 4,167E-5.T + 1,214E-7.T^2 - 5,184E-11.T^3$	273 a 1270 K
Oxigênio	$k = 0,00044994 * T^{0,7456} / (1 + 56,699/T)$	80 a 2000 K
Água	$k = 6,9295E-5 * T^{1,1254} / (1 + 847,68/T - 150000/T^2)$	373,1 a 1073 K
Nitrogênio	$k = 0,00033143 * T^{0,7722} / (1 + 16,323/T + 373,72/T^2)$	63,15 a 2000 K
Formaldeído	$k = 44,847 * (T^{-0,7096}) / (1 - 3493,5/T + 5,3532E6/T^2)$	254,1 a 994 K
Hidrogênio	$k = 8,099E-3 + 6,689E-4.T - 4,158E-7.T^2 + 1,562E-10.T^3$	115 to 1470 K
CO ₂	$k = 3,69 * (T^{-0,3838}) / (1 + 964/T + 1,86E6/T^2)$	194,7 a 1500 K
CO	$k = 5,067E-4 + 9,125E-5.T - 3,524E-8.T^2 + 8,199E-12.T^3$	115 a 1670 K

Nota: Valores de “T” em K e “k” em W/m.K. (REID ET AL., 1987)

2.7.2.2. Condutividade térmica da mistura

Método de Wassiljewa modificado por Mason e Saxena (REID ET AL., 1987)

$$k_{MIX} = \frac{\sum_{i=1}^N y_i \cdot k_i}{\sum_{j=1}^N y_j \cdot A_{ij}}$$

k_{MIX} : condutividade térmica da mistura;
 k_i : condutividade térmica do componente “i”;
 $A_{ij} = \phi_{ij}$
 $A_{ii} = 1$

2.7.3. Capacidade calorífica

2.7.3.1. Capacidade calorífica das substâncias puras

Equação para cálculo: $C_p = a + b.T + c.T^2 + d.T^3$

Espécie	Coeficientes			
	a	b	c	d
CO ₂	5.316	1.429E-02	-8.362E-06	1.784E-09
CO	6.726	4.001E-04	1.283E-06	-5.307E-10
H ₂ O	7.700	4.594E-04	2.021E-06	-8.587E-10
H ₂	6.952	-4.576E-04	9.563E-07	-2.079E-10
O ₂	6.085	3.631E-03	-1.709E-06	3.133E-10
HCHO	5.447	9.739E-03	1.703E-06	-2.078E-09
CH ₃ OH	4.550	2.186E-02	-2.910E-06	-1.920E-09

Nota: Valores de “T” em K e “C_p” em cal/mol.k

2.7.3.2. Capacidade calorífica da mistura

$$C_{P-MIX} = \sum_{i=1}^8 y_i \cdot C_{P,i}$$

2.7.4. Coeficiente de difusão

2.7.4.1. Método rigoroso de estimativa do coeficiente de difusão

Correlação de Hirschfelder, Bird e Spotz (1945)

$$D_{AB} = \frac{b.T^{1.5} \cdot \left[\left(\frac{1}{M_A} \right) + \left(\frac{1}{M_B} \right) \right]^{0.5}}{P \cdot \sigma_{AB}^2 \cdot \Omega_D}$$

D_{AB} : Coeficiente de difusão da espécie “A” na espécie “B” (m²/s)

T: Temperatura (K)

M_i : Peso molecular (g/mol)

P: Pressão do sistema (atm)

O termo “b” é um fator de proporcionalidade relacionado à constante de Boltzmann e definido como 0,001858 (WILKE E LEE, 1953).

σ_{AB} é chamado de diâmetro de colisão, calculado como a média aritmética dos diâmetros de colisão das substâncias “A” e “B”, definidas pela correlação de Papes-Cremasco (1995):

$$\sigma_i = (0,781 - 0,02885 \cdot \omega) \left(\frac{V_C}{1 + 2,4 \cdot \delta^2} \right)^{1/3}$$

V_C : Volume crítico (cm³/gmol)

ω : Fator acêntrico

O fator δ é calculado pela equação de Papes-Cremasco (1995):

$$\delta_i = \frac{3,6 \cdot 10^3 \cdot \mu_p^2 \cdot P_C}{(0,7915 + 0,1693 \cdot \omega) \cdot (2,3551 - 0,087 \cdot \omega)^3 \cdot T_C^2}$$

μ_p : Momento dipolar da espécie “i” (debyes)

P_C : Pressão crítica (atm)

T_C : Temperatura crítica (K)

O termo Ω_D é chamado de integral de colisão, calculado pela equação de Nuefeld, Janzen e Aziz (1972), corrigida pela correlação de Brokaw (1969).

$$\Omega_D = \frac{1,06036}{TR^2} + \frac{0,15610}{e^{0,47635 \cdot TR}} + \frac{1,03587}{e^{1,52960 \cdot TR}} + \frac{1,76474}{e^{3,89411 \cdot TR}} + \frac{0,196 \cdot \delta_{AB}^2}{TR}$$

Com $\delta_{AB} = \sqrt{\delta_A \cdot \delta_B}$

TR é a temperatura reduzida, calculada pela equação:

$$TR = \frac{T}{\varepsilon_{AB} / k}$$

Onde

“T” é a temperatura em K

$$\varepsilon_{AB} / k = \sqrt{\varepsilon_A / k + \varepsilon_B / k}$$

O termo “ ε_i/k ” é calculado pela correlação de Papes-Cremasco (1995):

$$\varepsilon_i / k = (0,7915 + 0,1693 \cdot \omega) \cdot (1 + \delta_i^2) T_C$$

2.7.4.2. Método teórico de estimativa do coeficiente de difusão

Chapman e Enskog desenvolveram a seguinte equação solucionando a equação de Boltzmann:

$$D_{AB} = \frac{3}{16} \cdot \frac{(4\pi kT / M_{AB})^{1/2}}{n \cdot \pi \cdot \sigma_{AB}^2 \cdot \Omega_D} f_D$$

Onde

$$M_{AB} = 2 \cdot \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{-1}$$

“n” é o número densidade de moléculas na mistura

“k” é a constante de Boltzmann

“T” é a temperatura em K

“ D_{AB} ” é o coeficiente de difusão em cm^2/s

“ f_D ” é um termo de correção entre 1,0 e 1,02

2.7.4.3. Método empírico simplificado de estimativa do coeficiente de difusão

Equação de Wilke e Lee:

$$D_{AB} = \frac{[3,03 - (0,98 / M_{AB}^{0,5})] 10^{-3} \cdot T^{1,5}}{P \cdot M_{AB}^{0,5} \sigma_{AB}^2 \cdot \Omega_D} f_D$$

Onde

“ M_{AB} ” tem a mesma definição acima

“P” é a pressão em bar

“ σ_{AB} ” é a média aritmética dos valores individuais para as espécies:

$$\sigma_i = 1,18 \cdot V_b^{1/3}$$

“ V_b ” é o volume molar líquido (cm^3/mol)

Para o cálculo de Ω_D utiliza-se a expressão:

$$\frac{\varepsilon}{k} = 1,15.T_b$$

“T_b” é o ponto normal de ebulição (K).

2.8. Dados de processo

A tabela a seguir apresenta os dados de processo extraídos de uma planta Prata industrial em operação, de médio porte, utilizados para o treinamento da RNA nos Capítulos 5 e 6.

Temperatura (oC)	Ar (kg/h)	Solução (kg/h)	Água (%)	Conversão	Seletiv. HCHO	Seletiv. CO2	Seletiv. CO
630,0	5600	4530	0,09	0,850	0,876	0,124	0,000
630,7	5151	3438	0,09	0,961	0,851	0,149	0,000
629,7	5684	4439	0,09	0,870	0,874	0,126	0,000
619,7	6032	4037	0,09	0,940	0,869	0,131	0,000
629,5	6363	4247	0,09	0,947	0,874	0,126	0,000
689,7	6042	4081	0,09	0,989	0,845	0,124	0,031
630,1	5848	4126	0,14	0,941	0,880	0,120	0,000
629,7	5756	4158	0,16	0,936	0,884	0,116	0,000
629,7	5778	4328	0,09	0,910	0,872	0,128	0,000
720,1	6062	4047	0,09	1,000	0,500	0,114	0,386
629,8	5935	4093	0,12	0,946	0,875	0,126	0,000
630,2	5952	4155	0,09	0,951	0,870	0,130	0,000
630,0	5999	4045	0,10	0,949	0,870	0,130	0,000
630,8	5454	3641	0,09	0,957	0,859	0,141	0,000
629,8	7878	5259	0,09	0,927	0,8930	0,107	0,000
629,7	5803	4142	0,15	0,939	0,882	0,118	0,000
581,0	6021	4046	0,09	0,900	0,840	0,160	0,000
629,5	6154	4017	0,07	0,954	0,866	0,134	0,000
599,2	6083	4042	0,09	0,920	0,857	0,143	0,000
630,1	7272	4854	0,09	0,936	0,884	0,116	0,000
669,5	6030	3999	0,09	0,975	0,861	0,129	0,010
630,1	4545	3034	0,09	0,972	0,839	0,161	0,000
630,2	6196	4001	0,06	0,957	0,865	0,135	0,000
630,0	6398	3697	0,09	0,980	0,818	0,172	0,010
679,3	6108	4000	0,09	0,980	0,853	0,127	0,020
629,8	6638	3442	0,09	0,990	0,780	0,200	0,020
631,0	4242	2831	0,09	0,975	0,836	0,164	0,000
715,3	6102	4023	0,09	1,000	0,639	0,116	0,245
630,4	6270	3964	0,04	0,961	0,862	0,138	0,000
629,6	5486	4622	0,09	0,820	0,878	0,122	0,000
710,2	6094	4059	0,09	1,000	0,740	0,120	0,140
629,9	5662	4190	0,18	0,930	0,888	0,112	0,000
629,7	7575	5056	0,09	0,931	0,889	0,111	0,000
630,1	5417	4692	0,09	0,800	0,880	0,120	0,000
629,7	6666	4450	0,09	0,944	0,876	0,124	0,000
630,1	5757	3843	0,09	0,952	0,867	0,134	0,000
631,0	6236	3984	0,05	0,958	0,863	0,137	0,000
611,0	6036	4029	0,09	0,930	0,861	0,139	0,000
629,2	5892	4110	0,13	0,942	0,877	0,123	0,000

650,3	6031	4079	0,09	0,960	0,867	0,123	0,010
589,5	6106	4075	0,09	0,910	0,851	0,149	0,000
630,0	5572	4227	0,20	0,924	0,893	0,107	0,000
629,7	4848	3236	0,09	0,966	0,844	0,156	0,000
629,8	6969	4652	0,09	0,940	0,881	0,119	0,000
630,8	6114	4033	0,08	0,951	0,870	0,130	0,000
629,2	6189	3911	0,09	0,971	0,843	0,157	0,000
700,9	6033	4091	0,09	1,000	0,820	0,120	0,060
639,9	6021	4003	0,09	0,955	0,869	0,131	0,000
630,8	6097	4041	0,09	0,950	0,870	0,130	0,000
659,1	6050	4047	0,09	0,969	0,867	0,123	0,010

As taxas de reação nas condições acima variaram no intervalo apresentado a seguir.

Taxa de formação de formaldeído:	$4,1 \cdot 10^0 - 2,9 \cdot 10^5$ kmol/m ³ .h
Taxa de combustão de formaldeído:	$1,2 \cdot 10^3 - 9,0 \cdot 10^3$ kmol/m ³ .h
Taxa de decomposição do formaldeído:	$2,9 \cdot 10^{-2} - 1,7 \cdot 10^4$ kmol/m ³ .h

Os gráficos comparativos entre as taxas de reação calculadas e as taxas experimentais, apresentadas no Capítulos 4 na forma normalizada, variaram em termos absolutos nas faixas mostradas acima.

2.9. Dados sobre o reator de Prata industrial utilizado como referência nessa Tese.

Condições operacionais de referência:

Temperatura do leito:	630 °C
Pressão:	1,2 atm
Vazão de ar:	6060 kg/h
Vazão de metanol:	3681 kg/h
Vazão de água:	364 kg/h
Conversão:	94,0 %
Seletividade formaldeído:	86,8 %
Seletividade CO ₂ :	13,2 %
Seletividade CO:	0,0 %

Condições de projeto:

Diâmetro do reator:	1,5 m
Comprimento do leito:	20 mm
Diâmetro médio do catalisador:	0,6 mm
Catalisador:	Prata eletrolítica

2.10. Pesos da RNA treinados para cálculo das taxas de reação, baseados nos dados de WATERHOUSE ET AL (2004b)

NEURÔNIOS DA CAMADA DE ENTRADA											
1	2	3	4	5	6	7	8	9	Bias		
1	-2,029E+00	-1,105E-02	-1,052E+00	3,962E-02	3,776E-01	-2,432E+01	6,598E-01	-3,709E-01	-2,151E+01	8,683E-02	
2	-5,531E-01	-9,622E-02	6,304E+01	4,238E+00	-7,828E+00	-6,184E-02	-7,631E+00	2,034E-01	-3,414E+00	4,552E-01	
3	7,044E-01	2,513E+00	9,905E+00	-2,016E+00	-1,055E-01	-5,081E+00	-8,553E+00	-6,477E-01	2,685E-01	-5,612E+00	
4	-5,738E-02	1,931E-02	1,031E+00	1,142E+01	-1,921E+00	-9,280E-01	-3,533E-02	-1,116E+01	-3,951E+01	-3,586E-01	
5	1,021E-01	1,132E-01	-3,986E-01	-1,084E+00	-4,331E-01	2,136E+01	-8,344E-01	2,956E+00	5,440E+00	-2,750E-02	
6	-6,431E+00	8,070E-02	7,941E-01	-4,452E-01	-1,976E-01	-7,547E-01	5,461E+00	-7,367E+00	-3,177E+00	2,104E-01	
7	1,412E+01	2,683E-02	4,886E-01	-1,105E-02	-2,049E-01	-5,260E-01	-3,370E+01	-7,916E-02	-4,106E-01	1,349E-01	
8	4,308E-01	3,541E+01	-1,607E+00	-3,298E-02	3,772E-02	3,747E-01	-1,161E+00	-1,465E-01	-6,628E-01	-1,591E+00	
9	6,578E-01	9,400E-01	8,149E+00	5,835E+00	-2,101E+01	2,213E-02	-3,859E-01	1,590E-03	2,241E-03	3,372E+00	
10	-3,656E+00	-1,142E-01	-9,832E-03	-2,502E-02	2,242E+00	-1,320E-01	2,142E-01	8,730E-03	3,025E-02	-3,711E-02	
11	-1,744E+00	-7,650E+00	5,478E+00	-8,798E-02	-3,046E-02	-4,140E+00	-5,491E-02	-8,642E-02	4,266E+00	2,006E+01	
12	2,121E-01	-1,329E+01	-9,642E+00	-1,863E-01	-4,583E-01	7,611E+00	6,726E+00	-4,365E+00	-7,771E-01	-4,855E-01	

NEURÔNIOS DA CAMADA DE SAÍDA			
1	2	3	
1	3,011E+00	1,689E+01	1,592E+00
2	1,693E+00	-1,131E-03	-1,224E+01
3	-2,096E-01	-5,224E-02	-4,591E-02
4	3,292E-01	-3,654E-02	2,096E+00
5	-2,560E+00	-1,036E+00	-4,203E+00
6	-1,446E+00	-3,297E+00	2,476E+00
7	5,709E-01	5,658E+00	9,409E+00
8	-1,351E+00	-9,455E-02	-1,639E-01
9	7,457E-01	3,836E+00	-2,040E-01
10	-3,284E-03	1,823E+01	9,648E-02
11	2,634E-01	-4,191E+00	4,733E-02
12	-6,932E-02	1,761E+01	1,352E+01
Bias	-1,007E+00	-5,769E+00	-5,625E-01

2.11. Fontes para obtenção de softwares

2.11.1. Redes Neurais Artificiais

- a) UNICAMP – Faculdade de Engenharia Química
 - Prof. Dr. Rubens Maciel Filho (maciel@feq.unicamp.br)
 - Antonio Carlos Papes Filho (acpapes@terra.com.br)
- b) www.din.uem.br/ia/neurais
- c) www.cs.bgu.ac.il/~omri/NNUGA/README
- d) Statistica – Statsoft (faleconosco@statsoft.com.br)

2.11.2. Algoritmo Genético

- a) UNICAMP – Faculdade de Engenharia Química
 - Prof. Dr. Rubens Maciel Filho (maciel@feq.unicamp.br)
 - Antonio Carlos Papes Filho (acpapes@terra.com.br)
- b) David Carroll: Department of Aeronautical and Astronautical Engineering
 - University of Illinois
 - www.staff.uiuc.edu/~carroll/gatips.html
- c) www.csc.fi/math_topics/Movies/GA.html
- d) <http://chemdiv-www.nrl.navy.mil/6110/sensors/chemometrics/practga.html>
- e) www.hao.ucar.edu/public/research/si/pikaia/pikaia.html
- f) www.geocities.com/CapeCanaveral/Launchpad/7651/gainita.htm

REFERÊNCIAS BIBLIOGRÁFICAS

ABIQUIM, Associação Brasileira da Indústria Química. Diretório da indústria química brasileira, www.abiquim.org.br, 2006.

ABRAF, Associação brasileira dos fabricantes de formaldeído. Relatório: Panorama da cadeia produtiva, www.abraf.com.br, 2004.

ANDREASEN, A., LYNNGAARD, H., STEGELMANN, C., STOLTZE, P. A microkinetic model of the methanol oxidation over silver. *Surface Science*, v.544, p.5-23, 2003.

ANDREASEN, A., LYNNGAARD, H., STEGELMANN, C., STOLTZE, P. Simplified kinetic models of methanol oxidation on silver. *Applied Catalysis A: General*, 289, pp.267-273, 2005.

BARTEAU, M., MADIX, R.J. *Surface Science*, 40, p.108, 1984.

BAZILIO, C.A., THOMAS, W.J., ULLAH, U., HAYES, K.E. The catalytic oxidation of methanol. *Proc. R. Soc. Lond. A*, 399, pp.181-194, 1985.

BELMAR, C.Y.C. *Analysis y modelacion del reactor de formaldehido de quimicos Coronel*. Concepción: Universidade de Concepcion, Chile, Informe de habilitacion profesional, 1995.

BERNE, R. M., LEVY, M. N. *Fisiologia*. Rio de Janeiro: Editora Guanabara, 2^a ed, 1990.

BHAGAT, P. An Introduction to Neural Nets. *Chemical Engineering Progress*, p.55, agosto 1990.

BHATTACHARYYA, S.K., NAG, N.K., GANGULY, N.D. Kinetics of vapor-phase oxidation of methanol on reduced silver catalyst. *Journal of Catalysis*, v.23, i.2, pp.158-167, 1971.

BOGGS, P.T., TOLLE, J.W. Sequential quadratic programming. *Acta Numerica*, pp. 1-52, 1996.

BOX, G.E.P, HUNTER, J.S. *Statistics for experimenters*. New York: Wiley and Sons, 1^a ed, 1978.

BROKAW, R.S. *Ind. Eng. Chem. Proc. Design and Dev.*, 8, 2, p.240, 1969.

- BUGAEVA, L.M. ET AL. An application of expert system to choice, simulation and development of gases purification process. *Computers and Chemical Engineering*, v.20, S401-S406, 1996.
- CANCHO, J.C., SANCHEZ, A.M.E., TENA, A.F., MORENO, M.C.M.. *Chem. Biochem.*, Q3, n. 1-2, p.51, 1989.
- CAO, E., GAVRIILIDIS, A. Oxidative dehydrogenation of methanol in a microstructured reactor. *Catalysis Today*, 110, pp.154-163, 2005.
- CARROL, D. Genetic Algorithms and Optimizing Chemical Oxygen-Iodine Lasers. *Developments in Theoretical and Applied Mechanics*, v.XVIII, pp.411-424, 1996a.
- CARROL, D.L. Chemical laser modeling with genetic algorithm. *AIAA Journal*, v.34, no 2, pp.338-346, 1996b.
- CHABRIS, C.F. *Artificial Intelligence & Turbo Pascal*. Multiscience Press Inc., 1^a ed., 1987.
- CHAN, C.W. An expert decision support system for monitoring and diagnosis of petroleum production and separation processes. *Expert Systems with Applications*, 29, p. 131, 2005.
- CHUMAKOVA, N.A., MADYAROV, A.I. Parametric sensitivity of methanol oxidation process as solution of boundary-value problem with an unknown parameter. *Chemical Engineering Journal*, 91, p. 159, 2003.
- COSTA, B.B.C., MACIEL FILHO, R. Evaluation of optimization techniques and control variable formulations for a batch cooling crystallization process, *Chemical Engineering Science*, 60, pp.5312-5322, 2005.
- COSTA, B.B.C. *Modelagem detalhada e otimização de processos de cristalização*. Campinas: Faculdade de Engenharia Química, Universidade Estadual de Campinas – UNICAMP, 2006. Tese de Doutorado.
- COWARD, H.F., JONES, G.W. Limits of Inflammability of Gases and Vapors. *US Bureau of Mines. Bull. 279*, 81-82, US Government Printing Office, Washington, 1939.
- CRANK, J., NICHOLSON, P. *Proceedings of Cambridge Phil. Soc.*, v.43, p.50, 1947.

DAI, W.L., CAO, Y, REN, L.P., YANG, X.L., XU, J.H., LI, H.X., HE, H.Y., FAN, K.N. Ag-SiO₂-Al₂O₃ composite as highly active catalyst for the formation of formaldehyde from the partial oxidation of methanol. *Journal of Catalysis*, 228, pp. 80-91, 2004.

DAVIS, L. *Handbook of Genetic Algorithms*. Boston: International Thomson Computer Press, 1991.

E.P.A. *Chemical summary for acetaldehyde*. August, EPA-749-F-94-003a, 1994.

FALIX, A, YETTER, R.A., FLOUDAS, C.A, BERNASEK, S.L., FRANSSON, M., RABITZ, H. Optimal control of catalytic methanol conversion to formaldehyde. *Journal of Physics Chemistry A*, 105, pp.2099-2105, 2001.

FOGLER, H.S. *Elements of chemical reaction engineering*, New Jersey: Prentice-Hall International, 2^a ed., 1992.

GARRARD, A., FRAGA, E.S. Mass exchange network synthesis using genetic algorithms. *Computers Chemical Engineering.*, v.22, n.12, pp.1837-1850, 1998.

GFRT. Global Formaldehyde & Resin Technologies. *Formaldehyde Industry Newsletter*, v.1, i.2, March 2007.

GOLDBERG, D.E. *Genetic Algorithms in Search, Optimization, and Machine Learning*. New York: Addison-Wesley Publishing Company, Inc, 1989.

GOLDBERG, D.E., DEB, K., CLARK, J.H. Genetic Algorithms, Noise and the Sizing of Populations. *Complex Systems*, 6, pp. 333-362, 1992.

GRAVILIN, V.N., POPOV, B.I. *Kinet. Catal.*, 6, p.799, 1965.

HIRSHFELDER, J.O., BIRD, R.B., SPOTZ, A. *Chem. Rev.*, 44, p. 205, 1949.

HOLLAND, J.H. *Adaptation in natural and artificial systems*, Ann Arbor: The University of Michigan Press, 1975.

HOLLAND, J.H. Adaptation. *Progress in theoretical biology*, 4, pp.263-293, 1976.

HOSTEN, L.H., FROMENT, G.F. Parametric sensitivity in co-currently cooled tubular reactors. *Chemical Engineering Science*, 41, p.1073, 1986.

IRDAM, E.A., KIEFER, J.H., HARDING, L.B., WAGNER, A.F. The formaldehyde decomposition chain mechanism. *International Journal of Chemical Kinetics*, v.25, pp.285-303, 1993.

KIM, T.H., RAMACHANDRA, B., CHOI, J.S., SAIDUTTA, M.B., CHOO, K.Y., SONG, S.D., RHEE, Y.W. Selective oxidation of methanol to formaldehyde using modified iron-molybdate catalysts. *Catalysis Letters*, v. 98, n. 2-3, pp. 161-165, 2004.

KIRK OTHMER. *Encyclopedia of Chemical Technology*. New York: Wiley & Sons, 4^a ed., 1991.

KIRK OTHMER. *Encyclopedia of Chemical Technology*. New York: Wiley & Sons, 1996.

LEFFERTS, L., OMMEN, J.G., ROSS, J.R.H. The oxidative dehydrogenation of methanol to formaldehyde over silver catalysts in relation to the oxygen-silver interaction. *Applied Catalysis*, 23, p.385, 1986.

LENNOX, B., MONTAGUE, G.A., FRITH, A.M., GENT, C., BEVAN, V. Industrial application of neural networks – an investigation. *Journal of Process Control*, v.11, pp.497-507, 2001.

LYNGGAARD, H., ANDREASEN, A., STEGELMANN, C., STOLTZE, P. Analysis of simple kinetic models in heterogeneous catalysis. *Progress in Surface Science*, v.77, pp.71-137, 2004.

MACIEL FILHO, R. *Internal report on the catalytic synthesis of acetaldehyde by oxidation of ethanol*. State University of Campinas, Sao Paulo, Brasil, 1985.

MACIEL FILHO, R., MACIEL, M.R.W., DOMINGUES, A., STINGHEN, A.O. Computer aided design of acetaldehyde plant with zero avoidable pollution. *Computers and Chemical Engineering*, v.20, S1389-S1393, 1986.

MACIEL FILHO, R., DOMINGUES, A. A multitubular reactor for obtention of acetaldehyde by oxidation of ethyl alcohol. *Chemical Engineering Science*, v.47, p.2571, 1992.

MACIEL FILHO, R., MCGREAVY, C. Multitubular Reactor Design for Waste Minimization. *Trans. Inst. of Chem. Eng.*, v.71, part B, pp.208-214, 1993.

MAO, C.F., VANICE, M.A. Formaldehyde oxidation over Ag catalysts. *Journal of Catalysis*, 154, pp.230-244, 1995.

MATUBAYASI, N., NAKAHARA, M. Hydrothermal reactions of formaldehyde and formic acid: free-energy analysis of equilibrium. *The Journal of Chemical Physics*, 122, 2005.

- MCGREAVY, C. et al. A concurrent engineering environment for chemical manufacturing. *Concurrent Engineering: Research and Applications*, 3, p. 281, 1995.
- MCGREAVY, C., WANG, X.Z., LU, M.L., YANG, S.H. Objects, Agents and Work Flow Modelling for Concurrent Engineering Process Design. *Computers chem. Engng.*, v.20, Suppl., S1167-S1172, 1996.
- MIHAIL, R., IORDACHE, C. *Chemical Engineering Science*, v.31, p.83, 1976.
- NAGY, A., MESTL, G. High temperature partial oxidation reactions over silver catalysts. *Applied Catalysis A: General*, 188, pp.337-353, 1999.
- NAGY, A., MESTL, G., RUHLE, T., WEINBERG, G., SCHLOGL, R. The dynamic restructuring of electrolytic silver during the formaldehyde synthesis reaction. *Journal of Catalysis*, 179, pp.548-559, 1998.
- NEUFELD, P.D., JANZEN, A.R., AZIZ, R.A. *J. Chem. Phys.*, 17, 2, p.236, 1972.
- PAPES FILHO, A.C. *Projeto e operação de reatores auxiliados por computador*. Campinas: Faculdade de Engenharia Química, Universidade Estadual de Campinas – UNICAMP, 1999. Dissertação de Mestrado.
- PAPES FILHO, A.C. Predição da resistência interna do papel utilizando redes neurais artificiais. *O Papel*, novembro 2001.
- PAPES FILHO, A.C., CREMASCO, M.A. Correlation for estimation of diffusion coefficient for gases. *Anais do 1º Congresso de Engenharia Química – Iniciação Científica*, Ed. UFSCar, 1995.
- PAPES FILHO, A.C., MACIEL FILHO, R. Concurrent Engineering Reactor Design. In XVIII Congress of Chemical Engineering, Porto Rico, Proceedings, 1998.
- PAPES FILHO, A.C., MACIEL FILHO, R. Concurrent engineering reactor design. In XIII Brazilian Congress of Chemical Engineering, Proceedings, 2000.
- PAPES FILHO, A.C., MACIEL FILHO, R. Concurrent Engineering Reactor Design. In III European Congress of Chemical Engineering, Nuremberg, Alemanha, Proceedings, 2001.
- PAPES FILHO A.C., MACIEL FILHO R. Concurrent Engineering Reactor Design. *Computer Aided Chemical Engineering*, v.20 A, Edited by Luis Puijagner and Antonio Espuña, Elsevier B.V., ISSN 1570-7946, pp.559-564, 2005.

PARK, B.D., WANG, X.M. Thermokinetic behaviour of powdered phenol-formaldehyde resins. *Thermochimica Acta*, 433, pp.88-92, 2005.

PERRY, R.H., CHILTON, C.H. *Manual de Engenharia Química*. Rio de Janeiro: Ed. Guanabara Dois, 5^a Ed, 1980.

PESTRYAKOV, A.N. Modification of silver catalyst for oxidation of methanol to formaldehyde. *Catalysis Today*, 28, pp. 239-244, 1996.

PHAM, D.T., PHAM, P.T. Artificial intelligence in engineering. *International Journal of Machine Tools & Manufacture*, v.39, pp. 937-949, 1999.

PICCOLI, R.L. *Kinetic study of methanol selective oxidation to formaldehyde on iron molybdate catalyst*. Bélgica:Rijksuniversiteit Gent, 1992. Dissertação de Mestrado.

PILATO, L.A., KNOP, A., GARDZIELLA, A. *Phenolic resins*. New York: Springer, 2nd ed., 2000.

PIZZI, A. *Advanced wood adhesives technology*. New York: Marcel Dekker Inc., 1^a ed., 1994.

PRESS, W.H., FLANNERY, B.P., TEUKOLSKY, S.A., VETTERLING, W.T. *Numerical Recipes*. Cambridge: Press Syndicate of the University of Cambridge, 1st ed., 1992.

PSICHOGIOS, D.C., UNGAR, L.H. A hybrid neural network-first principles approach to process modeling. *AIChE Journal*, v.38, 10, pp. 1499-1511, 1992.

QIAN, M., LIAUW, M.A., EMIG, G. Formaldehyde synthesis from methanol over silver catalysts. *Applied Catalysis A: General*, 238, pp.211-222, 2003.

REID, R.C., PRAUSNITZ, J.M., POLING, B.E. *The properties of gases and liquids*. New York: McGraw-Hill Book Company, 4^a ed., 1987.

ROBB, D.A., HARRIOT, P. The kinetics of methanol oxidation on a supported silver catalyst. *Journal of Catalysis*, 35, pp.176-183, 1974.

RUMELHART, D.E., HINTON, G.E., WILLIAMS, R.J. Learning internal representations by error propagation. *Parallel distributed processing*, v.1, pp.318-362, 1986.

SANDLER, S.I. *Chemical and engineering thermodynamics*. New York: John Wiley & Sons, 1989.

SANTACESARIA, E., MORBIDELLI, M. Kinetics of the catalytic oxidation of methanol to formaldehyde. *Chemical Engineering Science*, v.36, pp.909-918, 1981.

SAUER, J., EMIG, G. The catalyzed dehydrogenation of methanol to formaldehyde at high temperatures. *Chemical Engineering Technology*, 18, pp. 284-291, 1995.

SCHUBERT, H., TEGTMEYER, U., SCHLOGL, R. On the mechanism of the selective oxidation of methanol over elemental silver. *Catalysis Letters*, 28, pp.383-395, 1994.

SHENVI, N., GEREMIA, J.M, RABITZ, H. Efficient chemical kinetic modeling through neural network maps. *Journal of Chemical Physics*, 120, p.9942, 2004.

SILVER INSTITUTE, www.silverinstitute.org, 2006.

SOARES, A.P.V., PORTELA, M.F., KIENNEMANN, A. Methanol selective oxidation to formaldehyde over iron-molybdate catalysts. *Catalysis reviews*, v. 47, pp.125-174, 2005.

SRI INTERNATIONAL; "Formaldehyde", Report n° 23A, Menlo Park, 1978.

SU, S., ZAZA, P., RENKEN, A. Catalytic dehydrogenation of methanol to water-free formaldehyde. *Chemical Engineering Technology*, 17, pp.34-40, 1994.

SYSWERDA, G. Uniform crossover in genetic algorithms. Proceedings of the third international conference on genetic algorithms. San Mateo, California, Morgan Kaufmann publishers, 1989.

TANG, X., CHEN, J., LI, Y., LI, Y., XU, Y., SHEN, W. Complete oxidation of formaldehyde over Ag/MnO_x-CeO₂ catalysts. *Chemical Engineering Journal*, 118, pp.119-125, 2006.

THOMAS, M.D. Preparation of formaldehyde. *Journal of the American Chemical Society*, 42, p. 867, 1920.

TREYBAL, R.E. *Mass-transfer operations*. Singapore: McGraw-Hill International Editions, 3^a ed., 1981

ULLMANN. *Ullmann's Encyclopedia of Industrial Chemistry*. New York: VHC Publishers, v.A11, 5^a ed., 1988.

VAN VEEN, A.C, HINRICHSSEN, O., MUHLER, M. Mechanistic studies on the oxidative dehydrogenation of methanol over polycrystalline silver using the temporal-analysis-of-products approach. *Journal of Catalysis*, 210, pp. 53-56. 2002.

- VILLADESEN, J., MICHELSEN, M. *Solution of differential equation models by polynomial approximation*. New York: Prentice-Hall, 1978.
- WACHS, I.E., MADIX, R. The oxidation of methanol on a silver (110) catalyst. *Surface Science*, 76, pp. 531-558, 1978.
- WALKER, J.F. *Formaldehyde*. New York: Robert E. Krieger Publishing Company, 3^a ed., 1975.
- WANG, Q.J. Using Genetic Algorithms to Optimise Model Parameters. *Environmental Modelling & Software*, v.12, n.1, pp 27-34, 1997.
- WANG, J., LABORIE, M.P.G., WOLCOTT, M.P. Comparison of model-free kinetic methods for modeling the cure kinetics of commercial phenol-formaldehyde resins. *Thermochimica Acta*, 439, pp.68-73, 2005.
- WASSERMAN, P.D. *Neural Computing: Theory and Practice*. New York: Editora van Nostrand Reinhold, 1^a ed., 1989.
- WATERHOUSE, G., BOWMAKER, G., METSON, J. Mechanism and active sites for the partial oxidation of methanol to formaldehyde over an electrolytic silver catalyst. *Applied Catalysis A*, 265, pp.85-101; 2004a.
- WATERHOUSE, G., BOWMAKER, G., METSON, J. Influence of catalyst morphology on performance of electrolytic silver catalysts for the partial oxidation of methanol to formaldehyde. *Applied Catalysis A*, 266, pp.257-273, 2004b.
- WELSENAERE, R., FROMENT, G.F. Parametric sensitivity and runaway in fixed bed catalytic reactors. *Chemical Engineering Science*, 25, p.1503, 1970.
- WELTY, J.R., WICKS, C.E., WILSON, R.E. *Fundamentals of momentum, heat and mass transfer*. New York: John Wiley & Sons editor, 3^a ed., 1984.
- WILKE, C.R., LEE, C.Y. *Ind. Eng. Chem.*, 47, 6, p. 1253, 1953.
- WU, H. et al. Parametric sensitivity in fixed-bed catalytic reactors with reverse-flow operation. *Chemical Engineering Science*, 54, p. 4579, 1999.