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**“Simulação Computacional Aplicada à Melhoria do  
Processo de Purificação de Bioetanol”**

***“Computational Simulation Applied to the  
Improvement of the Bioethanol Purification  
Process”***

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**Simulação Computacional Aplicada à Melhoria do Processo  
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***Computational Simulation Applied to the Improvement of the  
Bioethanol Purification Process***

**Orientador: Prof. Dr. Antonio José de Almeida Meirelles**

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## **Dedicatória**

*“A vida é uma peça de teatro que não permite ensaios. Por isso, cante, chore, dance, ria e viva intensamente, antes que a cortina se feche e a peça termine sem aplausos” – Charles Chaplin*

*“Que os vossos esforços desafiem as impossibilidades, lembrai-vos de que as grandes coisas do homem foram conquistadas do que parecia impossível” – Charles Chaplin*

*“Não tentes ser bem sucedido, tente antes ser um homem de valor.” – Albert Einstein*

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## ***Resumo Geral***

A diminuição gradativa das reservas de combustíveis fósseis e a crescente preocupação com os efeitos do aquecimento global vêm impulsionando cada vez mais as pesquisas por fontes de energia limpa. Dentre essas energias, o etanol de cana-de-açúcar, utilizado no Brasil desde a criação do Programa Nacional do Álcool (PROALCOOL) em 1975, vem se consolidando cada vez mais e sofrendo modificações contínuas no seu processo produtivo. Essas modificações se devem, entre outros aspectos, ao surgimento do conceito de biorrefinaria, que visa um aproveitamento integral da biomassa da cana para produção de energia, e ao rápido e contínuo crescimento da indústria alcoolquímica brasileira, utilizando o etanol como matéria prima para a produção de diversos outros produtos, aumentando a demanda por etanol de melhor qualidade e impulsionando pesquisas no melhoramento do processo produtivo atual. Tendo em conta esse atual cenário, essa tese tem por objetivo estudar o processo de destilação alcoólica industrial, por simulação computacional, analisando a influência dos diversos contaminantes do fermentado de cana no funcionamento das colunas de destilação, investigando a possibilidade do desenvolvimento de uma nova planta industrial para a produção de álcool carburante e álcool neutro, um tipo especial de álcool de alto valor agregado com baixo teor de contaminantes utilizado na indústria de química fina e de bebidas. Para o cumprimento desse objetivo, esta tese está dividida em 6 capítulos: o Capítulo 1 apresenta uma revisão bibliográfica da produção científica associada à produção de álcool combustível, apontando as principais lacunas inerentes a esse tema; o Capítulo 2 discute a produção industrial de cachaça por sistema contínuo apresentando um cuidadoso estudo do equilíbrio de fase dos principais componentes do fermentado de cana de açúcar e analisando a influência dos mesmos no processo produtivo; o Capítulo 3 e o Capítulo 4 apresentam o estudo do processo de produção de álcool hidratado combustível discutindo a influência dos componentes do vinho no funcionamento das colunas, técnicas de otimização de processo aplicadas a um processo industrial real e técnicas de controle de processo aplicadas ao controle de acetaldéido e da graduação alcoólica no bioetanol; o Capítulo 5 apresenta uma

nova planta industrial para produção de álcool neutro e álcool hidratado discutindo detalhadamente as vantagens e desvantagens do novo processo frente a plantas industriais tradicionais brasileira e francesa; por fim, o Capítulo 6 apresenta as conclusões gerais do trabalho sugerindo temas para investigações futuras. A análise dos resultados obtidos permitiu concluir que, ainda que consolidado, o processo produtivo de etanol através de cana-de-açúcar apresenta lacunas importantes, principalmente quando se deseja produzir etanol de qualidade superior. Nesse sentido, uma nova planta industrial foi proposta com o objetivo de produzir etanol neutro e hidratado em uma única instalação com redução nos custos de instalação (menor número de colunas) e de consumo de vapor.

## ***Abstract***

The gradual reduction of fossil fuel reserves and growing concerns about the effects of global warming have encouraged more research on clean energy sources. Among these energies, ethanol from sugar cane, used in Brazil since the creation of the National Alcohol Program (PROALCOOL) in 1975, has undergone continuous changes in their production process. These changes were due to the emergence of the concept of biorefineries, aiming at a full utilization of sugarcane biomass for energy production, and the continuous and quick growth of the Brazilian alcohol-chemical industry, using the ethanol as raw material for the production of several other products, increasing the demand for ethanol with better quality and boosting the research to improving the current production process. Taking into account this present scenario, this thesis aims to study an industrial process for ethanol production, by computational simulation, analyzing the influence of the contaminants of the fermented sugar cane in the operation of distillation columns, investigating the possibility of developing a new plant for the industrial production of fuel alcohol and neutral alcohol, a particular type of hydrated alcohol of high economic value and low content of contaminants used in the manufacture of fine chemicals and beverages. To fulfill this objective, this thesis is divided into six chapters: Chapter 1 presents a literature review of scientific literature related to the production of fuel alcohol, pointing out the main shortcomings inherent in this theme; Chapter 2 discusses an industrial process for cachaça production by continuous distillation featuring a careful study of the phase equilibrium of the main components of the fermented sugar cane and analyzing their influence in the production process; Chapter 3 and Chapter 4 presents the study of an industrial plant for hydrated fuel ethanol production discussing the influence of the main components of the wine in the columns operation, techniques of process optimization applied to a real industrial process and techniques of control process applied to the control of acetaldehyde and alcoholic graduation in bioethanol; Chapter 5 presents a new plant for neutral and hydrated alcohol

productions, discussing in detail the advantages and disadvantages of the new process compared to traditional Brazilian and French industrial plants; finally, the Chapter 6 presents the overall findings of the study and suggesting topics for future investigations. Taking into account the results of this thesis, was possible to concluded that, although consolidated, the ethanol production process using sugar cane as raw material presents important gaps especially when related with high quality ethanol. Some of these shortcomings were solved by proposing a new industrial configuration in order to produce neutral and hydrated ethanol in a single installation with lower installation costs (less number of columns) and steam consumption.

## Introdução

O interesse mundial pelo desenvolvimento dos biocombustíveis vem aumentando vertiginosamente a partir de meados da presente década, em virtude de uma maior preocupação com o desenvolvimento de fontes energéticas renováveis e mais limpas, que permitam avançar na superação do atual paradigma, baseado nos combustíveis fósseis. Nesse cenário, destaca-se o Brasil, cujo programa de bioetanol de cana-de-açúcar apresenta resultados interessantes, desde a pesquisa de variedades de cana de maior rendimento até a fabricação de motores que funcionam com qualquer mistura de gasolina e etanol.

Segundo a primeira estimativa da produção de álcool e açúcar para a safra 2011/2012 realizada pela Conab, Companhia Nacional de Abastecimento, a produção total de álcool no Brasil será de pouco mais de 27 bilhões de litro, 1,8 % menor que a safra 2010/2011, em decorrência da grande estiagem ocorrida no verão passado. Desse total estimado, 33% serão de álcool anidro e 67% destinado à produção de álcool hidratado. A produção de álcool neutro esta englobada dentro das estimativas para produção de álcool hidratado e, segundo a União das indústrias de cana-de-açúcar (UNICA), deve ser responsável por aproximadamente 5 a 10% do total de álcool hidratado produzido no país.

O processo produtivo atual está centrado no modelo de primeira geração, através da fermentação do caldo de cana de açúcar ou pela fermentação de um mosto composto pelo caldo de cana de açúcar e melado. O primeiro caso é comumente utilizado em destilarias autônomas, ou seja, destilarias dedicadas exclusivamente à produção de álcool e, no segundo caso, utilizado em usinas de produção de açúcar com destilarias para produção de álcool anexas. Após a fermentação do caldo de cana e transformação do mesmo em vinho, este é separado das leveduras fermentativas e bombeado para a unidade de destilação. Essa unidade é composta por um complexo conjunto de colunas de destilação cuja configuração exata dependerá da qualidade desejada do produto, diretamente influenciados pela concentração dos componentes minoritários presentes no mosto fermentado. Em capítulos futuros será discutida uma

configuração industrial típica das destilarias brasileiras bem como a influência dos minoritários na complexidade do sistema de colunas de destilação.

Alternativamente à cana-de-açúcar, é possível utilizar outras matérias-primas para produzir este biocombustível tais como milho (EUA e China), beterraba (União Européia), mandioca, trigo e uva. Na maioria desses casos, entretanto, é preciso transformar o amido presente nestes alimentos em açúcar antes de fermentá-los. Esta etapa adicional diminui o rendimento do processo e aumenta os custos de produção. Enquanto os EUA gastam uma unidade de energia equivalente de combustível fóssil para gerar 1,3 unidades de etanol, no Brasil, a mesma unidade produz entre oito e nove unidades de etanol de caldo de cana (CTBE, 2009). Além das questões que tangem a eficiência energética, há também os aspectos ambientais. Análises realizadas mostraram que a substituição da gasolina por etanol de cana-de-açúcar levaria a uma redução no total de emissões de Gases de Efeito Estufa (GEE) em torno de 2,6t CO<sub>2</sub>eq./m<sup>3</sup> (etanol anidro) e 1,7t CO<sub>2</sub>eq./m<sup>3</sup> (etanol hidratado), ratificando que a produção de etanol de cana-de-açúcar é superior a qualquer outra tecnologia produtora de combustível a partir de biomassa do mundo no que diz respeito à relação energia renovável obtida / energia fóssil usada (CTBE, 2009). Apesar do excelente rendimento energético, custos reduzidos, alta produtividade e grande conhecimento do processo produtivo de etanol de cana-de-açúcar (etanol de primeira geração), é nítida a possibilidade de aperfeiçoamento do processo através da elevação dos rendimentos de conversão de produtividade global do processo, seja através do melhoramento genético da cana-de-açúcar ou através de modificações no sistema de fermentação e destilação.

Apesar da consolidação do etanol de primeira geração, é cada vez mais crescente no mundo a preocupação com a competição da terra para a produção de bioetanol e alimentos. Ainda que no Brasil as terras agricultáveis ocupadas sejam inferiores a 5% do total disponível, investimentos em pesquisas para produção de etanol de segunda geração se fazem necessários com o objetivo de se evitar, em longo prazo, a estagnação da produção e a competição das terras agricultáveis entre biocombustíveis e alimentos.

O etanol de segunda geração consiste no aproveitamento integral do material lignocelulósico ou da biomassa celulósica para a produção de etanol combustível, principalmente a partir de resíduos celulósicos agrícolas (dentre eles o bagaço de cana e outras frutas), culturas herbáceas (alfafa), resíduos florestais e madeira (madeiras duras, macias) (Huang et al., 2009). Segundo estimativas, a previsão é de que o aproveitamento do bagaço e parte das palhas e pontas da cana-de-açúcar eleve a produção de álcool em 30 a 40%, para uma mesma área plantada. A combinação das rotas de primeira e segunda geração na produção de etanol de cana-de-açúcar permitirá obter maior quantidade de combustível sem aumentar o volume de matéria-prima cultivada nem a área plantada, mas, em consequência, ter-se-á menor disponibilidade de bagaço para geração de energia elétrica. No momento em que a tecnologia de segunda geração estiver em escala comercial, as usinas seguirão a lógica do mercado, voltando sua produção para eletricidade ou etanol de modo semelhante ao que ocorre com a destinação do caldo que, a depender das condições, produzirá mais etanol ou mais açúcar (Embrapa, 2011).

O processo básico para a conversão de biomassa em etanol combustível celulósico consiste basicamente em oito etapas: manipulação da matéria prima e pré-tratamento, cujo objetivo é expor os materiais hidrolisáveis do material celulósico através da alteração ou remoção de impedimentos estruturais ou de composição; hidrólise do material celulósico, cujo objetivo é a liberação dos açúcares fermentescíveis; separação dos resíduos sólidos, fermentação, destilação, evaporação e combustão da lignina para a produção de eletricidade e vapor (Magnusson, 2006).

No Brasil, a principal forma de utilização do etanol é como combustível automotivo sob a forma de Álcool Etílico Anidro Combustível (AEAC), adicionado à gasolina na proporção de 20-25%, e Álcool Etílico Hidratado Combustível (AEHC), utilizado em carros a combustão exclusiva a álcool ou flex. Em menor escala e com um maior valor econômico agregado, temos o Álcool Neutro (AN), também conhecido como álcool fino ou extrafino, muito utilizado nas indústrias de química fina, farmacêutica e de bebidas. Devido ao seu baixo grau de impurezas o álcool

neutro que, segundo levantamentos da Companhia Nacional de Abastecimento (CONAB), praticamente desapareceu da cadeia produtiva nacional nos últimos quatro anos, vem ganhando força econômica novamente principalmente no atual cenário da indústria alcoolquímica.

A indústria alcoolquímica pode ser definida como um segmento da indústria química que utiliza o álcool etílico como matéria-prima para fabricação de diversos produtos químicos com amplo uso industrial como butadieno, acetaldeído, acetona, ácido acético, acetato de etila, etileno glicol, eteno, entre outros (Voss et al., 2011, Bussia et al., 1998, Lippits and Nieuwenhuys, 2010; Bi et al., 2010; Kamm and Kamm, 2004; Hamelinck et al., 2005). Dentre esses produtos, um destaque especial deve ser dado ao eteno. Principal matéria prima para a produção de importantes polímeros como o polietileno e o policloreto de vinila (PVC), esse composto vem se tornando um dos mais importantes pilares da indústria alcoolquímica no Brasil por ser precursor do chamado “plástico verde”. Segunda a UNICA, recentemente a Braskem, uma grande multinacional brasileira atuante na área de petróleo e química fina, desenvolveu uma tecnologia própria e passou a produzir polietileno tendo como matéria prima o etanol. Somente para a produção desse tipo de plástico, o mais utilizado no mundo, a Braskem prevê, para 2011, um consumo de cerca de 700 milhões de litros de etanol – o que corresponde cerca de 3% da produção total prevista para o ano no país e faz da empresa a maior compradora de álcool para fins industriais no Brasil. Nessa mesma linha, a Dow Chemical, maior empresa química dos EUA e maior produtora mundial de polietileno esta retomando um projeto anunciado em 2008 para a produção de 350 mil toneladas anuais de polietileno em Minas Gerais, o que gerará uma demanda de 700 milhões de litros anuais de etanol. No que se refere à produção de PVC, a Solvay Indupa, uma indústria belga de produtos químicos, também esta retomando o projeto desenvolvido anteriormente a crise de 2008, para a produção de 60 mil toneladas anuais de eteno para produção de PVC em Santo André – SP, gerando uma demanda de 150 milhões de litros de etanol por ano (Simpep, 2011).

O contínuo crescimento da produção de etanol para fins carburantes associado ao atual desenvolvimento da indústria alcoolquímica no Brasil contribuiu para o aumento da demanda de etanol no mercado nacional impulsionando a necessidade da busca de novas alternativas de produção e melhorias no processo produtivo já existente. É nessa atual conjuntura que o conceito de biorrefinaria começa a despontar no cenário industrial brasileiro e mundial.

Em suma, o conceito de biorrefinaria está relacionado ao uso de matérias-primas renováveis e de seus resíduos, de maneira integral e diversificada, para a produção, por rota química ou biotecnológica, de uma variedade de substâncias e energia, com a mínima geração de resíduos e emissões de gases poluidores. Esse conceito é muito semelhante às refinarias de petróleo que fabricam múltiplos produtos, como combustíveis (em grande volume) e também, com vistas a ampliar a lucratividade, uma parcela de produtos químicos de alto valor unitário. Assim, as biorrefinarias de etanol visam produzir combustíveis em larga escala, energia e, em menor quantidade, produtos químicos e/ou etanol de qualidade superior com maior valor agregado. Para o cumprimento desse objetivo as biorrefinarias utilizam diversos tipos de biomassa integrando, em um único complexo industrial, o processo produtivo de etanol de primeira e segunda geração (Rabelo et al, 2011; Zondervan et al, 2011; Alvarado-Morales et al., 2009; Fernando et al., 2006).

Para a discussão dos assuntos pertinentes à destilação alcoólica industrial essa tese é composta de 6 capítulos resumidos a seguir:

Capítulo 1: Apresenta uma revisão bibliográfica discutindo os principais trabalhos que associam simulação com destilação alcoólica e os fundamentos termodinâmicos envolvidos na simulação de processos de destilação alcoólica.

Capítulo 2: Este capítulo refere-se a um artigo publicado na revista Food Control intitulado “Computer simulation applied to studying continuous spirit distillation and product quality control”. A produção de bebidas por destilação contínua pode ser considerada uma etapa intermediária da produção de bioetanol. Assim, o estudo deste sistema permite inferir conclusões importantes sobre o comportamento dos componentes minoritários ao longo da coluna que serão fundamentais para o estudo de sistemas mais complexos de destilação, como

aqueles para produção de bioetanol. Neste artigo estudou-se a produção contínua de bebidas destiladas através do simulador comercial Aspen Plus e Aspen Dynamics. O trabalho discute a influência de algumas condições operacionais sobre a qualidade do produto obtido e apresenta técnicas de controle de processo para a minimização da contaminação da bebida com elementos voláteis (acetaldeído, acetato de etila, acetona e metanol). Para tal discussão, uma validação experimental do processo foi realizada através de coleta de amostras junto à usina Santa Adélia (Jaboticabal, SP). Esta usina trabalhou com uma moagem na safra 2010/2011 de mais de 4.500.000 toneladas de cana produzindo cerca de 300.000 m<sup>3</sup> de etanol total e mais de 160.000 toneladas de açúcar cristal (não refinado). As amostras coletadas na usina foram analisadas por cromatografia gasosa (GC), quantificadas, em termos da composição mássica de etanol, água e minoritários, sendo então comparadas com o resultado gerado pela simulação computacional do processo real. Visando uma minimização dos erros gerados na simulação, um rigoroso e cuidadoso estudo do equilíbrio líquido-vapor dos diversos binários formados com os componentes do vinho de cana-de-açúcar foi realizado. Esta análise do equilíbrio permitiu a classificação dos principais componentes envolvidos no processo em três categorias segundo suas volatilidades (componentes leves, intermediários e pesados), possibilitando uma melhor compreensão da distribuição dos mesmos ao longo das colunas de destilação.

Capítulo 3: Apresenta um trabalho completo publicado nos anais do International Symposium on Advanced Control of Chemical Processes – ADCHEM 2009, Istambul, Turquia de título “A Strategy for Controlling Acetaldehyde Content in an Industrial Plant of Bioethanol”. Este trabalho discute técnicas de controle de processos aplicadas ao controle do teor de acetaldeído no Bioetanol, via simulação computacional. Este componente pode, durante o processo de estocagem, ser oxidado a ácido acético aumentando a acidez do álcool combustível deixando o mesmo fora dos padrões de qualidade desejados. Para o estudo utilizou-se o simulador Aspen Plus conjugado com o simulador Aspen Dynamics.

Capítulo 4: Discute o artigo “Computational simulation applied to the investigation of industrial plants for bioethanol distillation” aceito para a publicação no periódico *Computers and Chemical Engineering*. Neste artigo uma planta industrial típica para produção de bioetanol é apresentada, discutida em detalhes e simulada através do simulador Aspen Plus. Com o objetivo de demonstrar a capacidade do simulador em reproduzir sistemas reais, uma etapa de validação experimental foi realizada através da coleta de amostras experimentais na usina Santa Adélia, comparando-se os perfis de componentes gerados pela simulação com os perfis experimentais. Posteriormente, técnicas de planejamento experimental foram utilizadas para investigar a influência de onze diferentes fatores relacionados à configuração do equipamento e condições operacionais sobre a graduação alcoólica do bioetanol produzido, o consumo de vapor, a perda de etanol pela vinhaça e flegmaça e a recuperação do etanol alimentado ao sistema. Com os resultados, foi possível definir um ponto ótimo de trabalho para as colunas de destilação produtoras de bioetanol combustível, comparando-se a qualidade do álcool produzido neste ponto ótimo com alguns padrões de qualidade consolidados no país. Por fim, com a planta otimizada foram realizadas simulações dinâmicas, através do simulador Aspen Dynamics, objetivando verificar a sensibilidade da mesma frente a variações na graduação alcoólica do vinho, com posterior desenvolvimento de malhas de controle.

Capítulo 5: É Apresentado o artigo “A new distillation plant for neutral alcohol production” a ser submetido à revista Fuel. O artigo conceitua o que é álcool neutro apresentando algumas de suas aplicações e sua relevância para a atual indústria alcoolquímica nacional. Discute em detalhes o atual processo produtivo apresentando e detalhando cada coluna de destilação envolvida no processo e suas respectivas funções. Relaciona a qualidade do álcool neutro simulado utilizando a configuração industrial atual com o padrão de qualidade de diversos países e com referências científicas. Propõe uma nova configuração de colunas para a produção do álcool neutro baseado na configuração industrial típica para produção de bioetanol combustível apresentada no capítulo 3, discutindo as vantagens da nova configuração com relação a atual em termos de

consumo de vapor, fatores de purificação e possibilidade de produção de mais de um tipo de álcool no mesmo sistema de colunas.

Capítulo 6: Discute-se as principais conclusões apresentando sugestões para trabalhos futuros.

## **Objetivos**

Tendo em vista a importância do etanol para a economia nacional, a grande preocupação mundial com a substituição dos combustíveis fósseis, o desenvolvimento das biorrefinarias e o aumento do peso da indústria alcoolquímica na economia nacional, esse trabalho tem por objetivo geral o estudo, por simulação computacional através do simulador Aspen Plus, do processo de produção de álcool hidratado a fim de se verificar a possibilidade de melhorias no processo de purificação e produção de alcoóis com maior padrão de qualidade destinado à indústria de alimentos, bebidas, farmacêuticas e alcoolquímica. Para tal propósito os seguintes objetivos específicos deverão ser alcançados:

- Levantamento de perfis de composição, temperatura, pressão, vazão, bem como informações relativas à construção dos equipamentos de destilação de álcool hidratado junto à Usina Santa Adélia, localizada na cidade de Jaboticabal no interior de São Paulo.
- Validação das ferramentas de simulação computacional do simulador Aspen Plus com base nos dados experimentais colhidos na planta industrial.
- Investigação, por simulação computacional, do processo de produção de bebidas destiladas por sistema contínuo.
- Proposição de uma nova configuração para produção de bioetanol com maior padrão de qualidade.
- Desenvolvimento e teste de malhas de controle através do simulador Aspen Dynamics.

# Capítulo 1

## Revisão Bibliográfica

### 1.1 – Publicações científicas relevantes

A complexidade do vinho (mosto fermentado de cana-de-açúcar) associada a fatores econômicos e estruturais que dificultam a realização de experimentos diretamente em uma planta industrial apontam para a simulação computacional como uma ferramenta poderosa para o aprimoramento de plantas já existentes, para o desenvolvimento de novos projetos, para o teste de condições extremas de operação, que são difíceis de serem analisadas numa planta industrial real, para a avaliação da resposta do sistema a distúrbios, para o estudo do impacto da variação da concentração dos diversos componentes do vinho no processo produtivo, dentre outras. A facilidade de acesso às ferramentas de simulação computacional, bem como a grande diversidade e complexidade de operações que esses softwares são capazes de reproduzir com alta confiabilidade, vem tornando possível um substancial aumento do número de publicações relacionadas à simulação de processos químicos. No entanto, as publicações relacionadas ao processo de produção de bioetanol através de simulação computacional, concentram-se, em sua maioria absoluta, na análise da destilação binária etanol-água, de processos de purificação do etanol para a produção de etanol anidro e, mais recentemente, um crescente aumento do número de publicações relacionadas à produção de etanol a partir de material celulósico, sendo dispensada pouca importância ao estudo da produção de álcool hidratado e/ou álcool neutro.

Figueiredo et al. (2011) otimizaram um sistema de colunas de destilação extrativa para produção de bioetanol anidro através do simulador comercial Aspen Plus. Neste estudo os autores utilizaram o etileno glicol como solvente e nenhum outro contaminante foi considerado. Junqueira et al. (2009), utilizaram-se do mesmo simulador comercial para estudar um processo de destilação azeotrópica para a produção de bioetanol anidro avaliando três configurações diferentes de

colunas. Os autores otimizaram o sistema em termos da formação de uma segunda fase líquida. Gil et al. (2008), simularam um processo de destilação extrativa para a produção de etanol anidro, utilizando solventes específicos, considerando apenas a mistura binária etanol-água. Verhoef et al. (2008), demonstraram a validade do simulador Aspen Plus simulando a produção de etanol anidro através de um processo híbrido de destilação pervorativa, também considerando apenas a mistura binária etanol-água, comparando os resultados obtidos com dados industriais. Simo et al. (2008) utilizaram a simulação computacional como ferramenta para apresentar técnicas alternativas à destilação para a produção de etanol combustível. Gomis et al. (2008) estudaram, tanto em escala laboratorial quanto por simulação computacional, o processo de produção de etanol anidro através de destilação azeotrópica com isooctano considerando apenas a mistura etanol-água-isooctano.

No que se refere à produção de etanol hidratado, poucos trabalhos estão disponíveis na literatura. Dentre os de maior relevância, Marquini et al. (2007) estudaram, por simulação computacional, um sistema industrial de colunas de destilação para a produção de etanol hidratado combustível, otimizando o sistema em termos de consumo de vapor considerando uma mistura binária etanol-água. Decloux and Coustel (2005) estudaram, através do simulador ProSim II, um sistema de colunas para a produção de álcool neutro. Para tal objetivo consideraram um vinho contendo etanol, água e mais quatro contaminantes, aumentando assim a complexidade da simulação e do sistema de colunas. Os mesmos simularam primeiramente a produção de um álcool intermediário (álcool hidratado combustível) seguida de uma etapa de purificação, através da adição de mais três colunas, para a produção de álcool neutro.

A grande experiência do grupo de trabalho (FEA/UNICAMP) com simulação de processos aliada a procedimentos experimentais voltados para a produção de etanol anidro, etanol hidratado ou outros produtos derivados do processo de destilação, possibilitaram um grande número de publicações nessa área (Batista e Meirelles, 2011; Batista et al., 2012; Batista e Meirelles, 2009; Meirelles et al., 1991; Meirelles et al., 1992; Batista e Meirelles, 1997). No que tange à produção

de álcool hidratado, Batista e Meirelles (2011) estudaram, por simulação computacional, um sistema industrial de colunas de destilação para produção de álcool hidratado combustível a partir de um vinho de cana de açúcar com 17 contaminantes além de etanol e água, objetivando otimizar esse sistema quanto ao consumo de vapor, recuperação de etanol, perda de etanol e graduação alcoólica do hidratado. Uma análise detalhada da influência dos contaminantes no processo produtivo foi discutida associada ao desenvolvimento de malhas de controle que permitam manter constante a graduação alcoólica do bioetanol frente a perturbações na graduação alcoólica do vinho. Batista e Meirelles (2009) apresentaram algumas técnicas de controle para a contaminação do álcool hidratado com acetaldeído, objetivando prevenir o aumento da acidez desse álcool por conta da oxidação desse composto durante o processo de estocagem, utilizando para isso ferramentas de simulação computacional (Aspen Plus). Meirelles et al. (2008) promoveram uma detalhada discussão dos processos de produção de bebidas destiladas e óleos essenciais, discutindo e analisando a presença de diversos contaminantes no processo, utilizando para isso ferramentas de simulação computacional. Em relação à simulação de processos de contato líquido-vapor e líquido-líquido de sistemas complexos contendo elevado número de componentes, o grupo de pesquisa do EXTRAE adquiriu também uma grande experiência com a investigação do processamento de óleos vegetais, óleos essenciais e recuperação de aromas (Ceriani et al., 2008; Ceriani e Meirelles, 2006; Ceriani e Meirelles, 2007; Haypek et al., 2000).

Pesquisas envolvendo produção de bioetanol através de material celulósico já produziram uma grande quantidade de artigos científicos, muitos deles utilizando ferramentas de simulação computacional como mecanismo de entendimento do processo. Em geral, esses trabalhos reproduzem o processo como um todo sem se preocupar com o detalhamento das operações unitárias envolvidas, nem mesmo com os possíveis contaminantes do processo. Dias et al. (2012) estudaram, por simulação computacional, um processo típico de produção de bioetanol por hidrólise do bagaço de cana-de-açúcar avaliando a possibilidade de integração com o processo de produção de etanol de primeira geração. Nesse

estudo não foram considerados contaminantes e os resultados apontaram que, economicamente, a integração dos dois processos de produção de bioetanol se demonstrou mais vantajoso. Fujimoto et al. (2011) investigaram a utilização de energia durante o processo de produção de bioetanol por material celulósico. Ferramentas de simulação computacional foram utilizadas e a taxa de recuperação de calor do processo foi determinada por análise pinch. No entanto, todo estudo foi focado na mistura binária etanol/água sem se preocupar com outros contaminantes do processo. Kumar et al. (2009) apresentaram alguns avanços no processo de produção de etanol por material lignocelulósico, discutindo as principais barreiras encontradas nas diversas etapas do processo. Soluções para essas barreiras foram apresentadas e a cinética química, tanto para o processo de hidrólise quanto para a fermentação, foram discutidos fornecendo uma boa base para o estudo do processo por simulação computacional. Piccolo e Bezzo (2009) promoveram um estudo técnico e econômico de duas configurações para a produção de etanol lignocelulósico. Para esse propósito, o simulador Aspen Plus foi utilizado para a simulação e otimização do processo. Alzate e Toro (2006) estudaram, por simulação computacional utilizando o simulador Aspen Plus, diversas configurações para a produção de etanol a partir de material lignocelulósico, avaliando cada uma dessas configurações quanto ao consumo de energia necessário para a produção de 1L de etanol. Detalhes das diversas configurações foram apresentados, permitindo um ótimo entendimento do processo, porém não houve a descrição dos contaminantes envolvidos. Galbe e Zacchi (1992) apresentaram um estudo por simulação computacional, também utilizando o simulador Aspen Plus, do processo de produção de etanol a partir da hidrólise enzimática de material lignocelulósico, investigando o efeito do reciclo de água na redução de vinhaça e no aumento da concentração de etanol no destilado. Novamente não foram apresentados os contaminantes do processo.

## 1.2 – Fundamentos do equilíbrio de fase e simulação computacional

Todo processo de simulação computacional está baseado na solução de equações que representem o processo desejado. Assim, para a simulação de qualquer processo de destilação contínua, deve-se lançar mão de um modelo capaz de representar, na íntegra, os balanços globais e por estágio, de massa e energia do sistema de destilação em questão. Esse modelo baseia-se em um método rigoroso capaz de descrever uma coluna de destilação como um conjunto de equações matemáticas, denominadas equações MESH (Kister, 1992), possibilitando determinar as condições de operação de uma coluna de destilação. Estas equações definem completamente a coluna através de um balanço global de massa e de energia, além das equações de somatória que definem a composição das correntes de saída da coluna. Internamente, estas definem condições de equilíbrio de fase, composição estágio a estágio e balanço material e de energia em cada estágio. Sendo assim, as equações MESH convertem a coluna num conjunto de equações tendo como principais variáveis independentes a temperatura dos estágios, vazão interna de líquido e vapor e composição do estágio ou vazão por componentes de líquido e vapor, que devem ser satisfeitas para caracterizar a mesma. Maiores detalhes sobre as equações MESH podem ser encontradas em Kister (1992).

### 1.2.1 – Equilíbrio de Fase

A correta simulação de processos de destilação alcoólica está diretamente ligada à qualidade da descrição do equilíbrio líquido-vapor dos compostos envolvidos uma vez que a força de separação dos componentes no interior das colunas está relacionada com a diferença entre a concentração atual e a concentração nas condições de equilíbrio sendo, portanto, o equilíbrio de fase a principal fonte de erros em simulações de processos de separação (Faúndez and Valderrama, 2004).

Um sistema em equilíbrio é definido, normalmente, em termos da energia interna ( $U$ ), entalpia ( $H$ ), energia livre de Helmholtz ( $A$ ) e energia livre de Gibbs ( $G$ ), todos sendo potenciais termodinâmicos extensivos. No entanto, critérios mais

úteis podem ser obtidos quando se analisam as quantidades intensivas inerentes ao equilíbrio, temperatura (T), pressão (P) e potencial químico do componente  $i$  ( $\mu_i$ ), de tal forma que o equilíbrio mecânico e térmico é caracterizado quando a pressão e a temperatura dentro de um sistema estiverem uniformes em todas as suas fases (Sandler, 2006). Com as condições de equilíbrio térmico e mecânico definidas, pode-se escrever as equações que regem o equilíbrio de fases, mostradas a seguir.

$$T^I = T^{II} = \dots = T^\pi \quad (1.1)$$

$$P^I = P^{II} = \dots = P^\pi \quad (1.2)$$

$$\mu_i^I = \mu_i^{II} = \dots = \mu_i^\pi \quad (1.3)$$

onde  $i$ , é o componente e os sobrescritos  $I, II, \dots, \pi$ , representam as fases em equilíbrio.

A manipulação das equações 1.1, 1.2 e 1.3 permitem a dedução da equação fundamental para o equilíbrio de fases (Sandler, 2006) mostrada a seguir:

$$f_i^I = f_i^{II} = \dots = f_i^\pi \quad (1.4)$$

Na equação 1.4,  $f$  representa a fugacidade do componente  $i$  em sua respectiva fase.

De uma forma geral, o equilíbrio de fases líquido–vapor (ELV) é representado pela condição de igualdade das fugacidades de cada um dos componentes na mistura, representada pela Equação 1.5.

$$f_i^L = f_i^v \quad (1.5)$$

onde  $v$  e  $L$  representam as fases líquida e vapor do componente  $i$ .

A sistemática de cálculo do equilíbrio a partir da Equação 1.5 depende da abordagem empregada. Basicamente podem ser empregadas as abordagens "phi-phi" ( $\phi - \phi$ ) ou "gamma-phi" ( $\gamma - \phi$ ). Para o cálculo do ELV a abordagem  $\gamma - \phi$  é mais comumente empregada. Sendo assim, de acordo com Sandler (1999) pode-se escrever a fugacidade da fase líquida e vapor em termos dos coeficientes de atividade (fase líquida) e fugacidade (fase vapor) como mostrado nas Equações 1.6 e 1.7.

$$f_i^L = \gamma_i x_i f_i^0 \quad (1.6)$$

$$f_i^v = \phi_i y_i P \quad (1.7)$$

onde  $\gamma$  é o coeficiente de atividade do componente  $i$  na fase líquida,  $x$  é a fração molar do componente  $i$  na fase líquida,  $f_i^0$  é a fugacidade do líquido  $i$  puro à temperatura e pressão do sistema,  $\phi$  é o coeficiente de fugacidade do componente  $i$  na fase vapor,  $y$  é a fração molar do componente  $i$  na fase vapor e  $P$  é a pressão do sistema.

Aplicando o critério de equilíbrio descrito na Equação 1.5 tem-se:

$$\gamma_i x_i f_i^0 = \phi_i y_i P \quad (1.8)$$

A fugacidade do líquido puro a temperatura e pressão do sistema  $f_i^0$  pode ser descrita por:

$$f_i^0 = P_i^{vap} \phi_i^S \exp \int_{P_i^{vap}}^P \frac{V_i^L}{RT} dP \quad (1.9)$$

Substituindo (1.9) em (1.8) e assumindo que  $F_i$  seja descrito pela Equação 1.10 a seguir, tem-se:

$$F_i = \frac{\phi_i^S}{\phi_i} \exp \int_{P_i^{vap}}^P \frac{V_i^L}{RT} dP \quad (1.10)$$

$$\gamma_i x_i P_i^{vap} F_i = y_i P \quad (1.11)$$

onde  $P_i^{vap}$  é a pressão de vapor do componente  $i$  para a temperatura de equilíbrio e  $F_i$  denominado Fator de Poynting. Essa grandeza representa a influência da pressão na fugacidade da fase líquida. Assim, a temperaturas abaixo da crítica, um líquido pode ser considerado incompressível, sendo o efeito da pressão na fugacidade da fase líquida desprezível, de forma que o Fator de Poynting se aproxima da unidade. Da mesma forma, um líquido puro não associado, a pressões não muito elevadas, também apresenta um  $\phi_i^S$  próximo à unidade. Sendo assim, a equação que rege todo o cálculo do equilíbrio líquido-vapor em um sistema de destilação, a baixas pressões, pode ser resumida a Equação 1.12 representada a seguir:

$$\phi_i y_i P = \gamma_i x_i P_i^{vap} \quad (1.12)$$

Para o correto cálculo do equilíbrio e conseqüente minimização dos erros gerados nas simulações, modelos termodinâmicos capazes de descrever corretamente o coeficiente de atividade, fugacidade e a pressão de vapor devem ser selecionados. Neste trabalho, após uma cuidadosa seleção apresentada na dissertação para obtenção do título de mestre do mesmo autor (Batista, 2008), o modelo NRTL (Reid, 1987) e a equação do virial modificado pelo modelo de Hayden e O'Connell (1975) foram selecionados para o cálculo do coeficiente de atividade e fugacidade, respectivamente. Com relação ao modelo para o cálculo da pressão de vapor, o simulador Aspen Plus condiciona todos os cálculos ao modelo de Antoine estendido (Reid, 1987) apresentado na Equação 1.13 a seguir.

$$\ln P^{vap} = A + \frac{B}{C+T} + D \cdot \ln(T) + E \cdot T^F \quad (1.13)$$

onde  $P^{vap}$  é a pressão de vapor de um componente puro a uma determinada temperatura,  $T$  é a temperatura do sistema e  $A, B, C, D, E$  e  $F$  são parâmetros da equação que dependem do componente em questão. A equação estendida pode ser reduzida à equação original fazendo-se os valores das constantes  $D, E$  e  $F$  serem iguais a 0. A grande vantagem da equação estendida está no fato de que a mesma permite uma melhor correlação da pressão de vapor ao longo de toda faixa de temperatura, garantindo cálculos mais precisos.

O sucesso da separação por destilação depende, entre outros fatores, da volatilidade relativa dos componentes. Essa grandeza é definida como uma relação entre o coeficiente de partição de um componente em relação a outro (Prausnitz et al., 1999; Sandler, 1999) dado por:

$$\alpha_{jk} = \frac{\frac{y_j}{x_j}}{\frac{y_k}{x_k}} = \frac{\gamma_j P_j^{vap}}{\gamma_k P_k^{vap}} \quad (1.14)$$

onde  $\alpha_{jk}$  é a volatilidade relativa do componente  $j$  em relação ao componente  $k$ ,  $y$  é a fração molar da fase vapor do elemento correspondente,  $x$  é a fração molar do líquido do componente correspondente,  $\gamma_j$  é o coeficiente de atividade do composto na mistura e  $P^{vap}$  é a pressão de vapor do mesmo.

Volatilidades relativas muito maiores ou menores do que a unidade indicam que os componentes podem ser separados facilmente por destilação. Quando a volatilidade se aproxima da unidade, a separação fica comprometida, sendo necessárias alterações no processo produtivo como aumento do número de bandejas, aumento substancial da razão de refluxo, destilação extrativa ou azeotrópica, levando a um aumento do custo do processo. Para a destilação de alcoóis especiais, ou seja, alcoóis com menor teor de contaminantes, a volatilidade relativa tem papel fundamental. Tomando como base o etanol (componente de interesse) ou a água ou ambos, é possível classificar os contaminantes em três classes diferentes, de acordo com suas volatilidades: *componentes leves*, que possuem volatilidades maiores que a água e o etanol

independente do teor de etanol na mistura; *componentes intermediários* (alcoóis superiores) que tem sua volatilidade alterada dependendo do teor de etanol na mistura apresentando volatilidades maiores do que o etanol e a água, entre o etanol e água e menores do que o etanol e água; e *componentes pesados*, que apresentam volatilidade sempre menor que o etanol e a água independente do teor de etanol na mistura. Essa classificação é de suma importância para identificar o local de concentração desses componentes nas colunas de destilação e, assim, identificar as bandejas corretas para retiradas laterais nas colunas a fim de esgotar esses contaminantes. Uma descrição mais detalhada pode ser encontrada no Capítulo 2 e Capítulo 3.

### *1.2.2 – Simulação Computacional*

Devido à complexidade dos processos em engenharia, o uso de simulações, tanto para o aprimoramento de plantas industriais já existentes, quanto para os projetos de novas plantas, podem trazer inúmeros benefícios tais como: a economia de experimentos, permitindo o estudo de processos já existentes de forma mais rápida e econômica do que na planta real; a extrapolação das condições operacionais, pois, com o uso de ferramentas matemáticas é possível testar condições extremas de operação, difíceis de serem analisadas numa planta industrial real; o estudo da estabilidade do sistema, uma vez que é possível avaliar a resposta do sistema a distúrbios relevantes; o estudo da comutabilidade e determinação de políticas alternativas, sendo possível a introdução ou remoção de novos elementos no sistema, enquanto o mesmo é examinado.

Atualmente uma grande variedade de algoritmos para a simulação computacional de colunas de destilação pode ser encontrada em livros e publicações científicas. No entanto, todos esses métodos têm como fundamento a resolução das equações Mesh (Kister, 1992), apresentando técnicas numéricas diferenciadas para a solução das equações, o que define qual o melhor ou pior algoritmo (Gani et al., 1986; Luyben, 2006; Skogestad and Morari, 1988, Truong et al., 2010; Li et al., 2011). Portanto, por estar baseado em resolução numérica, o

número de componentes envolvidos no processo de destilação está diretamente ligada ao número total de equações a serem resolvidas e, portanto, influenciam diretamente a complexidade da simulação podendo causar problemas de convergência, dificultando todo o estudo. Assim, com o rápido desenvolvimento da informática nos últimos 20 anos e o avanço do desenvolvimento de ferramentas de simulação computacional de processos químicos, operações de transferência de calor e massa envolvendo misturas complexas podem ser facilmente avaliadas gerando resultados altamente confiáveis. Essa alta confiabilidade possibilita uma base sólida para a otimização do processo e sugestão de novas alternativas para as configurações das colunas destilação envolvidas no processo destilação para a produção de álcool, principal foco desse trabalho, possibilitando uma melhora na eficiência da operação de concentração e purificação do mosto de cana de açúcar, bem como da sua versão correspondente obtida pela fermentação e/ou hidrólise de material celulósico.

No entanto, para assegurar a confiabilidade das análises de processo via simulação computacional, um criterioso estudo do processo deve ser feito de forma a caracterizar todas as etapas envolvidas em seus pormenores. Assim, no caso dos processos de destilação alcoólica, uma caracterização das correntes de entrada e saída (temperatura, composição, pressão), informações relativas ao equipamento (número de bandejas, eficiência de bandejas, consumo de vapor) e outras peculiaridades do processo, devem ser exaustivamente estudadas para que o simulador consiga reproduzir de maneira confiável o processo em questão. Dessa forma, uma etapa de validação experimental de algum processo real se faz absolutamente necessária, principalmente quando a simulação é utilizada com o objetivo do desenvolvimento de um novo processo, visando garantir a confiabilidade dos resultados gerados pela simulação. No caso deste trabalho, uma validação experimental do processo de produção de álcool hidratado carburante foi realizada tendo como base informações colhidas na usina Santa Adélia, localizada na cidade de Jaboticabal no interior de estado de São Paulo. Maiores detalhes podem ser obtidos no Capítulo 3.

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## Capítulo 2

# Computer simulation applied to studying continuous spirit distillation and product quality control <sup>1</sup>

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## Abstract

This work aims to study continuous spirit distillation by computational simulation, presenting some strategies of process control to regulate the volatile content. The commercial simulator Aspen (Plus and dynamics) was selected. A standard solution containing ethanol, water and 10 minor components represented the wine to be distilled. A careful investigation of the vapor-liquid equilibrium was performed for the simulation of two different industrial plants. The simulation procedure was validated against experimental results collected from an industrial plant for bioethanol distillation. The simulations were conducted with and without the presence of a degassing system, in order to evaluate the efficiency of this system in the control of the volatile content. To improve the efficiency of the degassing system, a control loop based on a feedback controller was developed. The results showed that reflux ratio and product flow rate have an important influence on the spirit composition. High reflux ratios and spirit flow rates allow for better control of spirit contamination. As an alternative to control the volatile contents, the degassing system was highly efficient in the case of low contamination. For a wine with high volatile contamination, the pasteurized spirit distillation unit was the best alternative.

Keywords: Spirits, distillation, simulation, Aspen Plus, degassing, control

## 2.1 – Introduction

Spirit beverages are produced by fermentation and distillation of different raw materials in many places around the world. Examples include *Whisky*, a typical UK spirit (Scotland, Ireland) produced by distillation of fermented grain mash and aged in wooden casks (Piggott et al., 1993; Gaiser et al., 2002; Suomalainen et al., 1974), *Rum*, a typical Caribbean drink produced by distillation of sugar cane molasses and aged in oak barrels (Pino, 2007; Porto & Soldera, 2008), *Vodka*, a typical Russian beverage obtained by distillation of alimentary ethanol from grain or potato fermented must, usually distilled to higher alcohol graduation and afterwards diluted (Savchuk et al., 2007; Legin et al., 2005) and *Cachaça* (ca-sha-sa), a

typical Brazilian spirit produced by the distillation of fermented sugar cane juice, with an alcoholic graduation within the range of 38% to 54% by volume (Brazil, 2005; Cardoso et al., 2003; Scanavini et al., 2009).

In general, the main differences between these spirits are the alcoholic graduation and the concentration of the congeners (minor compounds) in the beverage, as shown in Table 2.1. Usually these congeners, present in low concentrations ( $10^{-6}$  to  $10^{-4}$  mg/L) in the fermented *must* and in the beverage, are responsible for characterizing each type of spirit (Valderrama et al., 2002). The main congeners produced during fermentation are alcohols (methanol, propanol, and isoamyl alcohol), organic acids (acetic acid), carbonyl compounds (acetaldehyde) and esters (ethyl acetate) (Lurton et al., 1995). Table 2.1 shows some quality standards for different spirit beverages produced around the world according to their respective country legislation. In the case of aged spirits the alcohol content by volume of the distillate is higher, for instance: aged cachaça, distilled to 75 °GL, and whisky distilled to 93-96 °GL. After aging the spirit is diluted to the desired alcohol graduation.

Table 2.1 - Spirit quality standards

Component	Spirit (Country)					
	Cachaça (Brazil) <sup>a</sup>	Tequila (Mexico) <sup>b</sup>	Rum (Ecuador) <sup>b</sup>	Aguardiente (Spain) <sup>b</sup>	Vodka (Ukraine) <sup>b</sup>	Whisky <sup>b,d</sup>
Alcohol Graduation ( °GL )	38 – 54	38 – 55	35 – 48	79.5	38 – 40	40 – 50
Volatile acidity, in acetic acid (mg/100ml AETH <sup>c</sup> )	0 – 150	-	0 – 100	-	-	0 – 60
Esters, in ethyl acetate (mg/100ml AETH <sup>c</sup> )	0 – 200	2 – 270	0 – 100	0 – 100	0 – 18	5 – 70
Aldehydes, in acetaldehyde (mg/100ml AETH <sup>c</sup> )	0 – 30	0 – 40	0 – 20	0 – 20	0 – 3	2 – 12
Superior Alcohols (mg/100ml AETH <sup>c</sup> )	0 – 360	20 – 400	0 – 150	0 – 900	0 – 2	50 – 250
Methanol (mg/100ml AETH <sup>c</sup> )	0 – 20	30 – 300	0 – 10	0 – 80	0.03% (v/v)	0 - 15

<sup>a</sup> Brasil (2005); <sup>b</sup> Distill (2007); <sup>c</sup> Anhydrous Ethanol; <sup>d</sup> Ecuador, EUA, Scotland, Ireland

Carbonyl compounds are responsible for the most volatile aroma fraction of alcoholic beverages. The presence of these compounds is highly desirable but if their concentration is very high, the quality of the spirits is diminished and some problems for the health of consumers are generated (Nykanen, 1986). One of

these problems is the “hangover” syndrome caused by high levels of acetaldehyde (Nascimento et al., 1998);

Ethanol is the predominant alcohol found in spirit beverages and is responsible for their body. Higher alcohols, such as isoamyl alcohol, isobutanol, propanol and isopropanol, are the main group responsible for the spirit flavor. Isoamyl alcohol typically represents half the amount of higher alcohols (Oliveira, 2001). Propanol concentration is usually low in high quality spirits (Nykanen, 1986). Methanol is another alcohol that requires strict control since high ingestions of this compound can cause severe intoxication (Paine and Dayan, 2001).

The complexity of the fermented must makes it difficult to study the spirit distillation process. Nowadays computational simulators are able to accurately represent the most complex industrial processes. Using the commercial software PRO/II, Haypek et al. (2000) simulated an industrial plant for distilling aroma compounds evaporated during orange juice concentration. The feed stream was composed of 15 minor aroma compounds plus water, and the simulated results showed good agreement with the composition values measured in an industrial plant. Ceriani and Meirelles (2006, 2007) and Ceriani et al. (2008) simulated batch and continuous deodorizers for edible oils refining. Vegetable oils, such as palm, coconut, canola and sunflower oils, were considered as complex mixtures of fatty acids and acylglycerols with more than 50 components. Chemical reactions, such as transisomerization of unsaturated fatty components, were also taken into account. The obtained results are compatible with prior experimental data reported in the literature. Meirelles et al. (2008) also simulated the production of essential oils and spirits; they concluded that simulation tools helped to improve and optimize the distillation process of complex natural mixtures. When simulating batch distillation of Pisco, a typical spirit of Chile and Peru, Osório et al. (2005) optimized the process in terms of the preferences of enologists and specified the best operational conditions for the batch distillation column. Gaiser et al. (2002) tested the commercial software Aspen Plus for simulating whisky production by continuous distillation using a complex mixture composed of ethanol, water and 4

congeners to represent the grain fermented juice. They concluded that Aspen Plus was able to accurately represent continuous whisky distillation.

*Cachaça* is a typical Brazilian spirit produced by distillation of the sugar cane fermented juice, called must or wine, to an alcoholic content within the range of 38 to 54 °GL (Brasil, 2005). This wine is a hydroalcoholic mixture composed mainly of water and ethanol, but also containing a large number of minor components known as *congeners* (see Table 2.2). These congeners, in specific concentration ranges, are responsible for the highly appreciated sensory characteristics in the spirit. On the other hand, in higher concentrations they can reduce the commercial value and cause harm to the consumer's health.

Table 2.2 - Main components in industrial sugar cane wine (must)

Component	Boiling Point (°C)	Concentration range (w/w)	Fixed Value	Reference
Water	100.0	0.92–0.95	0.932000	By difference
Ethanol	78.40	0.05–0.08	0.066150	Oliveira (2001)
Methanol	64.70	0.0–3.0·10 <sup>-8</sup>	3.200·10 <sup>-07</sup>	Boscolo et al. (2000)
Isopropanol	82.40	1.020·10 <sup>-6</sup>	1.020·10 <sup>-06</sup>	Cardoso et al. (2003)
Propanol	97.10	(2.1–6.8)·10 <sup>-5</sup>	3.360·10 <sup>-05</sup>	Oliveira (2001)
Isobutanol	108.00	(1.3–4.9)·10 <sup>-5</sup>	2.780·10 <sup>-05</sup>	Oliveira (2001)
Isoamyl alcohol	132.00	(2.7–18.8)·10 <sup>-5</sup>	1.425·10 <sup>-04</sup>	Oliveira (2001)
Ethyl Acetate	77.10	(5.5–11.9)·10 <sup>-6</sup>	7.690·10 <sup>-06</sup>	Oliveira (2001)
Acetaldehyde	20.20	(1.0–8.3)·10 <sup>-5</sup>	1.580·10 <sup>-05</sup>	Oliveira (2001)
Acetone	56.53	-	1.500·10 <sup>-05</sup>	Estimated
Acetic Acid	118.10	(3.3–99.3)·10 <sup>-4</sup>	4.351·10 <sup>-04</sup>	Oliveira (2001)
CO <sub>2</sub>	-78.00	-	1.100·10 <sup>-03</sup>	Estimated

A typical industrial installation for continuous *cachaça* distillation is presented in Figure 2.1. The distillation column has a small rectifying section, composed of 2 or 3 trays, and a stripping section composed of 16 to 18 trays. No side stream for removal of higher alcohols (propanol, isopropanol, isobutanol and isoamyl alcohol) is necessary and normally a small reflux ratio is required for attaining the product specifications. Almost all ethanol fed to the column is recovered in the distillate stream. The bottom product should have a maximum ethanol content around 0.02% in mass, which corresponds to a loss of approximately 0.3 to 0.6% of the total ethanol fed to the distillation equipment.

Control of the volatile content (aldehydes, methanol, ketones and esters) present in the spirit is a very important factor in regards to product quality and food

safety for consumers, because of the association of these components to special beverage sensorial characteristics and some diseases (Nykanen, 1986; Nascimento et al., 1998). Changes in the equipment configuration are sometimes required in order to control the volatile concentration in the beverage. One of these changes is the inclusion of a *degassing system* as indicated in Figure 2.1 by the dashed line. This system is based on the association of two or more partial condensers at the top of the column. The vapor stream of each partial condenser is fed into the next condenser and the liquid streams return to the top of the column. In the last condenser, a small portion of the vapor phase is withdrawn as a degassing stream. According to the volatile concentration of the spirit, the temperature of the last condenser can be varied to generate a larger or smaller degassing stream, decreasing the volatile concentration in the spirit. Since it is used only for product quality control, the degassing flow rate is always very low in order to avoid significant ethanol losses.

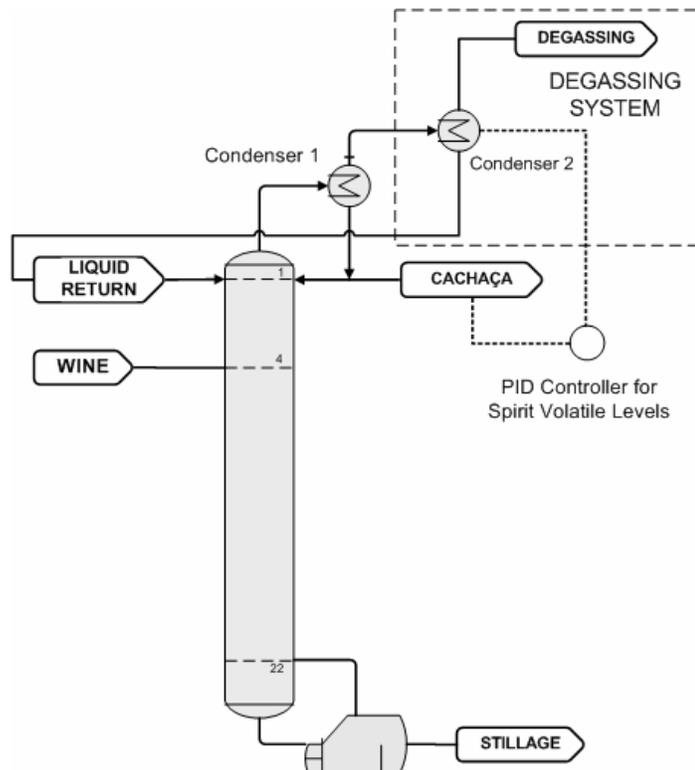


Figure 2.1 - Typical industrial installation for continuous cachaça production

Most of the research on spirit's production reported in the literature is focused on the sensorial quality of the beverage (Soufleros et al., 2004; Ledauphin

et al, 2006; Madrera et al, 2010 Piggott et al., 1993), but recently a modest effort has been undertaken to evaluate the influence of the distillation process on product quality. Taking this into account, the present work used the computational simulation to investigate the continuous distillation of a standard solution containing ethanol, water and ten minor compounds, aiming to improve product quality and process performance. For this objective, the prediction of phase equilibrium was improved by readjustment of the NRTL interaction parameters related to the minor components present in the wine, the process simulation using those interaction parameters was validated against experimental information collected from a industrial plant, the sensitivity of process simulation to changes in the interaction parameters was investigated, the performance of a typical industrial plant for continuous cachaça (Brazilian spirit) distillation was thoroughly investigated, considering the effects of spirit flow rate, reflux ratio, degassing system and second alcohol flow rate upon product quality, and finally a control loop was suggested for maintaining volatile components within the quality requirements for the final product.

## 2.2 - Material and Methods

### 2.2.1 – Vapor-Liquid Equilibrium

The complexity of the fermented must, due to its multicomponent composition and low concentration of congeners, makes difficult accurate prediction of the vapor-liquid equilibrium and it can be considered the main source of errors in the simulation of distillation processes (Faúndez and Valderrama, 2004). Taking this into account, the first step of this work was to thoroughly investigate the vapor-liquid equilibrium of the alcoholic wine.

The vapor-liquid equilibrium is given by the equality of fugacities in both phases, as described in Eq. 2.1 (Prausnitz et al, 1980; Sandler, 1999).

$$\phi_i y_i P = \gamma_i x_i P_{vpi} \quad (2.1)$$

Where,  $y_i$  is the molar fraction of component  $i$  in the vapor phase,  $P$  is the total pressure of the system,  $\gamma_i$  is the activity coefficient of component  $i$  in the liquid phase,  $x_i$  is the molar fraction of component  $i$  in the liquid phase,  $P_{vpi}$  is the vapor pressure of component  $i$  at the system temperature, and  $\phi_i$  the fugacity coefficient of component  $i$  in the vapor phase.

In the present case the NRTL model was chosen for calculating the activity coefficients ( $\gamma_i$ ) and the Virial equation, with the Hayden and O'Connell model (Hayden and O'Connell, 1975), was used to estimate the fugacity coefficients.

In order to check and eventually improve the representation of the vapor-liquid equilibrium (VLE) the following procedure was used. Experimental data for binary mixtures containing wine components (see Table 2.2) were collected from literature sources (Gmehling and Onken, 1981; Murti and Van Winkle, 1958; Freshwater and Pike, 1967; Resa et al., 1997; Ortega and Hernández, 1999; D'Avila and Silva, 1970; Bernetová et al., 2006). From 66 binary mixtures required for describing the wine VLE, experimental data were available for 43 mixtures. In such cases the equilibrium was calculated using the NRTL interaction parameters available in the Aspen Plus databank and compared with the experimental data. When the average absolute deviation ( $|\overline{\Delta y}|$ ) between experimental and calculated data was larger than 0.03, the NRTL parameters were readjusted on the basis of the corresponding experimental data. The above indicated deviations were calculated according to Eq. 2.2 below:

$$|\overline{\Delta y}| = \frac{\sum (y_{\text{experimental}} - y_{\text{calculated}})}{n} \quad (2.2)$$

Where  $y$  is the vapor phase concentration and  $n$  is the number of experimental points for the binary mixture.

For the others 23 binary mixtures without any reported experimental data available in literature, the Aspen Plus NRTL parameters were used since they were already available in the software databank or could be estimated using the UNIFAC group contribution method. These estimated parameters included all

binary mixtures with CO<sub>2</sub> and some others, such as acetaldehyde/isobutanol, acetone/isoamyl alcohol, and acetic acid/isoamyl alcohol.

Carbon dioxide is produced during fermentation and may have an important impact on the wine vapor-liquid equilibrium. In order to estimate its concentration in the wine it should be considered that industrial fermentation is conducted in closed vessels under a light over pressure (gauge pressure of 600 to 800 mm of water column) and temperature near 32 °C. Assuming that the gas phase inside the vessel is composed of carbon dioxide saturated with water and ethanol vapors, the carbon dioxide solubility in a wine with 8 °GL was estimated as varying within the range of 1050 to 1100 mg CO<sub>2</sub>/kg of wine. These estimated values were based on the NRTL model for ethanol-water mixtures and the Henry constants reported by Dalmolin et al. (2006) for CO<sub>2</sub> dissolved in hydroalcoholic solutions. An average value of 1100 mg CO<sub>2</sub>/kg of wine was selected for the wine composition (see Table 2.2).

Using the selected NRTL parameters, the relative volatilities for wine components ( $\alpha_{jk}$ ) were calculated according to Eq. 2.3.

$$\alpha_{jk} = \frac{y_j / x_j}{y_k / x_k} = \frac{\frac{\gamma_j P_j^{vp}}{\phi_j}}{\frac{\gamma_k P_k^{vp}}{\phi_k}} \quad (2.3)$$

Where  $\alpha_{jk}$  is the relative volatility of component  $j$  in relation to  $k$ ,  $x$  is the liquid phase concentration,  $\gamma$  is the liquid phase activity coefficient,  $\phi$  is the vapor phase fugacity coefficient and  $P^{vp}$  is the vapor pressure.

In order to obtain a better insight on the behaviors of the different congeners during alcoholic distillation, the relative volatilities of these compounds were calculated with the Aspen Plus simulator, using an isobaric flash drum at 1 atm. The congeners were always assumed to be at very low concentrations (mass fractions between 10<sup>-4</sup> and 10<sup>-6</sup>) and the ethanol concentration of the hydroalcoholic solution fed into the flash drum varied along the entire range of

mass fractions ( $10^{-4}$  to 0.99). According to the observed behaviors the congeners could be classified as *light components* when presenting volatility greater than ethanol, *intermediate volatility compounds* when their volatilities are greater than water but lower than ethanol and *heavy components* when they have volatility lower than water.

### 2.2.2 – Validation of the Process Simulation

In order to check whether the results generated by computational simulation are reliable, an experimental validation of the process simulation was conducted, comparing the obtained results with the information collected in an industrial plant. For this purpose experimental samples and data were collected from the industrial plant of Santa Adélia Mill, located in Jaboticabal town, State of São Paulo, Brazil. This industrial plant produces  $300 \text{ m}^3$  of anhydrous ethanol in a daily basis and is composed of three main parts, a stripping unit for recovering ethanol from the wine, an enriching section for concentrating ethanol up to the azeotropic point and a dehydration unit. The stripping unit is fed with the alcoholic wine and produces phlegm with ethanol content around 0.28 by mass and stillage with a very low ethanol composition. The main parts of the stripping unit are named, in the industrial practice, columns A, A<sub>1</sub> and D (Batista and Meirelles, 2009). In the case of Santa Adélia Mill, column A has 16 trays, column A<sub>1</sub> 8 trays and column D 6 trays. The recovery of ethanol from the wine is performed mainly in column A, while columns A<sub>1</sub> and D are used for extracting very light contaminants (acetaldehyde, ethyl acetate, etc.) from the liquid phase, withdrawing a very low stream as top product when high purity concentrated ethanol is being produced. In contrast to the prior situation, when ethanol for biofuel purposes is being produced, the light components are not extracted because the purity standards are not so high. In this case no top product is withdrawn and total reflux is used in the top of column D. Wine, at 94 °C and with a flow rate of  $100 \text{ m}^3/\text{h}$ , is fed into the top of column A1, corresponding to tray 24 (T24) counting from the bottom tray of the whole stripping unit. Phlegm is withdrawn from tray 16 (T16) and stillage from the bottom of this unit.

When no top product is withdrawn from column D, this stripping unit operates in a way similar to a distillation unit for *cachaça* production, except for the small rectifying section present in equipment used for distilling this spirit. In fact, both equipment have as main purpose the stripping of ethanol from the wine. Taking into account the similarity of this unit with a distillation unit for *cachaça* production, the validation of the process simulation focused the correct description of this stripping unit. For this purpose some sampling points were installed in tray 17 (T17), corresponding to the bottom of column A<sub>1</sub>, tray 16 (T16), corresponding to the top of column A, and tray 10 (T10). Samples of wine, phlegm and stillage were also collected. All samples were analyzed by gas chromatography (GC), as described below. Additional information about the temperatures of trays 16 and 1 (stillage withdrawal) was also acquired as well as information about the temperature and flow rate of the input stream. Using the input information mentioned above a static simulation was conducted with the Aspen Plus simulator and the simulated results compared with the experimental compositions and temperatures of those selected trays and output streams.

#### *2.2.2.1 - GC Analysis*

All the samples collected were filtered on filter paper with 0.2 µm of porosity. After clarification, the samples of trays T17, T16, T10 and of phlegm were weighed in glass flasks of 5 ml, and diluted with Milli-Q water (Millipore) using a ratio of 40 mg of original sample to 1 ml of final mixture. For samples of stillage and wine, by virtue of its low components concentration, the dilution ratio was adjusted to approximately 100 mg of original sample to 1 ml of final mixture.

The GC analysis was performed in a Capillary Gas Chromatograph model Shimadzu 6850 SERIES equipped with an autosampler and with a flame ionization detector (FID). The components of the liquid samples were separated in a column DB-624 crosslinked (6% cyanopropyl-phenyl 94% dimethylpolysiloxane) with dimensions of 60 m of length, 0.25 mm of internal diameter and 1.4 µm of film thickness. After several tests, the best column operational conditions was determined as follows: pressure column of 215 kPa (isobaric); injector and detector

temperature was fixed at 210 °C; the volume of sample injection was set at 1.5 µl with a split ratio of 1:30; the flow of carrier gas (helium) in the column was set at 2.4 ml/min with a linear velocity of 35 cm/s; the temperature gradient started at 40 °C (four minutes); 1 °C/min until 80 °C; 10 °C/min until 180 °C, staying at this temperature for five minutes.

The components were quantified by the external standard technique through the construction of calibration curves to eleven components. All standard components were chromatographic grade produced by Sigma Aldrich, with purity  $\geq$  99.9%. Calibration curves were constructed using eight points, analyzed in triplicate, for the following components and their respective range concentrations: Acetaldehyde (1220-0.3 mg/l), Methanol (1110-0.3 mg/l), Ethanol (41000-0.2 mg/l), Acetone (800-0.3 mg/l), Isopropyl alcohol (1000-0.3 mg/l), Propanol (3500-0.3 mg/l), Ethyl Acetate (1000-0.3 mg/l), Isobutanol (3600-0.3 mg/l), Acetic Acid (500-0.3 mg/l) and Isoamyl Alcohol (7500-0.3 mg/l). It was observed that all components produced identifiable peaks when their concentrations were higher than 0.1 mg/l (0.000001 in mass fraction), being this value fixed as a lower detection limit. The composition of the industrial wine was used as the feed stream for the simulation run performed for validation purpose. In case of minor components not identified during the wine GC analyses, their composition in the feed stream was fixed at the minimum chromatography detection limit value. Its occurs, for instance, for isopropyl alcohol. The mass fraction of water was quantified by difference.

### 2.2.3 – *Simulation of Spirit Production*

Static simulations were conducted with the Aspen Plus simulator, using the RADFRAC package. This package uses the MESH equations (Kister, 1992) for rigorously calculating distillation columns. Initially, an industrial plant without degassing system (see Figure 2.1) was investigated. The distillation column has 23 stages, including reboiler and condenser, and the tray efficiency was fixed at 0.7 (70%). Wine was fed at stage 4 (numbered from top to bottom) with mass flow of 10000 kg/h and temperature of 97 °C. The wine composition is given in Table 2.2. Column top and bottom pressures were fixed at 100 kPa and 137.4 kPa,

respectively. The spirit mass flow and reflux ratio were varied from 1000 to 2000 kg/h and 0.001 to 1.5, respectively. In sequence, the *degassing system* was included and strategies for controlling the spirit volatile content were investigated. Acetaldehyde and ethyl acetate concentrations in wine were increased to 26 mg/kg and 175 mg/kg, respectively, in order to generate the risk that their concentrations in cachaça may be outside the range of values fixed by the Brazilian legislation (see Table 2.1). The temperature of the final condenser in the degassing system was varied from 25 to 75°C in order to produce a larger or smaller degassing flow rate, expressed as a spirit (distillate) percentage, so that its influence on spirit volatile content, spirit alcohol graduation and ethanol losses in the degassing stream could be investigated. Furthermore, a control loop based on feedback control (PID) was developed using Aspen Dynamics. The temperature of the final condenser was manipulated in order to control spirit's volatile content. The control loop response was tested via a disturbance in the wine acetaldehyde and ethyl acetate concentrations.

Finally, a distillation column configuration based on the work of Whitby (1992) and presented by Gaiser et al. (2002) was tested. This column, shown in Figure 2.2, is a typical industrial installation for whisky production. It has 35 stages in the rectifier section and 27 stages in the beer stripper. Spirit is withdrawn from stage 8 (from the top) and fusel oils (higher alcohol) from stage 33. Ethanol is separated from fusel oil in a simple side column with 10 plates, where the aqueous phase is withdrawn from the top and the organic phase from the bottom. At the top of the main column, a small stream (called second alcohol stream), rich in volatile compounds, was withdrawn. The liquid phase from the degassing system is recycled to the first tray of the main column, and the aqueous phase from fusel oil sidestream is pumped back to the feed to the main column. This configuration is particularly appropriate for producing spirits with high alcohol graduation, mainly those submitted to an aging process, such as whisky and aged cachaça. In the present study this system was named *pasteurized spirit distillation unit*.

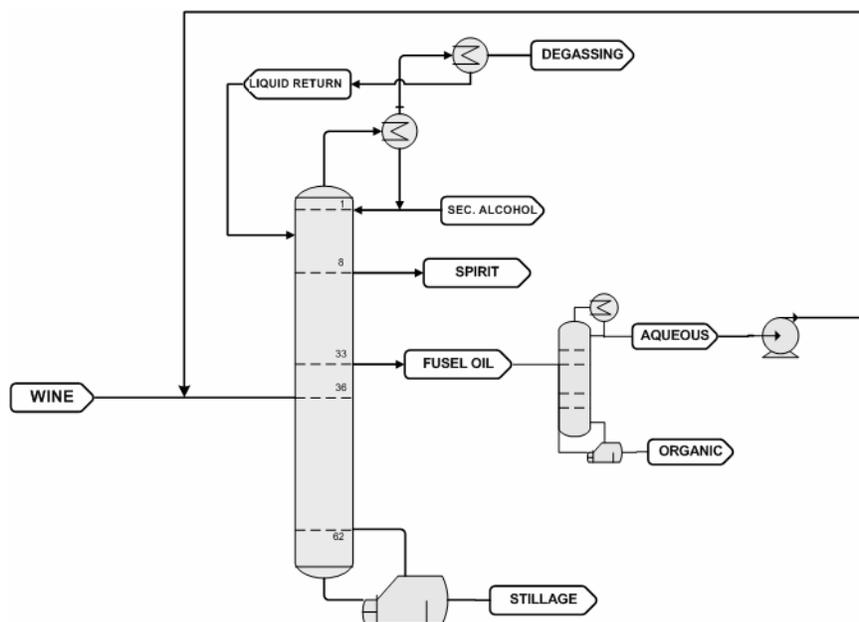


Figure 2.2 – Pasteurized spirit distillation unit

#### 2.2.4 – Sensitivity analysis to the NRTL binary interaction parameters

Aiming to verify the sensitivity of the distillation process state variables in relation to the NRTL binary interaction parameters, a sensitivity analysis was performed taking into account a fermented must containing water, ethanol and one congener of each component class mentioned before, i.e. light components (Acetaldehyde), intermediate volatility compounds (Isoamyl Alcohol) and heavy components (Acetic Acid). To perform this sensitivity analysis some simulations were conducted with the same operational conditions presented in the Spirits Production topic above and with the wine containing ethanol and the three minor components indicated before with the same concentrations shown in Table 2.2. In these simulations a change of  $\pm 5\%$  in the values of the NRTL binary interaction parameters was considered. The liquid phase mass fractions of those components in all column trays and the temperature of these trays were compared to the simulation results performed with the NRTL original parameters. An absolute deviation, calculated in relation to the values obtained with the NRTL original parameters, was obtained following Eq. 2.4 below.

$$\varepsilon = \frac{\sum |S_0 - S_1|}{n} \quad (2.4)$$

Where  $\varepsilon$  is the deviation value,  $S_0$  is the value of the distillation process state variable (compositions or temperatures) obtained with the NRTL original binary parameters,  $S_1$  is the value of state variable obtained taking into account a change of  $\pm 5\%$  in the NRTL parameters and  $n$  is the number of column trays.

## 2.3 - Results and discussion

### 2.3.1 – Vapor-liquid equilibrium

For calculating the vapor phase non-ideality, the Virial equation of state coupled with the Hayden and O’Connell model (Hayden and O’Connell, 1975) was used. This approach is the most appropriate, especially in the case of binary mixtures containing acetic acid, since this organic compound dimerizes in the vapor phase.

In the case of activity coefficients calculated by the NRTL equation, interaction parameters were readjusted for 33 binary mixtures from the set of 43 mixtures with experimental data available in literature. Before readjustment, the average absolute deviation for the vapor phase molar fraction was 0.0130 (maximum of 0.0570). After the necessary readjustment, the average absolute deviation was reduced to 0.0085 (maximum of 0.0282). In the case of equilibrium temperature, the average absolute deviation was 0.78 °C (maximum of 2.53 °C) before readjustment and 0.40 °C (maximum 1.72 °C) after. As shown by the results, the new NRTL interaction parameters could significantly reduce the deviations in the phase equilibrium calculations, a result that contributes to a more reliable process simulation.

Figure 2.3a presents the relative volatility of the *light elements* in relation to water for different ethanol mass fractions in the liquid phase. These light elements are generally represented by aldehydes (acetaldehyde), ketones (acetone) and esters (ethyl acetate). As can be observed, the relative volatilities of light

components decreases steadily as the ethanol concentration in the mixture increases, but their values are always greater than one; this means that these components tend to be concentrated in the vapor phase. Figure 2.3b presents the relative volatility of ethanol and methanol, two light elements, and acetic acid, a heavy element, in relation to water. Methanol is more volatile than water along the entire concentration range, but ethanol volatility approaches one for concentrations within the mass fraction range of 0.9-1.0, because of the azeotropic behavior of ethanol-water mixtures. Based on Figure 2.3a and b it is possible to conclude that acetaldehyde, acetone and ethyl acetate are also more volatile than ethanol for the whole range of concentrations. Because of this characteristic, these components tend to concentrate at the top of the column, significantly affecting spirit quality. Methanol has a volatility relatively close to that of ethanol, showing values slightly lower in the ethanol diluted region (ethanol mass fraction in liquid phase lower than 0.47) and slightly higher in the ethanol concentrated region. This occurs because the larger ethanol activity coefficient in the diluted region compensates the larger values of methanol vapor pressure. In any case, methanol-ethanol separation is difficult since their relative volatility is small and they tend to exhibit a similar distillation behavior. Fortunately, methanol concentration in wine is usually very low, except when sources of methoxilated pectins are added to the must before fermentation (Meirelles et al, 2008). The volatility of acetic acid is always lower than water and ethanol (see Figure 2.3b), so this component concentrates in the column bottom and is mostly eliminated in the stillage (vinasse).

Figure 2.3c and d show the relative volatility of the higher alcohols in relation to water. These components exhibit a decrease in volatility as the ethanol concentration in the liquid phase increases, acting as light components in the ethanol diluted range and as heavy components in the ethanol concentrated range. Because of this behavior they should be classified as components with intermediate volatility. Although the higher alcohols present vapor pressures always lower than the corresponding values for ethanol, they are more volatile than ethylic alcohol in the ethanol diluted concentration range because their activity coefficients in aqueous solutions tend to be very large. As the ethanol

concentration in the liquid phase increases, these activity coefficients decrease steadily and the same occurs for their volatilities

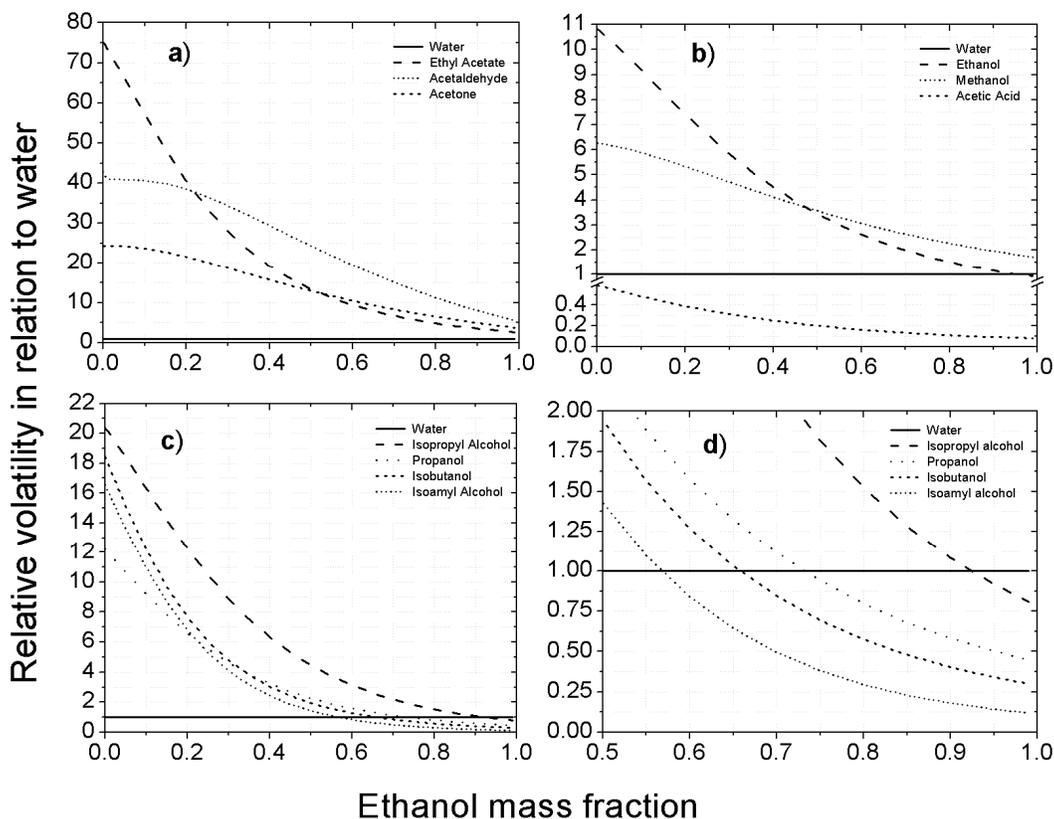


Figure 2.3 - Relative volatility for the wine components in relation to water.

### 2.3.2 – Validation of Process Simulation

As mentioned above, the samples from the industrial plant for alcohol distillation were analyzed by GC. Linear calibration curves were obtained for all standards with high values of determination coefficients ( $R^2$ ), always higher than 0.992. Aiming to verify the reproducibility of the calibration curves two different solutions, containing water, methanol, ethanol, propanol, acetic acid and isoamyl alcohol at known concentrations, were analyzed by GC. A maximum deviation between the value obtained by the GC analysis and the original composition of the above mentioned mixtures was obtained for acetic acid and this deviation has a value of 15%. A higher deviation was expected in case of acetic acid because the selected chromatographic column is not so appropriate for analysis of organic acids due to its relatively low polarity. This column was selected because it is the

most appropriate for ethanol and for all other minor compounds. For this reason the deviations for other components were much lower, with a maximum value of 5.5% and an average value of 2.5%. Such results indicate a very good quality of the experimental analysis when one takes into account the range of compositions for some minor compounds, with values sometimes lower than  $1.7 \cdot 10^{-4}$  in mass fraction, for isoamyl alcohol for instance. The comparison of the compositions of the experimental samples analyzed by GC and the simulated results was performed in terms of the mass fractions of water, ethanol and of the minor components as a group, as well as in terms of the temperatures of some trays. Table 2.3 presents the comparison between experimental and simulated values.

Table 2.3 – Simulated and experimental values (compositions in mass fractions)

		<b>Ethanol</b>	<b>Water</b>	<b>Minor Components</b>	<b>Temperature (°C)</b>
<b>Wine</b>	Exp <sup>1</sup>	0.057516	0.941822	0.000662	-
<b>T25</b>	Exp <sup>1</sup>	0.524082	0.465191	0.010727	-
	Sim <sup>2</sup>	0.530174	0.458927	0.010899	-
<b>T23</b>	Exp <sup>1</sup>	0.448853	0.540000	0.011147	-
	Sim <sup>2</sup>	0.457914	0.530161	0.011925	-
<b>T17</b>	Exp <sup>1</sup>	0.064354	0.935112	0.000534	-
	Sim <sup>2</sup>	0.063200	0.936111	0.000689	-
<b>T16</b>	Exp <sup>1</sup>	0.042423	0.957302	0.000275	104.0
	Sim <sup>2</sup>	0.046918	0.952727	0.000355	103.0
<b>T10</b>	Exp <sup>1</sup>	0.004325	0.995652	0.000023	-
	Sim <sup>2</sup>	0.004972	0.995011	0.000017	-
<b>Stillage</b>	Exp <sup>1</sup>	0.000394	0.999326	0.000280	108.2
	Sim <sup>2</sup>	Trace <sup>3</sup>	0.999700	0.000300	108.7
<b>Phlegm</b>	Exp <sup>1</sup>	0.283419	0.714623	0.001958	104.0
	Sim <sup>2</sup>	0.286600	0.711715	0.001685	103.0

<sup>1</sup> Exp – Experimental values

<sup>2</sup> Sim – Simulation result

<sup>3</sup> Trace  $\leq 10^{-6}$  mg/mg (Aspen Technology, 2003)

Table 2.3 shows that the simulated and experimental values for water and ethanol mass fractions are very close to each other respectively. The same was observed for the temperatures. Such results indicate that the simulator is able to reproduce with good accuracy the behavior of the mass fractions of the major components and of the temperatures measured in an industrial plant for bioethanol distillation. For the congeners, represented in Table 2.3 as a group of components, the experimental and the corresponding simulated values always have the same order of magnitude, even in the case of very low experimental mass fractions, such as the value observed in tray T10 (0.000023). Nevertheless, the relative deviations

are higher, attaining values around 30% in case of trays T25, T17 and T16. Table 2.4 gives the complete experimental and simulated compositions for the phlegm and stillage stream. As can be seen, the experimental and simulated results for all minor components have the same order of magnitude, although the deviations are high, in relative terms.

Considering all the results obtained in this validation test it is possible to conclude that, for the major components and for temperatures, the simulation results are correct from a qualitative as well as a quantitative point of view. In case of the minor components, process simulation should be considered as able to provide good qualitative results that reproduce correctly the major trends of their distillation behavior, but does not give low deviations in relation to the experimental values. However, it should be noted that for all components with mass fraction below the chromatography detection limit, with the exception of isopropyl alcohol, the simulated results are below  $10^{-12}$  or  $10^{-6}$ . Furthermore, it should be considered that isopropyl alcohol was not detected in the industrial wine and, in fact, one does not know whether this component is not present in the wine or its composition is below the minimum GC detection limit. Taking into account that the experimental and simulated results for all minor components have the same order of magnitude, the simulation results can be considered as a reliable estimate of their distillation behavior and of its dependence on the operational conditions and equipment design.

Table 2.4 – Experimental and simulated compositions for Phlegm and Stillage

Component	Phlegm		Stillage	
	Experimental	Simulated	Experimental	Simulated
Acetaldehyde	< DL <sup>1</sup>	$1.121 \cdot 10^{-8}$	< DL	Trace <sup>2</sup>
Methanol	0.0000499	0.0000802	< DL	Trace
Ethanol	0.2834743	0.2866373	0.0003636	$8.540 \cdot 10^{-8}$
Acetone	< DL	0.0000003	< DL	Trace
Isopropyl Alcohol	< DL	0.0000353	< DL	Trace
1-Propanol	0.0005359	0.0004588	< DL	Trace
Ethyl Acetate	0.0000221	0.0000117	< DL	Trace
Isobutanol	0.0004423	0.0002741	< DL	Trace
Acetic Acid	< DL	$2.394 \cdot 10^{-7}$	0.0002761	0.000267
Isoamyl Alcohol	0.0009259	0.0008423	< DL	Trace
Water	0.7146496	0.7117416	0.9993804	0.999733

<sup>1</sup> DL = Minimum detection limit for the GC analyses ( $10^{-6}$  mg/mg)

<sup>2</sup> Trace  $\leq 10^{-6}$  mg/mg (Aspen Technology, 2003)

### 2.3.3 – Simulation of Spirit Production

Figure 2.4a gives the spirit alcohol content by volume as a function of product flow rate and reflux ratio (RR). For low reflux ratios, in some cases very low ratios, such as  $RR = 0.001$ , the alcoholic graduation is relatively low but larger than the minimum value required by the legislation for Brazilian cachaça (38 °GL, see Table 2.1). For lower spirit flow rates, the reflux ratio must be increased in order to avoid larger losses of ethanol in the stillage, as can be seen in Figure 2.4b. From an industrial point of view these ethanol losses should be no larger than 0.6% of the ethylic alcohol amount fed into the column (see the short dash dot horizontal line in Figure 2.4b), corresponding to a maximum ethanol concentration of 200 mg/kg in the stillage. Larger reflux ratios increase the spirit alcoholic graduation (see Figure 2.4a), in some cases to concentrations much greater than the maximum required by legislation (54 °GL for cachaça). Greater alcohol graduations are sometimes required, either by legislation or for improving the beverage aging process. Whisky (Suomalainen, 1974; Gaiser, 2002), Absinthe (Lachenmeier, 2007) and Vodka (Savchuk et al., 2007; Legin et al., 2005), by virtue of their specific legislation, should be distilled to higher alcohol graduations and later diluted to acceptable levels for human consumption (see Table 2.1). In case of Brazilian cachaça, only the aged spirit is distilled to higher alcohol graduations and diluted after the aging process. For this investigation (feed stream of 10000 kg/h with 8.5 °GL), cachaça flow rates and reflux ratios varying from 1000 to 2000 kg/h and 0.001 to 1.5, respectively, allow for spirit production with an alcohol graduation within the appropriate concentration range (38-54 °GL, see Table 2.1). The industrial plant shown in Figure 2.1 is not appropriate for distilling spirits to high alcoholic graduations, for instance to 96 °GL. In such case, the pasteurized spirit distillation unit (see Figure 2.2) is recommended and some results for this type of industrial unit will be discussed later.

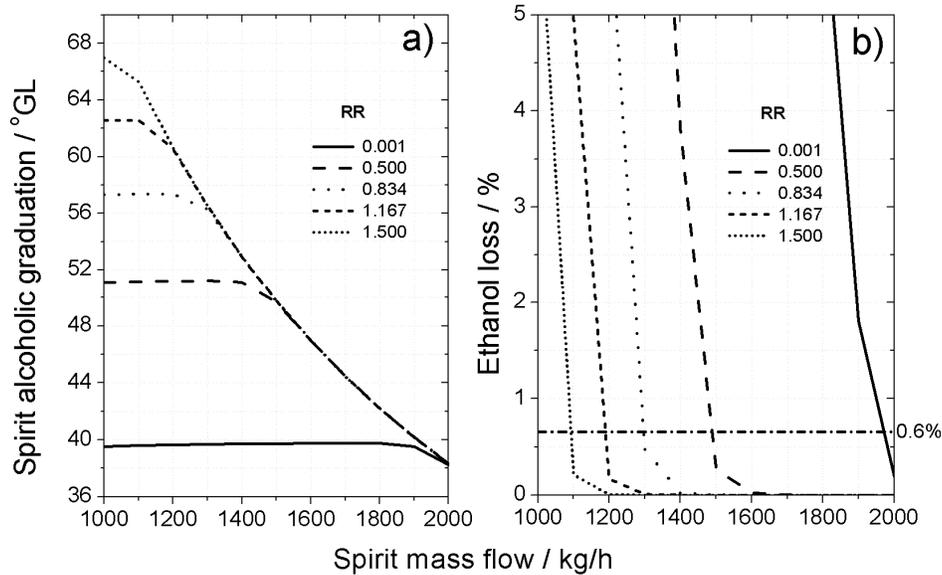


Figure 2.4 - Spirit alcohol graduation (a) and ethanol loss (b) as a function of spirit mass flow and reflux ratio (RR)

Figure 2.5 shows the concentration of volatile congeners, represented by acetaldehyde, in alcoholic beverages. As can be observed, low acetaldehyde contaminations are obtained only by using large spirit flow rates or by combining low spirit flow rates with large reflux ratios. A similar behavior was also observed for other volatile compounds, but the component concentration range depends on the specific component. In the case of ethyl acetate, the concentration range in spirits varies from 9.2 to 17.8 mg/100 ml anhydrous ethanol (AE) for the same range of operational conditions. The corresponding range of values for acetone is from 17.9 to 33.3 mg/100 ml AE. As shown in Table 2.1, congener concentrations are usually evaluated in mg of the component by ml of AE contained in the spirit. For acetaldehyde, the range of values obtained in the simulations, 19.0 to 34.0 mg/100 ml AE, corresponds to the range from 6.8 mg/100 ml of spirit (79.0 mg/kg spirit) to 12.8 mg/100 ml of spirit (158.0 mg/kg spirit). Both graphs in Figure 2.5 represent the same simulation results, but the unities of concentration used in Figure 2.5b (mg/kg of spirit) make it clear that the reflux ratio has only a very slight influence on the acetaldehyde content of the spirit. This is also true for other congeners, such as ethyl acetate and acetone. In fact, this behavior points out that the effect of reflux ratio observed in Figure 2.5a is due to the use of concentrations

expressed in mg of congeners/ml of AE, since the reflux ratio has a large influence on the spirit alcohol graduation (Figure 2.4a).

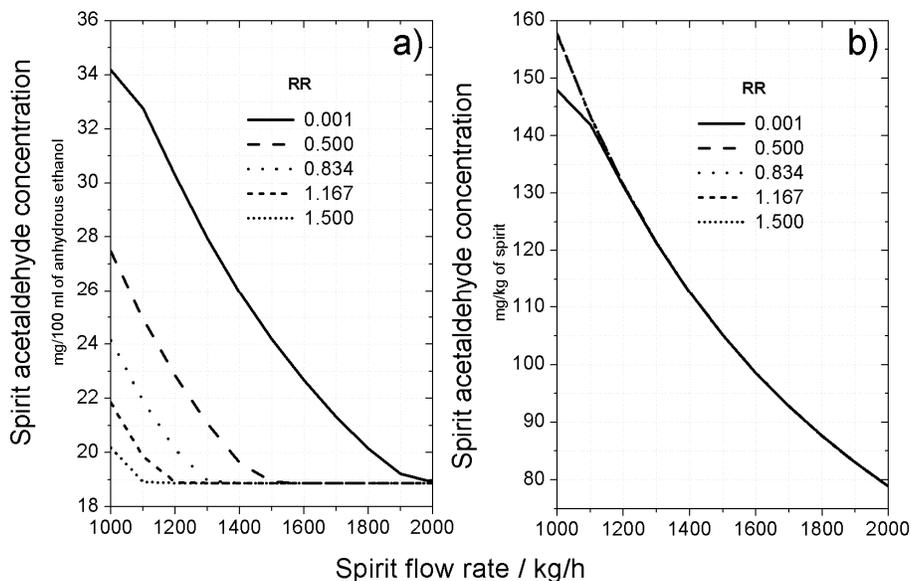


Figure 2.5 - Spirit Acetaldehyde concentration as a function of spirit mass flow and reflux ratio (RR)

As previously mentioned, control of the volatile content is important for the spirit quality. According to Table 2.1, this is especially true for whisky and vodka, beverages that require a more strict control of the volatile content. In this case, the use of the degassing system and/or a more complex configuration of the distillation unit are recommended.

Another important congener class is represented by the higher alcohols, composed mainly of isoamyl alcohol (over 60% of the total quantity of higher alcohols). Figure 2.6 shows that their concentrations in the spirit, expressed in mg of congeners/100 ml of AE and mg of congeners / kg of spirit, increase for low spirit flow rates and low reflux ratios.

Spirit acidity as a function of the product mass flow and reflux ratio shows a somewhat different behavior (see Figure 2.7). Since acetic acid is a heavy component, its concentration in the beverage decreases as the reflux ratio is increased, an effect that is to some extent, mitigated by the increase of the product mass flow.

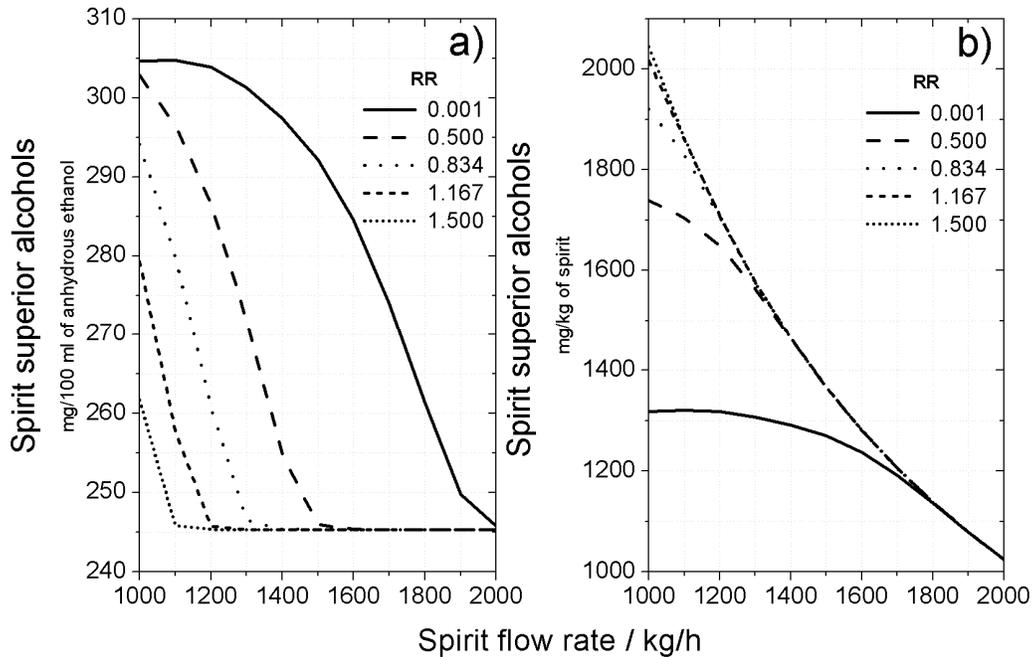


Figure 2.6 - Total higher alcohols in spirits as function of spirit mass flow and reflux ratio (RR)

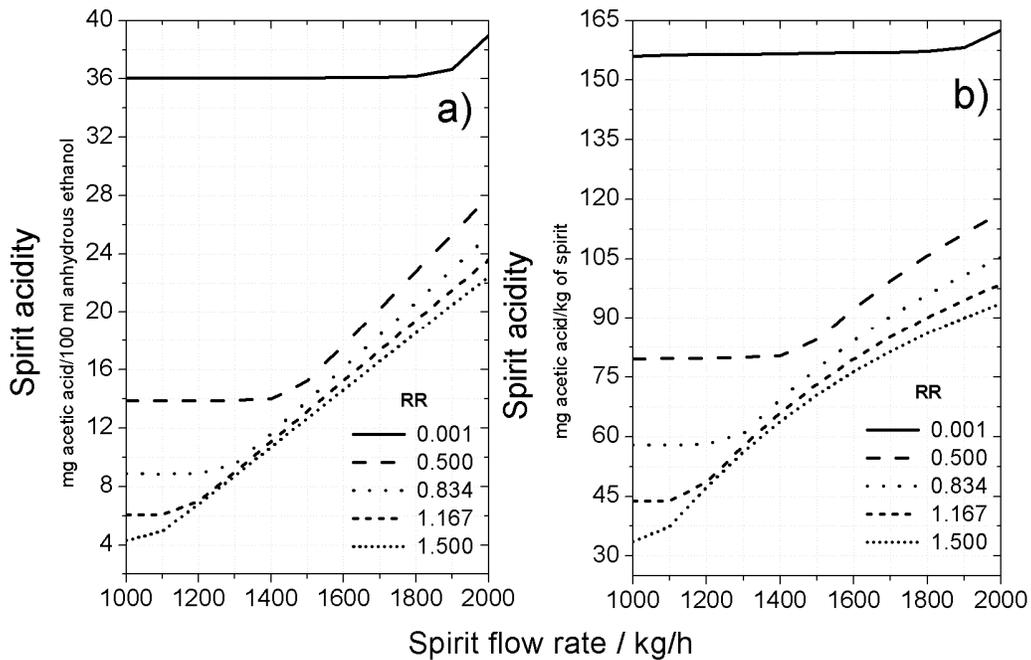


Figure 2.7 - Spirit acidity as function of spirit mass flow and reflux ratio (RR)

Based on the prior simulation results, a specific set of operational conditions (spirit mass flow = 1500 kg/h and reflux ratio = 0.5) was selected in order to investigate the performance of a degassing system included in the equipment

configuration, as indicated by the dashed line in Figure 2.1. The levels of acetaldehyde and ethyl acetate in the wine were increased to 26 mg/kg and 175 mg/kg, respectively, so that a spirit produced without the degassing system would be outside of legislation limits.

Alcoholic fermentation is an anaerobic process that generates a relatively large concentration of carbon dioxide in the wine. As an extremely light component, its presence in the top product can be easily decreased by the degassing system, with the further advantage that it also facilitates control of the other volatile congeners in the spirit. Figure 2.8 presents the influence of the degassing system on the spirit alcohol graduation and ethanol loss. The increase in temperature of the final condenser raises the ethanol loss in the degassing system and slightly decreases the spirit alcohol graduation. The main component in the degassing stream is carbon dioxide, but most of the light components fed into the column are withdrawn in this stream (see Figure 2.9) and small amounts of ethanol are lost. In the case of Brazilian cachaça, a final condenser temperature of 55 °C, representing a degassing ratio of 0.6% (3 kg/h of degassing stream) and an ethanol loss of 0.35%, is sufficient to meet the limits specified by legislation for acetaldehyde and ethyl acetate.

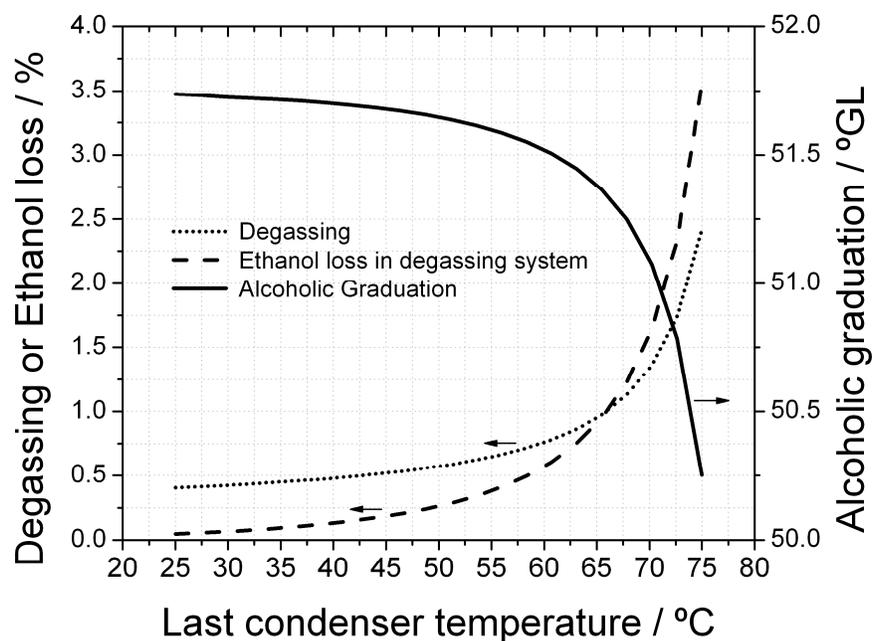


Figure 2.8 - Influence of the degassing system on spirit alcohol graduation and degassing ethanol loss

A control loop for the final condenser temperature, based on a PID controller, makes it possible to avoid that any disturbance in acetaldehyde and ethyl acetate concentration in the wine compromises their concentration in the product. Figure 2.10 shows the results for this control system simulated by Aspen Dynamics. The perturbation caused in the wine concentration, increasing acetaldehyde and ethyl acetate concentration in a unique step from 26 to 30 mg/kg and 175 to 200 mg/kg, respectively, was easily stabilized by the control loop based on the final condenser temperature.

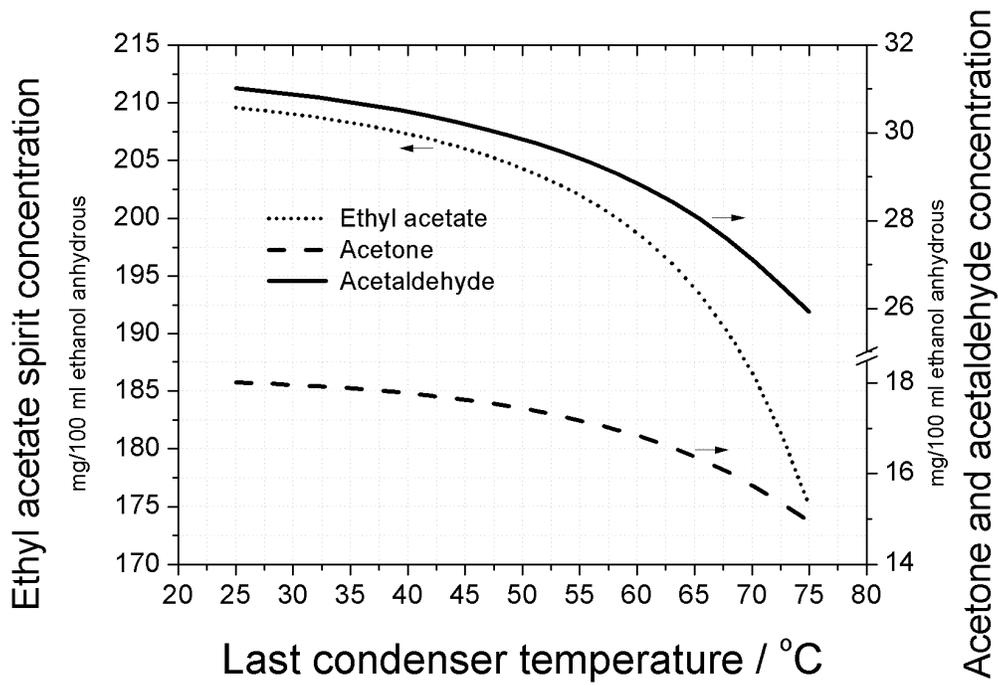


Figure 2.9 - Influence of the degassing system in volatile spirit concentration

Unfortunately, perturbations larger than those investigated above cannot be controlled using only a degassing system. In the case of acetaldehyde and ethyl acetate concentrations greater than 30 mg/kg and 200 mg/kg respectively, the final condenser temperature would be so large that the degassing stream would correspond to almost the entire vapor stream fed into the last condenser. This indicates that this kind of system is efficient for controlling volatile concentration only within a restrict range of wine contamination. In fact, in some spirits the limits of volatile content are so strict and the alcoholic graduation so high that a modification in the configuration of the distillation unit is required. For these

beverages the industrial plant presented in Figure 2.2 is the best option. In order to test the efficiency of this configuration, a simulation was performed with a wine having the same composition shown in Table 2.2.

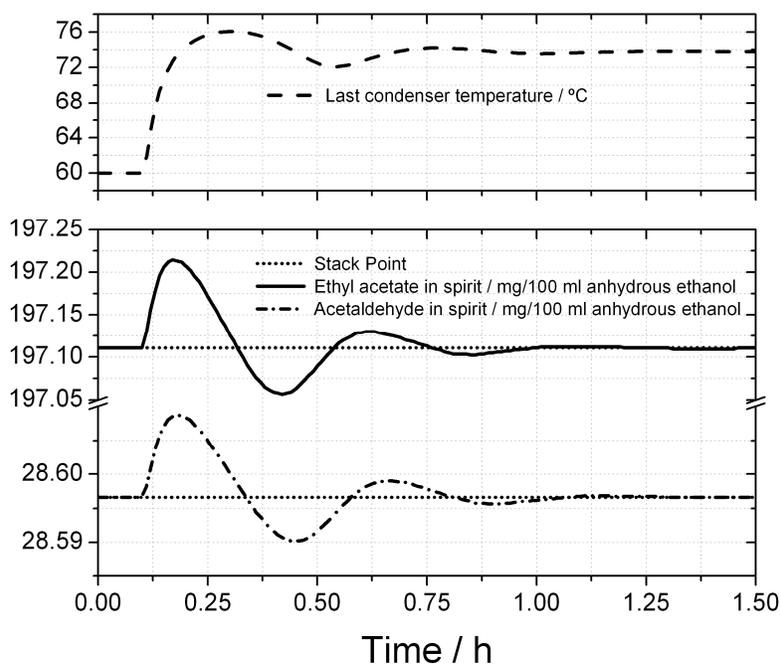


Figure 2.10 - Results of a PID control system for volatile content in spirits

The simulation results show a spirit with the following characteristics: 96 °GL, 0.13 mg of acetaldehyde/100 ml of AE, 0.64 mg of ethyl acetate/100 ml of AE, 1.03 mg of total higher alcohols/100 ml of AE and 0.26 mg of methanol/100 ml of AE. This spirit is in accordance with the standards set for whisky (see Table 2.1). On the other hand, the distillation unit shown in Figure 2.2 is able to produce spirits with different standards by simply adjusting the operational conditions. For beverages whose allowable content of minor components is larger, the following operational conditions can be used: lower reflux ratios, higher spirit flow rates and no withdrawal of the second alcohol and fusel oil streams. This leads to energy saving and minimal ethanol loss. In the case of beverages that are submitted to a more strict concentration standard for minor components, higher reflux ratios and lower spirit flow rates are required and the second alcohol and fusel oil streams must be withdrawn. Aiming to investigate the influence of the second alcohol stream on the spirit volatile concentration, a series of static simulations was

performed while maintaining constant the acetaldehyde and ethyl acetate concentrations in the wine (26 mg/kg and 175 mg/kg respectively) and the degassing flow rate (0.6% of spirit flow rate). Figure 2.11 show that the increase of the second alcohol stream can reduce spirit volatile contamination. On the other hand, the spirit alcohol graduation decreases only slightly until the second alcohol stream reaches 60 kg/h (4 % of the spirits flow rate) and then shows a steep decrease for greater flow rates of this byproduct. This indicates that, for spirits that require high alcohol graduation (vodka and whisky) and are obtained from wines with high volatile contaminations, a larger ethanol loss from the second alcohol stream will be necessary in order to promote the volatile control in the spirits. In the particular case simulated in the present work, a flow rate of 45 kg/h for the second alcohol stream is sufficient to stabilize the spirit ethyl acetate concentration at 18 mg/100 ml AE and to produce a beverage according to the quality standards required for vodka and whisky (see Table 2.1). In case of acetaldehyde, it is possible to produce a spirit according to legislation for all values of second alcohol flow rate (30 to 100 kg/h) investigated in the present study. These results suggest that a control loop to manipulate the second alcohol flow rate may be a good option to maintain spirit volatile contents within the required limits.

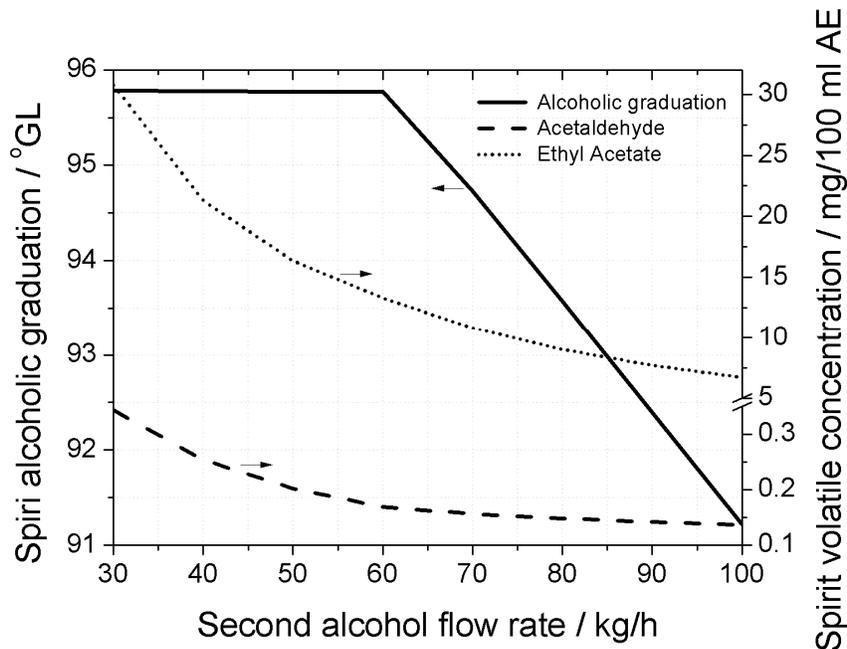


Figure 2.11 - Influence of the second alcohol stream on spirit volatile content and alcohol graduation for the pasteurized spirit distillation unit

### 2.3.4 – Sensitivity analysis of Process Simulation Results

Table 2.5 shows the results for the sensitivity analysis of the process state variables in relation to the NRTL binary interaction parameters. These deviations were calculated according to Eq. 2.4 and represent average absolute differences between the simulated results obtained with the original set of parameters and those obtained after a change of  $\pm 5\%$  in their values.

Taking into account the compositions observed along the entire column, Table 2.4 indicates that the average absolute deviations for the major components, ethanol and water, was less than 0.002 in mass fraction. In case of the minor components these average differences have values always lower than 0.000005, also in mass fraction. The absolute differences are a little bit higher in case of the spirit composition, 0.0062 for the major components and lower than 0.000025 for the minor components, but even in relative terms these differences are not large. For instance, a maximum difference of 1.4% was obtained for spirit alcoholic graduation, indicating a small variation of its composition. For the minor components the relative differences in spirit composition were always lower than 2.7%, suggesting that also in this case the change in the parameters did not have a large effect.

Table 2.5 – Sensitivity analysis results

Component	Column		Cachaça		Composition <sup>3</sup>
	$\epsilon_{+5\%}$	$\epsilon_{5\%}$	$\epsilon_{+5\%}$	$\epsilon_{5\%}$	
Water <sup>1</sup>	$1.5 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	$5.8 \cdot 10^{-3}$	$6.2 \cdot 10^{-3}$	0.557949
Ethanol <sup>1</sup>	$1.5 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	$5.8 \cdot 10^{-3}$	$6.2 \cdot 10^{-3}$	0.440995
Isoamyl alcohol <sup>1</sup>	$3.4 \cdot 10^{-6}$	$4.9 \cdot 10^{-6}$	$2.1 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	0.000950
Acetaldehyde <sup>1</sup>	$3.1 \cdot 10^{-8}$	$3.4 \cdot 10^{-8}$	$2.6 \cdot 10^{-7}$	$2.9 \cdot 10^{-7}$	0.000105
Acetic Acid <sup>1</sup>	$4.1 \cdot 10^{-7}$	$5.2 \cdot 10^{-7}$	$8.9 \cdot 10^{-7}$	$1.1 \cdot 10^{-6}$	0.000081
Temperature (°C)	$8.9 \cdot 10^{-2}$	$1.2 \cdot 10^{-1}$	$1.6 \cdot 10^{-1}$	$2.3 \cdot 10^{-1}$	
Steam Consumption <sup>2</sup>	$8.7 \cdot 10^{-5}$	$7.5 \cdot 10^{-4}$	-	-	

<sup>1</sup> Composition in mass fraction

<sup>2</sup> kg of steam per liter of spirit

<sup>3</sup> Obtained with the original set of parameters

For the temperature, the average absolute deviation was not higher than 0.39 °C, a value that corresponds to a relative deviation of 0.40%. In case of steam consumption, a variable very important for evaluating the energy performance of

continuous distillation, the absolute deviation was less than  $7.5 \cdot 10^{-4}$  kg of steam per liter of spirit, representing a relative deviation of 0.08%.

The results presented above suggest that the changes considered in the set of NRTL parameters used in the present work do not have a large impact on product quality, tray temperatures and energy performance of the equipment, indicating that process simulation based on these parameters can be a powerful and reliable tool for evaluating the effects of variations in the operational conditions and in the design of equipments for spirit distillation. Nevertheless, such results should not be overestimated. The original set of parameters used in the present work was thoroughly readjusted in order to better describe the phase equilibrium of the alcoholic wine, so that it could be considered a kind of optimum set of parameters for calculating this specific equilibrium. Eventually the changes considered in the parameters values were not able to take them out of this optimum region. On the other hand, the changes of  $\pm 5\%$  were performed in the set of parameters as a whole and eventually changes of similar magnitude performed in part of the whole set could have a larger impact on the obtained results. Furthermore, even in the present case the changes in NRTL parameters may have a significant impact on specific results. This occurs in the case of light components concentration in the bottom trays. For instance, the decrease of 1.4% in the alcoholic graduation mentioned above corresponds to a change of approximately 33% in the ethanol concentration in stillage, from 0.0002 to 0.0003.

## **2.4 - Conclusions**

The main difference between spirits produced around the world is the concentration of congeners in the beverage. Small changes in the concentration of these congeners are enough for differentiating each spirit. The results presented in this work showed that simple modifications in the distillation column configuration and operational conditions (reflux ratio, second alcohol, degassing stream, spirit flow rate and column trays) are sufficient for producing spirits of different standards. Beverages with moderate alcoholic strength (cachaça, rum, tequila) are easily obtained by simple column systems with a small rectification section. On the

other hand, spirits with high alcoholic graduation (whisky, vodka, absinthe and others) require a high reflux ratio and low spirit flow rate, implying higher steam consumption. For these spirits a more complex column system is required. Rectification and stripping sections with a larger number of trays are necessary together with the withdrawal of higher alcohols and second alcohol streams, increasing ethanol losses but allowing for a greater alcoholic graduation (93-96 °GL). For spirits with a low volatile contamination, a simple PID controller linked to the degassing system is sufficient to avoid spirit contamination. For spirits with a high alcoholic graduation, the influence of a degassing system on volatile control is not significant because the legislation limits are stricter in this case. Perhaps in this case a control system based on the manipulation of the second alcohol stream is required. These conclusions were made possible because of the ability of commercial simulators, such as Aspen Plus and Aspen Dynamics, to reliably represent the spirit distillation process.

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## Capítulo 3

# **A strategy for controlling acetaldehyde content in an industrial plant of bioethanol <sup>2</sup>**

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## **Abstract**

This work presents a strategy for controlling acetaldehyde content in Brazilian bioethanol, based in simulation results of a typical industrial distillation plant. The major problem of acetaldehyde in bioethanol is that, during the storage period, it can oxidize to acetic acid, increasing fuel acidity above the legislation limit. This work tested, by dynamic simulation, simple loops to control acetaldehyde in bioethanol. The dynamic simulation generated a disturbance in the wine to be distilled by increasing acetaldehyde content, and verified how those loops were able to control the acetaldehyde level in bioethanol. Two different column system configurations were investigated. The first one includes a degassing system and a second one that produces pasteurized alcohol without or with a degassing system. Suggestions for the best control system of acetaldehyde contamination in bioethanol were formulated according to the acetaldehyde level in the wine.

*Keywords:* Fuel ethanol, bioethanol, dynamic simulation, degassing system, aspen plus.

## **3.1 – Introduction**

There is an increasing interest in bioethanol as a renewable energy source as well as a commodity to be used in other industrial branches, such as the chemical, pharmaceutical, and beverage industries. Brazil is one of the largest bioethanol producers and the largest exporter. For more than 30 years bioethanol is used directly as a biofuel, in this case with a concentration close to the azeotropic one, or added to petrol and, in this last case, it should be anhydrous. The rapid increase in its use as biofuel, the increase of its exports and of its use in other industrial branches is requiring a better control of product quality. Several minor components are generated during bioethanol production by fermentation and most of them are contaminants present in the end product. Although ethanol distillation is a largely investigated subject, most of the research works focus on energy consumption, alternative dehydration techniques and control strategies for separating the binary mixture ethanol-water, not taking into account the series of minor components that influence the distillation process. Those research works

also rarely consider the peculiarities of the column systems used for ethanol distillation in the industrial practice.

Some recent works are applying simulations tools in order to investigate spirits and bioethanol distillation, taking into account at least part of the complexity of the multicomponent alcoholic mixture and of the industrial equipments used for its distillation. Gaiser et al. (2002) used the commercial software Aspen Plus for simulating a continuous industrial unit for whiskey distillation, validating the results against industrial data. Meirelles et al. (2008) simulated a continuous distillation column for spirits production from sugar cane fermented must. Decloux and Coustel (2005) simulated a typical distillation plant for neutral alcohol production, using the software ProSim Plus. Neutral alcohol is a very pure ethanol product that requires a series of distillation columns to be produced. Taking into account the increasing importance of bioethanol and the largely untreated subject of controlling its contaminants, this work is focused on investigating strategies for controlling the acetaldehyde content in bioethanol. Acetaldehyde is the contaminant responsible for the increase in biofuel acidity during storage time.

### **3.2 - Description of Process**

A typical industrial installation for bioethanol production in Brazil, according to Marquini et al. (2008), is shown in Figure 3.1. This industrial installation is composed by 3 columns, two stripping ones (A and B1) and the rectifying column B. Column A, a equipment for wine stripping, is composed by 22 plates, 1 reboiler and no condenser. These plates have Murphree efficiency of 0.65, the total pressure drop of this column is 18437 Pa, the pressure of stage 1 is 138932 Pa and the reboiler pressure 157369 Pa. The wine or beer, industrial denominations of the fermented sugar cane must, is represented by the standard solution given in Table 3.1. This mixture is fed into the top of column A. The stream named PHLEGM, a vapor stream with ethanol concentration within the range 35-45 mass%, is fed into the bottom of column B. STILLAGE and WHITE STILLAGE, streams withdrawn from the bottoms of columns A and B1, respectively, must have an ethanol content not larger than 0.02 mass%. Column B, the phlegm rectification

column, is composed by 45 plates plus a condenser, has Murphree efficiency of 0.50, a total pressure drop of 38932 Pa, condenser pressure of 100000 Pa and bottom stage pressure of 138932 Pa. Bioethanol is extracted as top product of column B with 93 mass% of ethanol. Column B1, the phlegm stripping column, is fed with the bottom product of column B. This column is composed by 18 plates plus a reboiler, has Murphree efficiency of 0.60, total pressure drop of 8042 Pa, and the reboiler pressure equal to 146974 Pa.

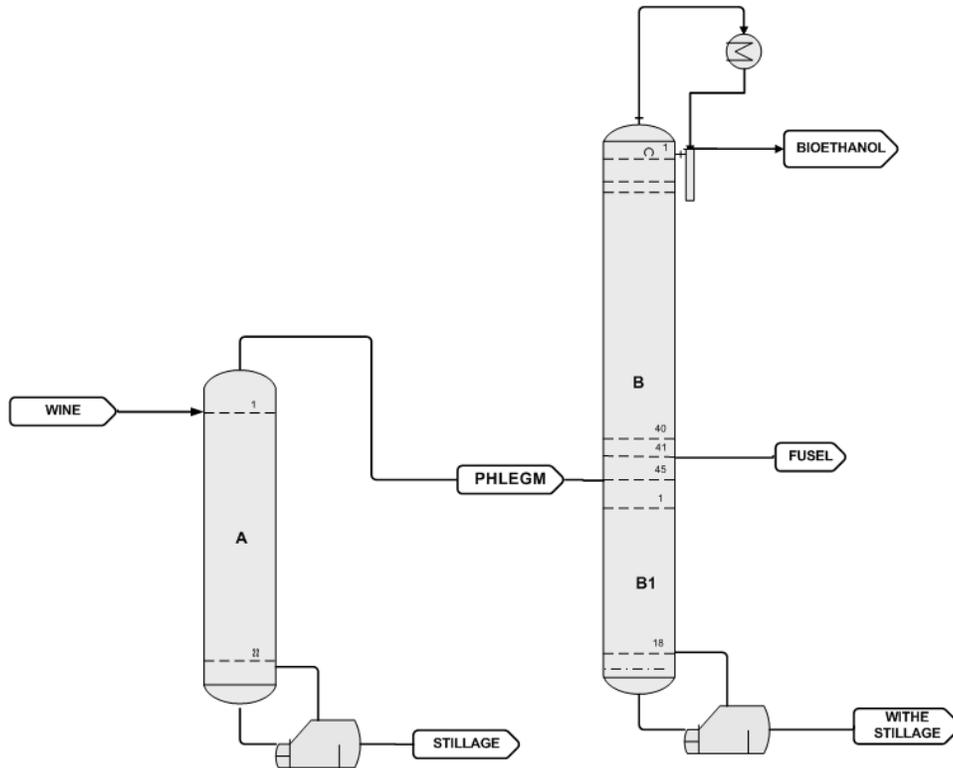


Figure 3.1 - Simplified Brazilian Bioethanol Industrial Plant

Table 3.1 - Typical composition of industrial wine used in the simulations

<b>Component</b>	<b>Concentration (mass fraction)</b>	<b>Reference</b>
Water	0.93495357	By difference.
Ethanol	$6.450 \times 10^{-2}$	Oliveira (2001)
Methanol	$3.200 \times 10^{-7}$	Boscolo et al. (2000)
Isopropanol	$1.020 \times 10^{-6}$	Cardoso et al. (2003)
Propanol	$3.000 \times 10^{-5}$	Oliveira (2001)
Isobutanol	$2.780 \times 10^{-5}$	Oliveira (2001)
Isoamyl alcohol	$4.250 \times 10^{-5}$	Oliveira (2001)
Ethyl Acetate	$7.690 \times 10^{-6}$	Oliveira (2001)
Acetaldehyde	$2.000 \times 10^{-6}$	Oliveira (2001)
Acetic Acid	$4.351 \times 10^{-4}$	Oliveira (2001)

### 3.3 – Materials and Method

The first part of the present work focused on the steady-state simulation of a typical industrial unit, such as that shown in Figure 3.1. The simulations were conducted using the commercial software Aspen Plus, by Aspen Tech, and aimed to investigate the operation of the industrial system by analyzing the effects of operational conditions upon the concentration profiles in columns A, B and B1. The second part was conducted using the module Aspen Dynamic, by Aspen Tech, so that some control strategies could be tested in order to keep the acetaldehyde level in bioethanol within the required limits. In this way the acidity increase of the biofuel during storage period could be prevented. The package RADFRAC for simulating distillation columns within Aspen Plus was selected in order to represent the whole industrial system. This package uses a rigorous method of calculation for solving the set of balance and equilibrium equations based on the MESH system described in detail by Kister (1992). According to a detailed and rigorous analysis (Meirelles et al., 2008), previously performed for the vapor-liquid equilibrium of the binary mixtures formed by the wine components (Table 3.1), the NRTL model and a corresponding set of parameters were selected for representing the liquid phase non-ideality and the Virial equation, together with the approach based on Hayden and O'Connell (1975), for estimating the vapor phase fugacities.

Wine was fed into column A (see Figure 3.1) with a mass flow of 202542 kg/h, at 94 °C and the composition given in Table 3.1. The ethanol concentration in the bottom product of column A was fixed in 200 mg/kg (0.02 mass %) and the mass flow of bioethanol was varied around 14000 kg/h with at least 93 mass% of ethanol, corresponding to an approximately daily production of 465 m<sup>3</sup>. In the bottom of column B1 the ethanol concentration was not fixed but its level was ever less than 200 mg/kg. In accordance with industrial information, the fusel stream mass flow was fixed in 41 kg/h, almost 0.3% of the bioethanol mass flow. Reflux and bioethanol stream mass flows were varied and the corresponding concentration profiles investigated.

For the dynamic simulation, in a first step a PID controller was used with the aim of controlling the acetaldehyde content (controller variable) in bioethanol, by

manipulating the reflux stream and bioethanol mass flows (manipulated variables), after a perturbation in acetaldehyde concentration was imposed to the feed stream (wine). In a second step, the degassing system was tested to control the acetaldehyde content in bioethanol.

The degassing system is based on the association of two or more partial condensers in the top of column B. The vapor stream of each partial condenser is fed into the next one and the liquid streams return to the top of the column. In the last condenser, a small amount of vapor phase is withdrawn as a DEGASSING stream. According to the maximum level of allowed acetaldehyde contamination, the temperature of the last condenser can be varied and more or less mass of degassing can be generated.

### **3.4 – Results and Discussions**

Almost all bioethanol fed into column A was stripped from the liquid phase and transferred via the PHLEGMA stream to column B. Except for acetic acid, all congeners (minor components in wine) are concentrated in the PHLEGMA stream and also transferred to column B. Figure 3.2 shows the concentration profiles of water and ethanol along columns B (stages 1, condenser, to 46) and B1 (stages 47 to 65, reboiler). An alcoholic graduation of 93.0 mass% was obtained. Note that this value is within the concentration range required by the Brazilian legislation for hydrous bioethanol (see Table 3.2). Figure 3.3 shows the concentration profiles for high alcohols. High alcohols, containing mainly isoamyl alcohol, are extracted from column B as a side stream named FUSEL stream. Figure 3.4 shows the concentration profile for acetaldehyde and acetic acid in columns B and B1. Acetaldehyde profile indicates that this contaminant is concentrated in the biofuel stream.

ANP, the Brazilian National Petroleum Agency, is the public institution responsible for setting quality standards for fuels and biofuels. Copersucar, one of the largest Brazilian trading companies for sugar and bioethanol export, also sets specific quality standards according to the requirements of its clients. Table 3.2 shows the main specifications for bioethanol according to ANP (AEHC) and

Copersucar (H1 and H2), and also some of the results obtained by steady-state simulation of the industrial plant (SIM). According to the simulation results the bioethanol produced fulfil the requirements of the Brazilian legislation and even most of the requirements set by Copersucar.

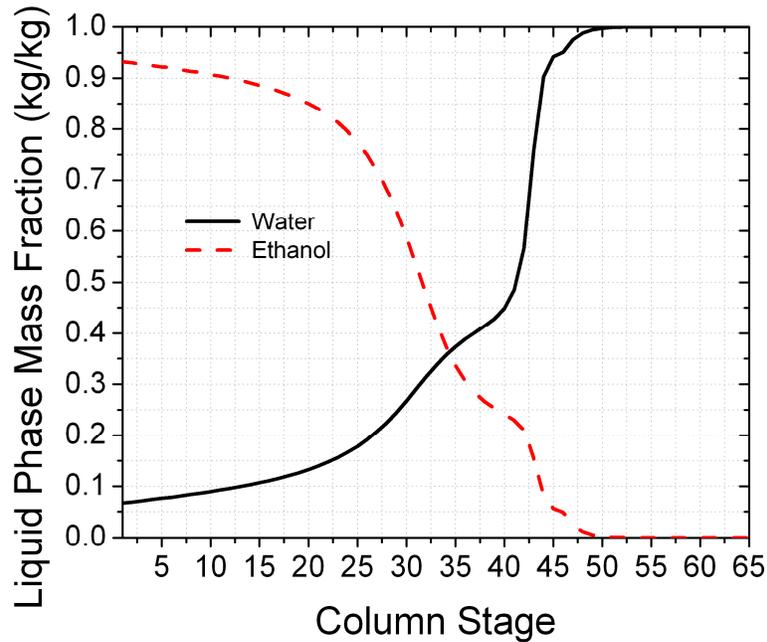


Figure 3.2 – Concentrations profile of ethanol and water in columns B (stages 1-46) and B1 (stages 47-65)

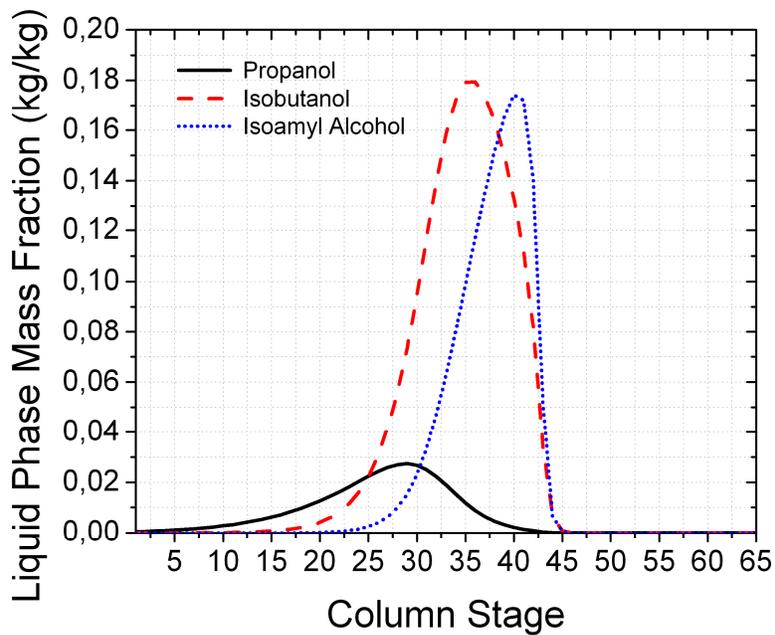


Figure 3.3 – Superior alcohols profiles in columns B (stages 1-46) and B1 (stages 47-65)

Acetaldehyde concentration is not a quality parameter fixed by ANP for the biofuel (see Table 3.2). In case of the simulation results, the obtained acidity values, were far below the limit set by the Brazilian legislation. However, during the storage period acetaldehyde can oxidize to acetic acid and deteriorate the biofuel quality, increasing its acidity. If all acetaldehyde content present in the simulated fuel ethanol (see Table 3.2) oxidizes to acetic acid, the product acidity would be increased to 33.5 mg/L. With this value, the biofuel would be outside the standards qualities established by the Brazilian legislation (see Table 3.2). For this reason, the concentration of acetaldehyde in biofuel must be strictly controlled to prevent that the acidity level exceeds the legislation limits along the storage time. On the other hand, Brazil is nowadays the largest bioethanol exporter and the use of this bioproduct is increasing worldwide not only as an alternative energy source as well as an input material for chemical, pharmaceutical, perfume and beverage industries. Although these other uses may require further purification steps, sometimes conducted at the importing country, the Brazilian exporters are opting for defining stricter quality standards, such as the values specified by Copersucar (see Table 3.2). This highlights the importance of monitoring and controlling the contamination levels of minor components, such as acetaldehyde and high alcohols, in bioethanol.

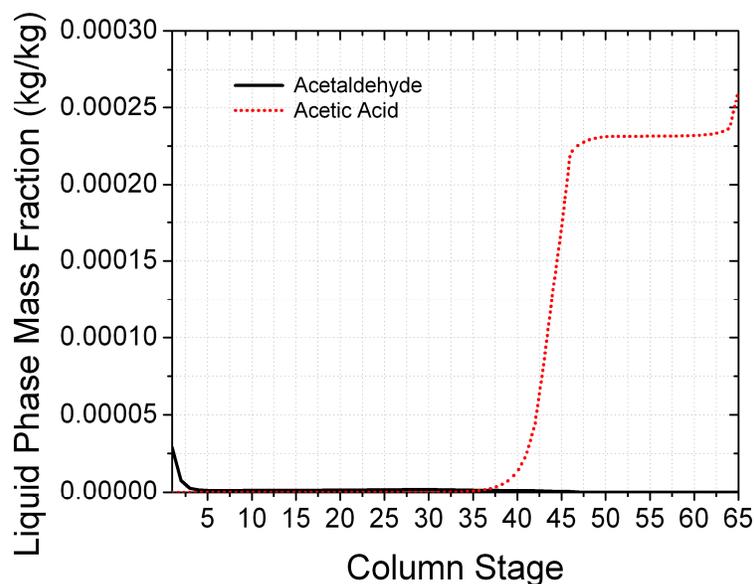


Figure 3.4 – Acetaldehyde and acetic acid profiles in columns B (stage 1-46) and B1 (stages 47-65)

Table 3.2 – Bioethanol quality standards, ANP (AEHC), Copersucar (H1 and H2) and the simulation results (SIM)

<b>Spec</b>	<b>Unities</b>	<b>Bioethanol</b>			
		<b>AEHC</b>	<b>H1</b>	<b>H2</b>	<b>Sim.</b>
<i>Alcoholic Graduation</i>	<i>Mass %</i>	<i>92.6 – 93.8</i>	<i>≥ 92.8</i>	<i>≥ 93.8</i>	<i>93.2</i>
<i>Acidity (Acetic Ac.)</i>	<i>mg/L</i>	<i>≤ 30</i>	<i>≤ 20</i>	<i>≤ 10</i>	<i>Trace</i>
<i>Density (20°C)</i>	<i>Kg/m<sup>3</sup></i>	<i>807.6 – 811.0</i>	<i>-</i>	<i>-</i>	<i>807.1</i>
<i>Acetaldehyde</i>	<i>mg/L</i>	<i>-</i>	<i>≤ 50</i>	<i>≤ 10</i>	<i>24.6</i>
<i>Higher Alcohol</i>	<i>mg/L</i>	<i>-</i>	<i>≤ 400</i>	<i>≤ 50</i>	<i>332.5</i>

Data on the mechanism and kinetics of acetaldehyde oxidation to acetic acid can be found in WANG et al. (1992) and XU et al. (2000). In order to avoid the risk of this oxidation during biofuel storage one of the possible strategies is to reduce acetaldehyde content in biofuel to a minimal value. In the second part of this work, some strategies to control the acetaldehyde content were investigated. All the strategies were based in a PID loop control, with the aim of keeping acetaldehyde concentration in bioethanol constant even if a perturbation increases its content in the wine. Figure 3.5 shows the simplest configuration of column simulated in the present work. As acetaldehyde is a very light component, the total amount of this substance present in the wine will contaminate bioethanol if this configuration is used. For this reason no control strategy would be able to avoid an increase of acetaldehyde contamination in bioethanol in case of a slight increase in its concentration in the wine. In fact, attempts to avoid this contamination, by using reflux and/or bioethanol flow, according to the loop control represented in Figure 3.5, failed. Thus two alternative solutions are suggested and they include changes in the industrial installation.

The first alternative installation includes a degassing system, as that shown in Figure 3.6 and explained above. Such a system makes easier the control of acetaldehyde content in bioethanol. As a very light component, acetaldehyde concentrates in the vapor streams and is eliminated by the DEGASSING stream. Controlling the DEGASSING flow makes possible to eliminate part of the acetaldehyde contamination, although this also causes small losses of the bioproduct.

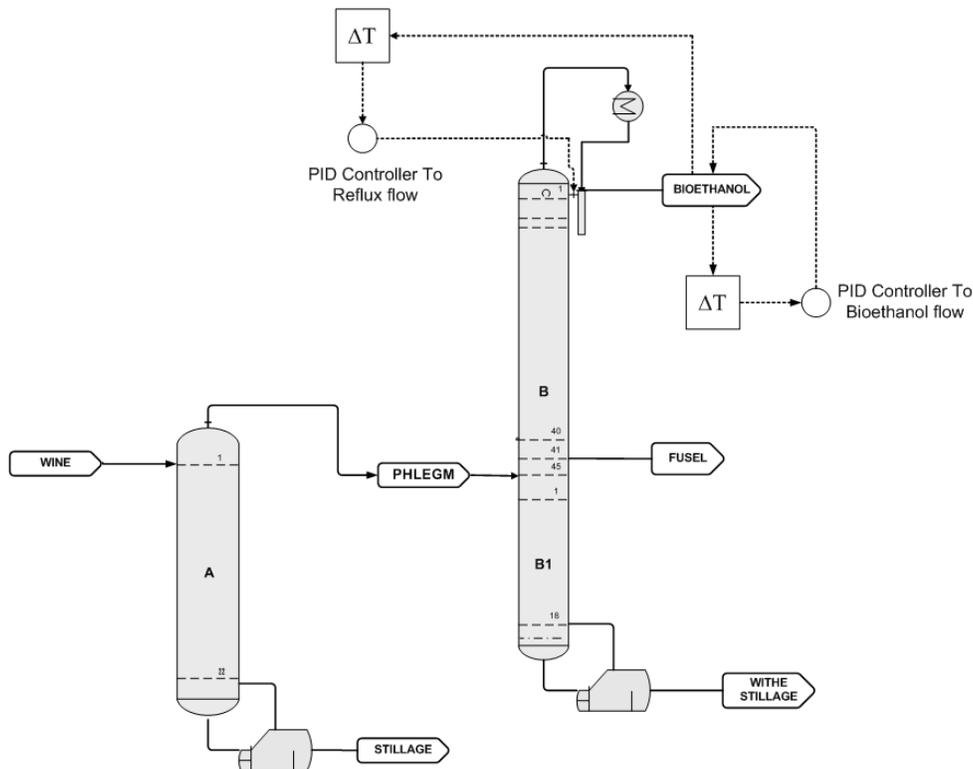


Figure 3.5 – Loop control for acetaldehyde concentration in bioethanol

Figure 3.7 shows steady-state results for DEGASSING flow, ethanol mass flow in degassing and acetaldehyde content in bioethanol as a function of the last condenser temperature. The increase of this temperature increases the degassing flow, and by consequence increases the mass flow of ethanol in degassing stream, and decreases the acetaldehyde concentration in the bioethanol. These results show that the control of the temperature of the last condenser in the degassing system can control the concentration of acetaldehyde in the bioethanol. Taking this into account, a simple PID controller was developed to control the temperature of the last condenser of the degassing system (see Figure 3.6). In this loop control, the controller variable was the acetaldehyde content in bioethanol and the manipulated variable was the temperature of the last condenser. The stack point (maximum level of the acetaldehyde in bioethanol) was fixed in 25.3 ppm ( $2.530 \cdot 10^{-5}$  kg/kg). With this concentration, even if all the acetaldehyde oxidize to acetic acid, the mass of acid formed will not be sufficient to exceed the acidity maximum level fixed by ANP (Table 2). In order to better represent the industrial process, carbon dioxide ( $\text{CO}_2$ ) produced during fermentation was included in the

wine composition in a concentration of 0.0011 kg/kg. This value was determined assuming that the alcoholic fermentation industrial process is performed in closed vat with light over pressure (600 to 800 mm of water) and temperatures close to 35 °C. Considering that gas phase inside the vat is composed of saturated CO<sub>2</sub> with vapors of ethanol and water, the NRTL model and the Henry constant for CO<sub>2</sub> (Dalmolin et al., 2006) was used in order to estimate the solubility of CO<sub>2</sub> in the wine. The estimated values varied within the range 1050 to 1150 mg/kg. The acetaldehyde concentration in the wine was increased to  $2.100 \cdot 10^{-6}$  kg/kg and after 3 hours decreased to  $1.900 \cdot 10^{-6}$  kg/kg, in order to demonstrate the efficiency of the degassing system. The concentration of the other wine components were kept constant in the values indicated in Table 3.1, except for water whose value was appropriately adjusted. The results are present in the Figure 3.8.

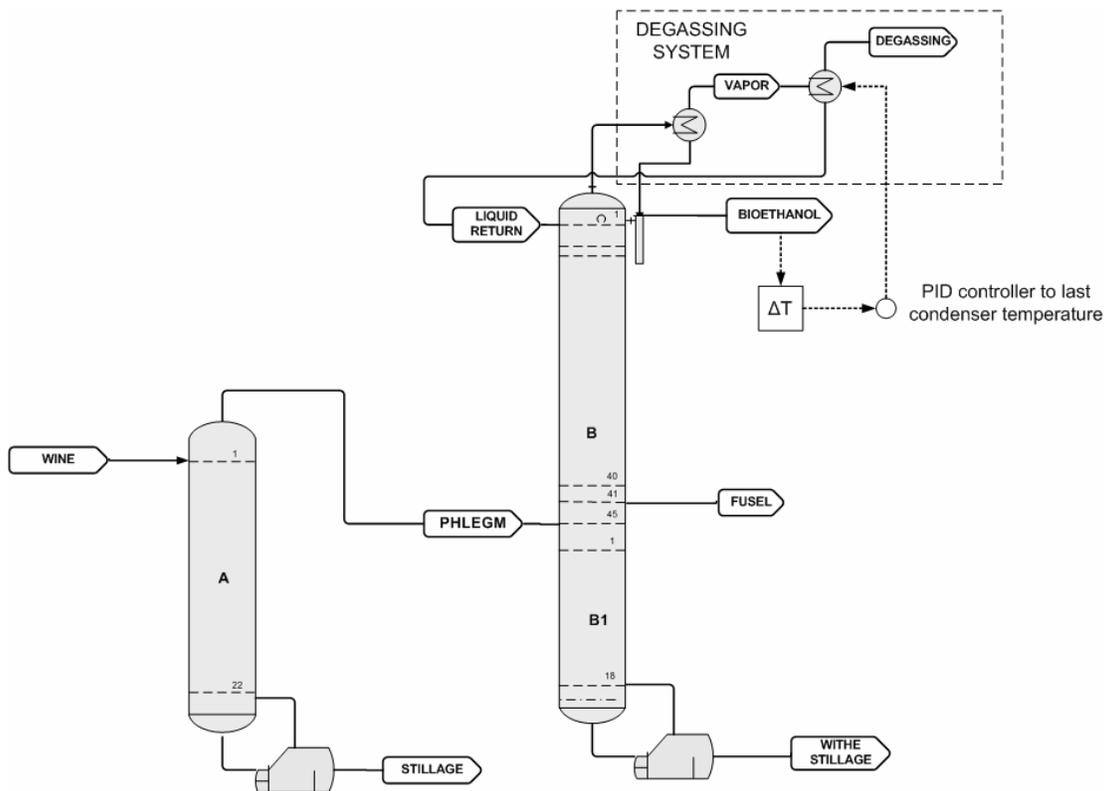


Figure 3.6 – Industrial plant with degassing system

As is possible to observe in Figure 3.8, the control system based in a PID controller has a good performance in avoiding a contamination of acetaldehyde in bioethanol. A direct dependence between the controller variable (biofuel acetaldehyde concentration) and the manipulated variable (last condenser temperature) was observed. In case of an increase of acetaldehyde concentration in the wine the PID controller increases the last condenser temperature and, in consequence, a large degassing flow is withdrawn of the equipment. The acetaldehyde level in bioethanol reaches safe values after 40 minutes and stabilizes after one hour. The reverse process occurs when the concentration of acetaldehyde in wine is decreased (see Figure 3.8).

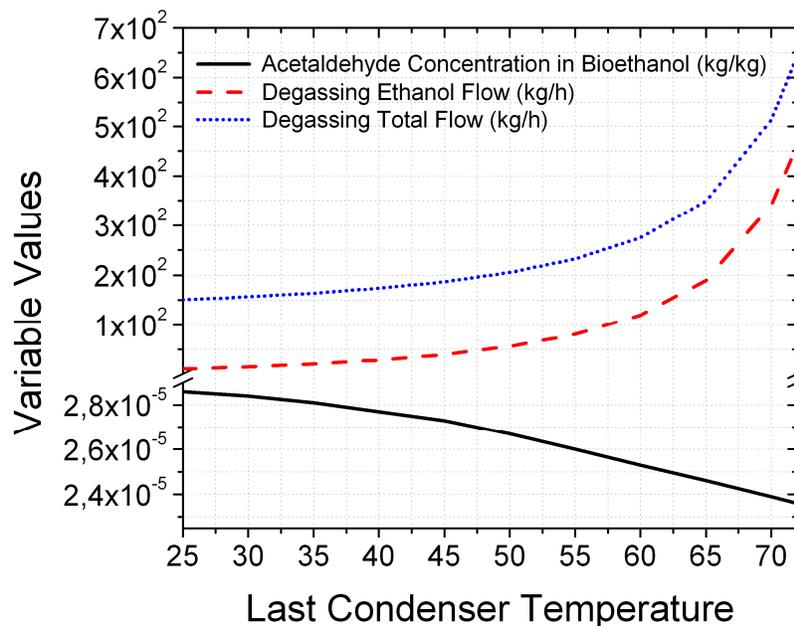


Figure 3.7 – Acetaldehyde content and degassing flow as a function of last condenser temperature

Despite this good performance, the configuration with a degassing system may exhibit some difficulties in case of a large wine contamination with acetaldehyde. Large concentrations of acetaldehyde in wine require larger flow of degassing stream in order to reduce the biofuel contamination. A larger degassing mass flow increases ethanol losses (see Figure 3.7). Therefore, the total loss of the ethanol in the production system can reach levels higher than those accepted by industry. A better alternative configuration for a wine with larger acetaldehyde

contamination is the pasteurized bioethanol installation shown in Figure 3.9. In this kind of installation two news columns (D and A1) are added to the original system. These columns concentrate the major part of wine volatile compounds, including acetaldehyde, and eliminate part of them via the Second alcohol stream withdrawn from the top of column D.

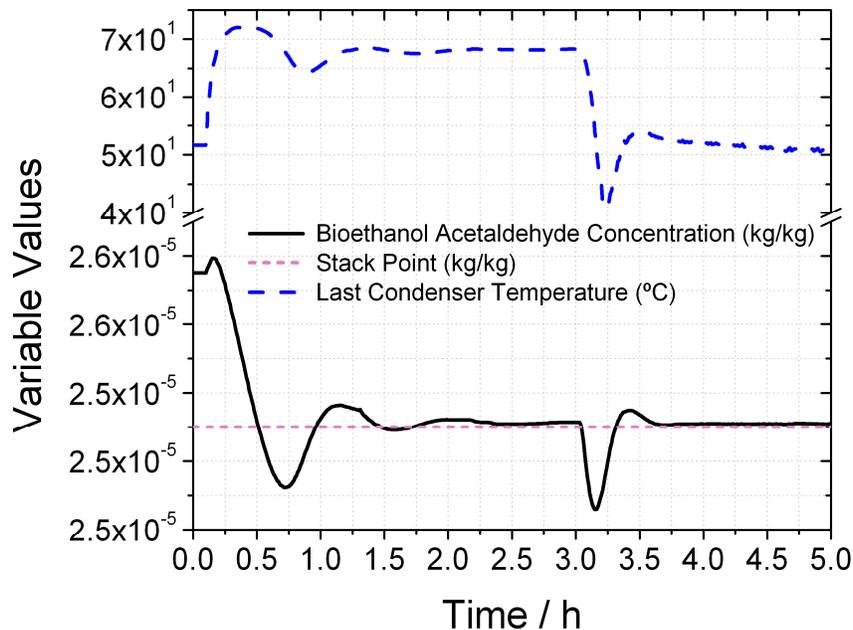


Figure 3.8 – Results of PID controller in degassing system (industrial installation)

In column B bioethanol is withdrawn from a tray close to the column top. In the top of Column B a further SECOND ALCOHOL stream is also withdrawn. According to Figure 3.4 acetaldehyde is concentrated in the trays located close to the top of column B. For this reason streams such as the two SECOND ALCOHOL ones are concentrated in acetaldehyde and other light minor components, for instance ethyl acetate. These contaminants are taken away by the top streams and bioethanol, withdrawn from column B as a side stream, has its acetaldehyde content decreased. On the other hand, small amounts of ethanol are not recovered as the main product (bioethanol), being extracted in those byproduct streams. Such scheme is more appropriate for producing bioethanol from a wine with larger contamination of light components or in case the bioproduct must have a higher purity.

Figure 3.10 shows the results of steady state simulations performed for the pasteurized bioethanol installation. For this simulation acetaldehyde concentration in the wine was increased to approximately 10 times the value of the previous simulations (new concentration equal to  $1.900 \times 10^{-5}$  kg/kg), representing a larger contamination, closer to the industrial wine, according to Oliveira (2001).

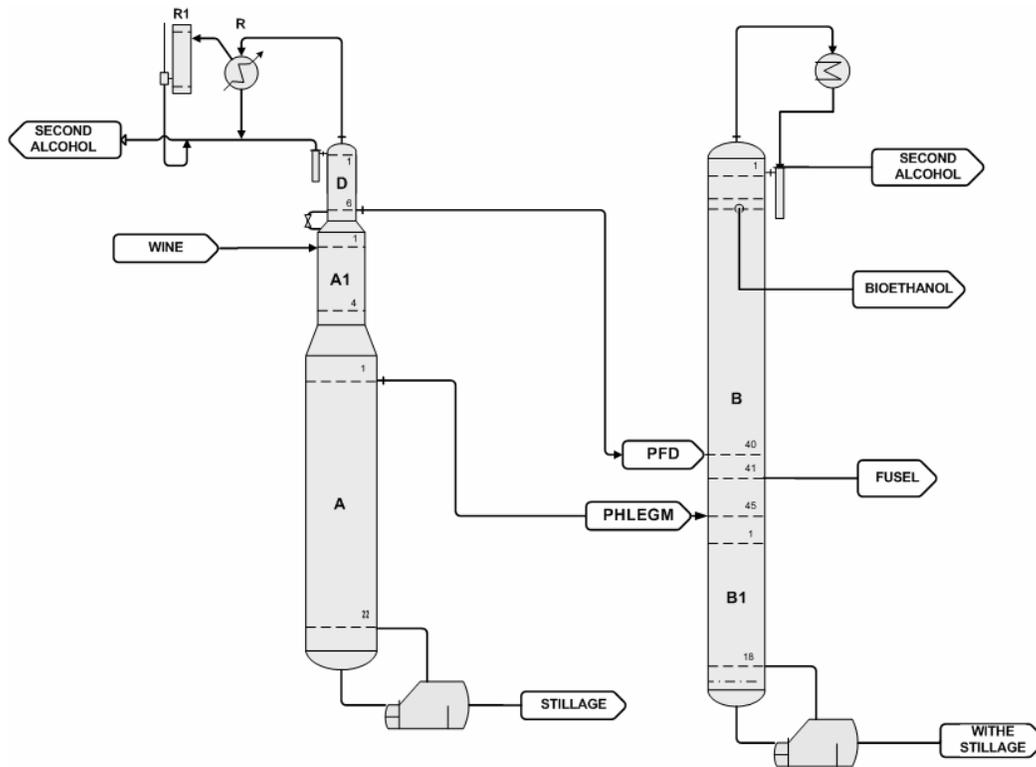


Figure 3.9 – Industrial plant for bioethanol with second alcohol streams

The main objective of those simulations was to show that, varying the mass flow of the second alcohol stream in column B, it is possible to reduce considerably the concentration of acetaldehyde in bioethanol. According to Figure 3.10, the increase of the mass flow of the second alcohol stream reduces acetaldehyde contamination without influencing, in a significant way, the bioproduct alcoholic graduation. In these simulations only the second alcohol stream in top of column B was varied, keeping the second alcohol stream in top of column D fixed at the value 400 kg/h. This means that a relative larger acetaldehyde contamination is contained in the second alcohol stream, a result that makes easier the control of this contamination in the main product (pasteurized bioethanol) by means of the

degassing system. For this reason a loop control similar to that of Figure 3.6, connecting the acetaldehyde concentration in pasteurized bioethanol (controller variable) to the last condenser temperature (manipulated variable), was tested. The wine acetaldehyde concentration was increased to  $2.000 \times 10^{-5}$  kg/kg and the last partial condenser temperature was varied to stabilize the bioethanol acetaldehyde concentration at  $2.450 \times 10^{-5}$  kg/kg. With this value, the problem of acetaldehyde oxidation during storage time was eliminated. The result of this simulation, presented in Figure 3.11, shows that in almost 2 hours the acetaldehyde concentration reaches the required value although the stabilization time is approximately 7 hours suggesting that the degassing system is an excellent alternative for acetaldehyde control in bioethanol, provided that the wine contamination with acetaldehyde is not too large.

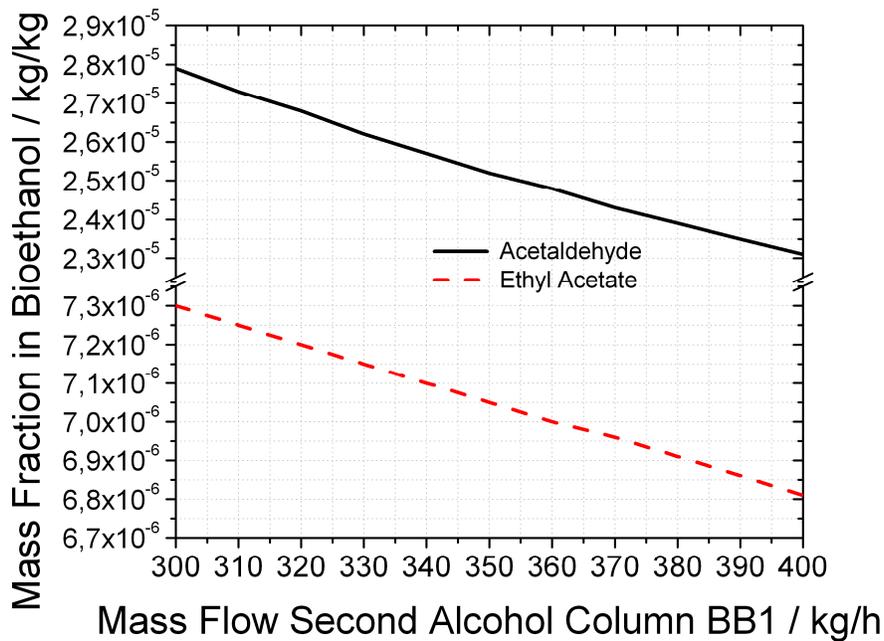


Figure 3.10 – Volatiles content in bioethanol in function of second alcohol flow of column BB1

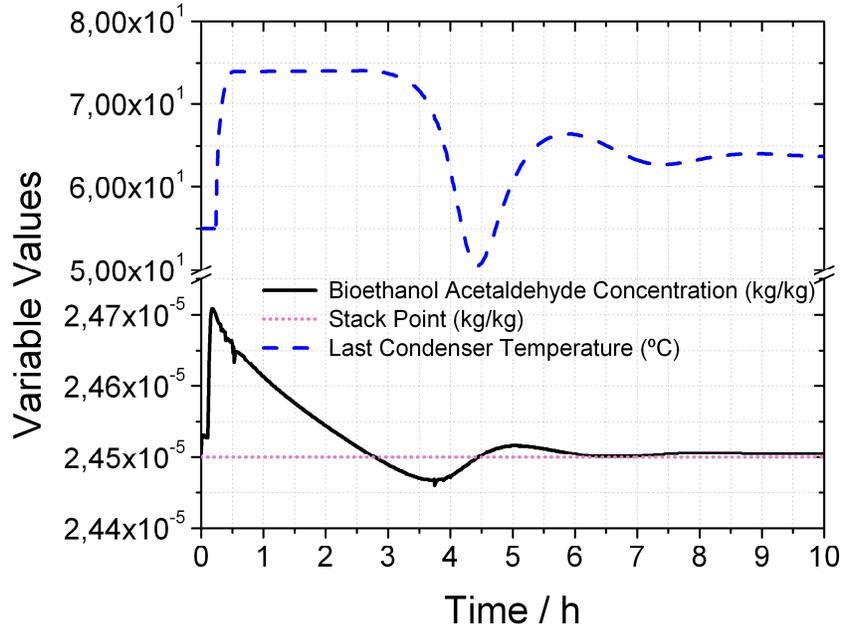


Figure 3.11 – Results of PID controller in degassing system (pasteurized bioethanol installation)

### 3.5 - Conclusion

Production of bioethanol as a renewable fuel or as an input commodity to be used in other industrial branches requires the reduction and control of several contaminants contained in the fermented must. In the present work special attention was focused on controlling acetaldehyde contamination. Analyzing the results presented it is possible to conclude that the wine (must) acetaldehyde concentration will determine the type of industrial installation and the type of control to be used to regulate the acetaldehyde in bioethanol and prevent problems with its oxidation during storage. Thus, for wine with less than  $2.0 \times 10^{-6}$  kg/kg of acetaldehyde, the industrial installation without degassing system is appropriate. For wine concentrations within the range  $2.0 \times 10^{-6}$  to  $2.2 \times 10^{-6}$  kg/kg, the degassing system is required. In case of wine concentrations within the range  $2.2 \times 10^{-6}$  to  $2.0 \times 10^{-5}$  kg/kg, the pasteurized bioethanol installation is the most appropriate one. For concentrations within the range  $2.0 \times 10^{-5}$  to  $2.2 \times 10^{-5}$  kg/kg the degassing system should be included in the pasteurized bioethanol installation. Finally, for musts with higher acetaldehyde concentration ( $\geq 2.2 \times 10^{-5}$  kg/kg) the pasteurized bioethanol installation with a PID controller to regulate the mass flow of second

alcohol is probably the best way to prevent problems with acetaldehyde oxidation during storage.

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## Capítulo 4

# Computational simulation applied on investigation of industrial plants for bioethanol distillation <sup>3</sup>

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## **Abstract**

This work aimed to investigate a typical bioethanol distillation process considering an alcoholic wine with 19 components and to validate the simulation results against experimental data collected from a Brazilian sugar mill. The process was investigated in terms of bioethanol alcoholic graduation, ethanol recovery, energy consumption and ethanol loss. Two optimizing approaches were tested: the central composite design (CCD) and the Sequential Quadratic Programming (SQP). Both approaches allowed the optimization of the equipment configuration used nowadays and provided similar optimal conditions. The results showed that the simulation approach was capable of correctly reproducing a real plant of bioethanol distillation and that the optimal conditions guaranteed the bioethanol production according to legislation, with low consumption of steam and high recovery of ethanol. On the other hand, substantial fluctuations in wine composition may require adjustments of operational conditions or the use of specific control loops to prevent an off-specification product.

*Keywords: bioethanol, aspen plus, distillation, fusel oil, wine distillation, minor components.*

## **4.1 – Introduction**

There is a growing interest in bioethanol as a renewable energy source, as well as a raw material to be used in other industrial branches, such as the chemical, pharmaceutical, and food industries. Brazil is one of the largest bioethanol producers and the largest exporter. For over 30 years bioethanol has been used directly as fuel when its concentration is near the azeotropic point, or added to gasoline, in which case it should be further dehydrated. The rapid increase in its use as a biofuel, the increase of its exports and its use in other industrial sectors requires better product quality control and improvements in the production process.

Although ethanol distillation is a topic widely investigated in literature, most research studies focus on energy consumption, dehydration techniques and alternative control strategies to separate the ethanol-water binary mixture, not

taking into account the set of minor components that influence the distillation process. Usually these compounds are only considered in investigations related to alcoholic beverages because of their influence on the sensorial quality of the product (Soufleros et al., 2004; Ledauphin et al, 2006; Madrera et al, 2010; Piggott et al., 1993; Gaiser et al., 2005). This absence is even more surprising if one considers the important influence of such minor compounds on the performance of industrial distillation units and the existence of very powerful simulation tools nowadays. Such tools can accurately represent the thermodynamic properties of complex solutions, such as those containing a large quantity and variety of compounds, and they can also use reliable algorithms to describe the main unity operations involved in ethanol production.

Computer simulation has been used as a tool for investigating and improving bioethanol dehydration processes by azeotropic or extractive distillations (Ravagnani et al., 2010; Vasquez et al., 2007; Gomis et al., 2007; Cho et al. 2006; Verhoef et al., 2008, Simo et al., 2008, Figueredo et al., 2011) and thermal integration (Dias et al, 2010), invariably as mentioned earlier, considering that the feed stream is the binary mixture ethanol-water. In the case of wine distillation for producing azeotropic bioethanol, little information on the industrial distillation process is available in literature. Two works on this subject are the articles of Marquini et al. (2007) and Decloux and Coustel (2005). Marquini et al. (2007) investigated an industrial distillation system for producing approximately 15,500 L·h<sup>-1</sup> of azeotropic ethanol, but they also considered the alcoholic wine as a mixture composed only of ethanol and water. Decloux and Coustel (2005) studied, by computer simulation with ProSim II, a column system for producing neutral alcohol, a hydrated alcoholic product with very low levels of contaminants used in the cosmetics, perfumery, pharmaceutical, food and fine chemical industries. This system usually requires a sequence of five distillation columns, the first two for distilling bioethanol according to the legislation for biofuels and the subsequent three columns for further purification and removal of organic contaminants. For this purpose they considered a wine containing ethanol, water and six contaminants, so

that the simulation complexity increases as a consequence of the mixture composition as well as the equipment configuration.

Batista and Meirelles (2011) simulated a continuous distillation system for spirits production, taking into account the presence of 10 minor components. Due to the equipment for continuous spirits distillation is similar to a portion of the entire process used for bioethanol concentration, they validated some of their simulation results against experimental data collected in an industrial plant for bioethanol distillation. The same approach was tested by the authors (Batista and Meirelles, 2009) for developing a control loop in order to prevent the contamination of hydrated ethanol with acetaldehyde. Acetaldehyde concentration in ethanol as a biofuel is not restricted by legislation, but this contaminant can oxidize to acetic acid during storage, increasing the ethanol acidity above the value required by legislation ( $30 \text{ mg}\cdot\text{L}^{-1}$ ). In both cases alcoholic wine was represented by a standard solution containing ethanol, water and ten minor compounds.

In Brazil, bioethanol is produced by fermentation of sugar cane juice or from a must composed of cane juice and molasses. The fermentation broth is deyeasted by centrifugation and the obtained alcoholic wine, with a composition similar to that shown in Table 4.1, is pumped to the distillation plant. Figure 4.1 shows a typical Brazilian industrial installation for bioethanol distillation. This installation is based on one of the industrial plants belonging to Santa Adélia Mill, located in Jaboticabal, São Paulo State. This plant produces around  $300 \text{ m}^3\cdot\text{day}^{-1}$  of hydrated bioethanol used for the later production of anhydrous ethanol and is composed of two distillation columns (Figure 4.1). Nevertheless, in industrial practice these distillation columns are named according to their sections, for instance the stripping sections A and B1 are the *wine* and *phlegm exhausting columns*, respectively, and the rectification section B is the *ethanol concentration column*.

The alcoholic wine is fed into the top tray of section A1, which usually has eight trays and whose main purpose is to decrease wine contamination with light components, especially the volatile acidity. Section D, denominated the *second alcohol column*, is fed with a vapor stream withdrawn from the top tray of section A1, has around six trays, and is used for concentrating the light components.

These components are partially removed either by a degassing stream linked to the R1-condenser or by the second alcohol stream, depending on the contamination level of the wine and the desired purity of the main product stream (bioethanol). The bottom product of section D (PFD) and the phlegm contain almost all the bioethanol present in the wine and both streams are fed in section B to be concentrated to the required level. The *wine exhausting column* (section A) typically has 16 trays and should recover almost all ethanol fed into the process, so that its concentration in the vinasse is around or less than 0.02 % by mass. Stillage also contains most of the heavy contaminants, including soluble solids and solids in suspension, such as non-fermentable sugars, salts and very fine particles of bagasse that are removed from the process in this diluted aqueous solution. The phlegm stream is withdrawn from the top tray of section A as a vapor flow, has an ethanol concentration within the range of 25-35% by mass and is fed into the bottom tray of the *ethanol concentration column* (section B). This last section is usually composed of 43 trays and should concentrate ethanol to the level specified by legislation (see Table 4.2). Bioethanol is usually withdrawn as a liquid stream from a tray located 2-4 plates below the top tray and in industry this stream is referred to as pasteurized alcohol.

Table 4.1 – Main components in industrial fermented sugar cane (must, wine or beer)

Component	Boiling Point (°C)	Standard Wine	Industrial Wine	Reference
Water	100.00	0.932	0.942	By difference
Ethanol	78.40	$6.615 \cdot 10^{-02}$	$5.748 \cdot 10^{-02}$	Oliveira (2001)
Methanol	64.70	$3.200 \cdot 10^{-07}$	$1.630 \cdot 10^{-05}$	Boscolo et al. (2000)
Isopropanol	82.40	$1.020 \cdot 10^{-06}$	$1.000 \cdot 10^{-06}$	Cardoso et al. (2003)
Propanol	97.10	$3.360 \cdot 10^{-05}$	$5.737 \cdot 10^{-05}$	Oliveira (2001)
Isobutanol	108.00	$2.780 \cdot 10^{-05}$	$4.748 \cdot 10^{-05}$	Oliveira (2001)
N-Butanol	118.00	-	$1.000 \cdot 10^{-06}$	-
2-Butanol	99.00	-	$1.850 \cdot 10^{-05}$	-
Isoamyl alcohol	132.00	$1.425 \cdot 10^{-04}$	$1.712 \cdot 10^{-04}$	Oliveira (2001)
2-Methyl-1-Butanol <sup>a</sup>	127.50	-	$4.898 \cdot 10^{-05}$	-
1-Pentanol	138.00	-	$1.000 \cdot 10^{-06}$	-
1-Hexanol	158.00	-	$1.000 \cdot 10^{-06}$	-
Methyl Acetate	56.9	-	$1.000 \cdot 10^{-06}$	-
Ethyl Acetate	77.10	$7.690 \cdot 10^{-06}$	$1.877 \cdot 10^{-05}$	Oliveira (2001)
Acetaldehyde	20.20	$1.580 \cdot 10^{-05}$	$1.090 \cdot 10^{-05}$	Oliveira (2001)
Acetone	56.53	$1.500 \cdot 10^{-05}$	$1.000 \cdot 10^{-06}$	Estimated
Acetic Acid	118.10	$4.351 \cdot 10^{-04}$	$2.340 \cdot 10^{-04}$	Oliveira (2001)
Propionic Acid	141.00	-	$5.043 \cdot 10^{-05}$	-
CO <sub>2</sub>	-78.00	$1.100 \cdot 10^{-03}$	$1.100 \cdot 10^{-03}$	Estimated <sup>b</sup>

<sup>a</sup> 2-Methyl-1-Butanol = Amyl alcohol; <sup>b</sup> See Batista and Meirelles (2011) for the details.

The vapor phase from the top tray of section B is used for heating the wine feed stream, and after its condensation a small second alcohol stream may be removed as distillate and recycled to the top of section D. Fusel oil is withdrawn as a liquid stream from some trays between the 35<sup>th</sup> and 40<sup>th</sup> plates (top to bottom). Fusel oil is composed mostly of heavy alcohols such as isoamyl and amyl alcohols, butanol and isobutanol (Salis et al, 2005). In its crude form, fusel oil has low commercial value, but after purification it can be used in the cosmetics industry. As explained elsewhere (Batista and Meirelles, 2011), fusel oil must be removed as a side stream to allow that the required alcoholic graduation of the biofuel is reached. In fact, the so-called higher alcohols behave as components of intermediate volatility in an ethanol-water environment, accumulating in the vapor phase when dissolved in dilute aqueous solutions which occur along section A, and in the liquid phase when the ethanol concentration is higher, as is found on the trays close to the top of section B.

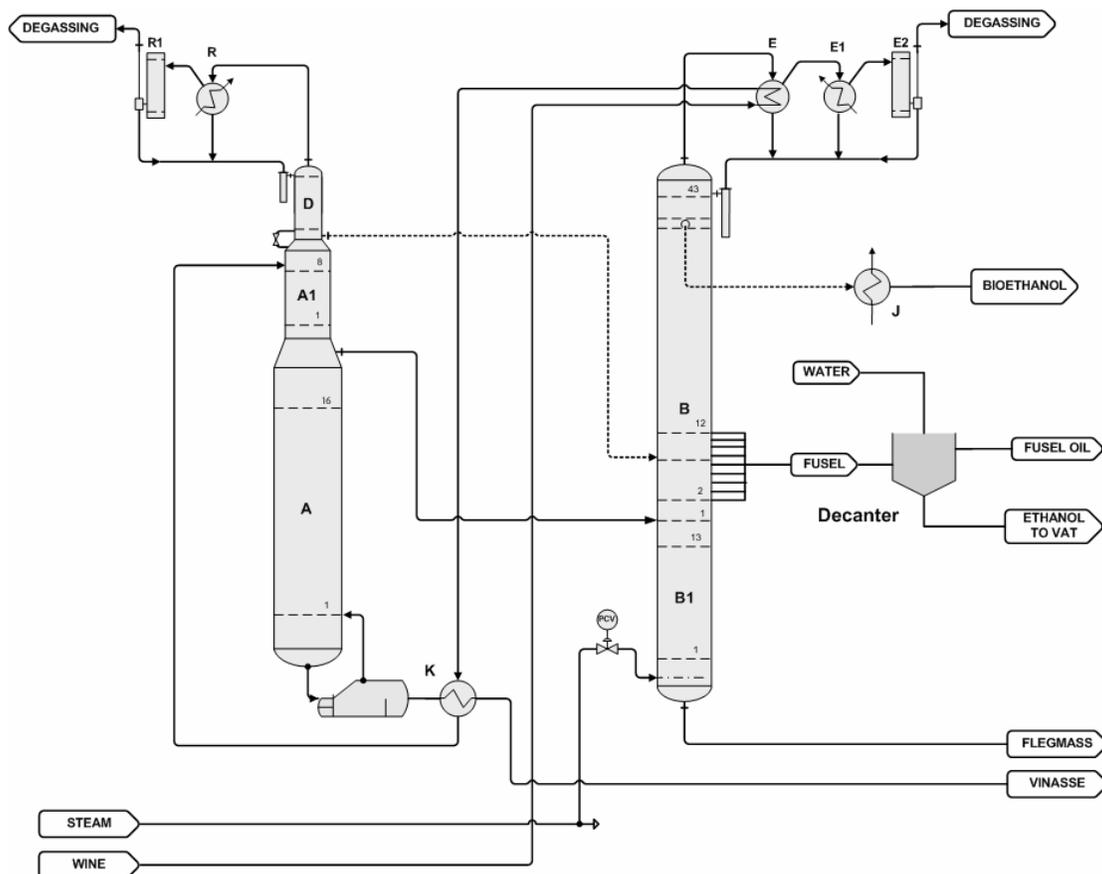


Figure 4.1 – Typical Brazilian Bioethanol Industrial Plant

The liquid phase from the bottom tray of section B is fed into the top of the *phlegm exhausting column* (section B1). Section B1 has around 12 trays and must remove almost all ethanol present in the liquid phlegm stream leaving section B. Similar to the stillage stream, flegmass or white stillage must contain around or less than 0.02 % ethanol by mass, but in contrast to the stillage stream is cleaner and does not contain non-volatile solids. The absence of these solids (salts, non-fermentable sugars and particles in suspension) in section B1 is important from an operational point of view, especially for avoiding incrustation, a problem that can be potentially serious when fluctuations in equipment performance increase the ethanol concentration in the top trays of the exhausting sections.

Degassing may be accomplished at the tops of sections D and B by controlling the temperatures of the condensers R1 and E2. Degassing is performed with the aim of reducing the volatile acidity of bioethanol below the required level, but the corresponding values of the degassing stream must be very small. This approach for controlling acidity of bioethanol should be used only when the losses of ethanol in the degassing stream are negligible. In the cases in which wine has a higher acidity or the alcoholic product requires a lower acidity, degassing can be inefficient or the ethanol losses become prohibitive. In such cases, the removal of volatile acidity and eventually other light contaminants (acetaldehyde, acetone, ethyl acetate, etc.) must be performed via the second alcohol stream.

The exact configuration of the industrial installation for bioethanol distillation, including the number of trays in each section and the eventual use of additional columns, depends on the desired product purity. Table 4.2 provides the specifications of different ethanolic products. Such specifications are defined either by the Brazilian National Petroleum Agency (ANP - Brazil), as is the case for hydrated and anhydrous fuel bioethanol, or by producers and producer associations, as is the case for the alcoholic products specified by Copersucar, one of the largest Brazilian Producers and Trading companies for sugar and bioethanol, congregating several sugar mills and distilleries. As can be seen in Table 4.2, there is a variety of ethanolic products with different degrees of purity. Ethanol with highest purity is indicated in Table 4.2 as Copersucar (HN), also denominated

neutral or extra-fine ethanol, which is used in cosmetics, pharmaceutical, and spirits production. The products with intermediate degrees of purity (H1 and H2) are used as solvents in many industrial segments and increasingly as a raw material, replacing the petrochemical naphtha in the production of specific chemicals.

Table 4.2 – Quality Standards for Brazilian Bioethanol

Characteristics	Unity		Bioethanol <sup>a)</sup>				
			Anhydrous	Hydrated	Hydrated		
					H1 <sup>b)</sup>	H2 <sup>b)</sup>	HN <sup>b)</sup>
<b>Alcoholic Graduation</b>	mass%	Min.	99.3	92.6-93.8	92.8	93.8	94.0
	vol%	Min.	-	-	-	96.0	96.1
<b>Density (at 20°C)</b>	kg/m <sup>3</sup>	-	≤791.5	807.6-811.0	-	-	-
<b>Water content</b>	mass%	Max.	-	-	-	-	-
<b>Acidity (Acetic Acid)</b>	mg/L	Max.	30	30	20	10	10
<b>Conductivity</b>	μS/m	Max.	500	500	500	500	50
<b>pH</b>	-	-	-	6.0-8.0	6.0-8.0	6.0-8.0	6.0-8.0
<b>Fe</b>	mg/kg	Max.	-	5	5	5	5
<b>Na</b>	mg/kg	Max.	-	2	2	2	2
<b>Sulfate</b>	mg/kg	Max.	-	4	4	4	0.2
<b>Copper</b>	mg/kg	Max.	0.07	-	-	-	-
<b>Nitrogen</b>	mg/kg	Max.	-	-	-	-	-
<b>Phosphorus</b>	mg/L	Max.	-	-	-	-	-
<b>Acetaldehyde</b>	mg/L	Max.	-	-	50	10	5
<b>Methanol</b>	mg/L	Max.	-	-	40	20	5
<b>Ethyl Acetate</b>	mg/L	Max.	-	-	120	80	5
<b>Acetone</b>	mg/L	Max.	-	-	-	-	1
<b>Isopropanol</b>	mg/L	Max.	-	-	20	5	2
<b>n-Propanol</b>	mg/L	Max.	-	-	180	30	8
<b>n-Butanol</b>	mg/L	Max.	-	-	10	10	0.5
<b>Isobutanol</b>	mg/L	Max.	-	-	120	20	2
<b>Acetal</b>	mg/L	Max.	-	-	100	50	5
<b>Isoamyl Alcohol</b>	mg/L	Max.	-	-	200	10	3
<b>Higher Alcohols</b>	mg/L	Max.	-	-	400	50	15

<sup>a)</sup> ANP;

<sup>b)</sup> [http://www.copersucar.com.br/produtos/ing/alcool\\_etilico.asp](http://www.copersucar.com.br/produtos/ing/alcool_etilico.asp);

The above explanation clearly emphasized the importance of the minor components and their influence on the design and performance of equipments for bioethanol distillation. It also revealed that studies on the distillation of ethanol based on a simple binary mixture are not the most reliable for investigation of the industrial process. Although some research results based on this type of

simplification have aided in improving the performance of industrial equipments, their exact configuration and the operational conditions used nowadays are largely the result of a trial and error approach performed on the industrial scale. As mentioned earlier, simulation studies that take into account, at least in part, the complexity due to equipment configuration and the presence of minor components are very scarce. However, these studies can help to optimize existing equipments or even allow the suggestion of new and more efficient configurations.

Simulation studies on the distillation and stripping of multicomponent mixtures, such as those found in the recovery of aromas, in the production of alcoholic beverages or in the physical refining of edible oils, allow for achieving a better insight into the performance of industrial equipments (Haypek et al, 2000; Batista and Meirelles, 2011; Meirelles et al, 2008; Ceriani et al, 2008; Ceriani and Meirelles, 2006; Ceriani and Meirelles, 2007). Results of these studies, particularly in the case of minor components, should be treated with some caution due to the low concentrations of these compounds and the large deviations of the simulated values, but even in this case they provide, from a qualitative point of view, important information in terms of the distillation behavior of such compounds that help improve equipment performance and design.

Taking such aspects into account, the present study investigated by computational simulation a typical industrial plant for bioethanol distillation from a wine feed stream containing 17 minor components. The simulation approach was preceded by the definition of wine components based on literature data and chromatographic analysis of industrial samples, by the collection and modeling of phase equilibrium data for the binary mixtures containing wine components and by the collection of information related to the configuration of the industrial equipments, the corresponding operating conditions and the temperature and concentration profiles along the distillation columns. Process simulation was performed using ASPEN PLUS and validated against the experimental information collected from the industrial plant. Afterwards the influence of the main operational and constructive variables was investigated using simulation results and two optimizing approaches: the factorial design, especially the central composite

design (CCD) (Box et al, 1978), and the Sequential Quadratic Programming (SQP). Both approaches allowed for the optimization of the equipment configuration used nowadays for bioethanol distillation (Figure 4.1). The optimized equipment was dynamically tested and control loops were developed for compensating changes in wine concentration.

Except for the work of Decloux and Coustel (2005), no prior work reported in the scientific literature took into account a series of minor components important for the distillation of hydrous ethanol. Additional contributions of the present work include: i) the improvement of the phase equilibrium description, considering additional wine minor components and readjusting NRTL parameters, ii) the rigorous validation of the simulation results against experimental data collected in the industrial plant, iii) the detailed discussion of the behavior of congeners based on the bioethanol purification factors, iv) the optimization of the industrial distillation unit and v) the suggestion of a control loop able to prevent an off-specification product.

## **4.2 - Materials and Methods**

The complexity of the fermented must, due to its multicomponent composition and low concentration of congeners, complicates the accurate prediction of the vapor-liquid equilibrium and this can be considered one of the main sources of errors in the simulation of distillation processes (Faúndez and Valderrama, 2004). Batista and Meirelles (2011) performed a detailed investigation on the vapor-liquid equilibrium of the alcoholic wine. They took into account ten minor components plus ethanol and water and selected the NRTL model for the liquid activity coefficients and the Virial equation, with the Hayden and O'Connell model (Hayden and O'Connell, 1975), for the fugacity coefficients. Using the ASPEN data bank for NRTL interaction parameters as an initial estimate of values and experimental data collected from the literature and DECHEMA data bank, some binary interaction parameters were adjusted in order to improve the equilibrium description, as indicated in detail in Batista and Meirelles (2011). These authors also classified the congeners in light components, intermediate volatility

compounds and heavy components, an important classification for understanding the configuration of the distillation columns and the profiles of the minor components. In the present study such equilibrium studies were extended to the binary interactions involving seven additional minor components: n- and 2-butanol, amyl alcohol, 1-pentanol, 1-hexanol, methyl acetate and propionic acid. The new included minor components require NRTL interaction parameters for 98 additional binaries. Available experimental data was obtained from literature for 60 of those binaries involving the new minor components; the Aspen Data Bank parameters were tested against the experimental data and in the case of higher average deviations in vapor phase molar fractions,  $|\Delta y| > 0.03$ , the NRTL interaction parameters were readjusted. In the case of binaries with no available experimental data the NRTL parameters were obtained via Aspen Plus using the UNIFAC predictions of the simulation software.

#### *4.2.1 - Validation of the process simulation*

In order to verify the reliability of the simulations results, experimental validation of the process simulation was conducted, comparing the obtained results with the information collected in an industrial plant. Experimental samples and data were collected from the industrial plant of Santa Adélia Mill (see Figure 4.1). In order to simplify the simulation procedure, sections A, A1 and D were grouped into a single column, as well as sections B and B1 into a second unique distillation equipment. Industrial wine at 94 °C, with a volumetric flow rate of 100 m<sup>3</sup>/h, was fed into the top of section A1, at tray 7 (T7) from the top of column A1. The phlegm is withdrawn from the top of section A represented by tray 15 (T15) and the stillage from the bottom of section A. In column BB1, hydrated ethanol is withdrawn from tray 2 (T2) with a flow rate of 6.8 m<sup>3</sup>/h, and fusel oil from tray 40 (T40) from the top. Considering that during the experimental trials no second alcohol stream was withdrawn, both columns were simulated as operating with total reflux, where the top of section D was represented by tray 1 (T1) of column AA1D, and the top of section B by tray 1 (T1) of column BB1. In column AA1D, samples points were installed in tray 1 (T1), tray 6 (T6) corresponding to the bottom of section D, tray 14

(T14) corresponding to the bottom of section A1, tray 15 (T15) and tray 20 (T20). In column BB1, sample points were installed in tray 2 (T2) corresponding to the tray of bioethanol withdraw, tray 4 (T4), tray 9 (T9), tray 15 (T15), tray 19 (T19), tray 32 (T32), tray 34 (T34), tray 36 (T36), tray 38 (T38), tray 40 (T40) corresponding to the tray of fusel oil withdrawn. Samples of industrial wine, vinasse (bottom of section A), phlegm and flegmass (bottom of section B1) were also collected. All samples were analyzed by gas chromatography (GC) according to the methodology described below. Additional information on the temperatures of trays 15 (phlegm withdrawal) and vinasse stream of column AA1D and trays 40 and 55 of column BB1 were also acquired, as well as information on the temperatures and flow rates of the input and output streams. Using the input information mentioned above, static simulations were conducted with Aspen Plus simulator and the simulated results compared with the experimental compositions and temperatures of the selected trays and output streams. Murphree tray efficiency for columns AA1D, and sections B and B1 were fixed at 0.65, 0.5 and 0.6, respectively. The total column pressure drop was fixed in 0.48 atm for column AA1D and 0.41 atm for column BB1. Local atmospheric pressure in Santa Adélia Mill varied within the range of 0.898 to 0.928 atm.

#### *4.2.1.1 - GC Analysis*

The methodology for GC analysis was originally developed by Batista and Meirelles (2011)<sup>4</sup> and further complemented in the present work, taking into account 17 components to be identified within the following concentration ranges: Acetaldehyde (1220-0.3 mg/l), Methanol (1110-0.3 mg/l), Ethanol (41000-0.2 mg/l), Acetone (800-0.3 mg/l), Isopropyl Alcohol (1000-0.3 mg/l), Methyl Acetate (500-0.3 mg/l), Propanol (3500-0.3 mg/l), Ethyl Acetate (1000-0.3 mg/l), 2-Butanol (1200-0.3 mg/l), Isobutanol (3600-0.3 mg/l), Acetic Acid (500-0.3 mg/l), n-Butanol (2500-0.3 mg/l), Isoamyl Alcohol (7500-0.3 mg/l), 2-Methyl-1-Butanol (4500-0.3 mg/l), Propionic Acid (500-0.3 mg/l), 1-Pentanol (800-0.3 mg/l) and 1-Hexanol (800-0.3 mg/l). It was observed that all components produced identifiable peaks when their

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<sup>4</sup> Vide Capítulo 2, item 2.2.2.1

concentrations were greater than 0.1 mg/l (0.000001 in mass fraction), where this value was fixed as a lower detection limit. The composition of the industrial wine was used as the feed stream for the simulation runs performed for validation purposes. In the case of minor components not identified during the wine GC analyses, but identified in the more concentrated samples taken along the columns, their composition in the feed stream was fixed at the minimum chromatographic detection limit value. Mass fraction of water was quantified by difference. The composition of one of the industrial wines collected, analyzed and used in the simulations for validation is shown in Table 4.1, under the tag Industrial Wine.

#### *4.2.2 - Simulation of bioethanol production*

The complexity of the bioethanol industrial plant is determined by the desired product quality standard. The absence of a universal bioethanol quality standard requires that the major traders determine bioethanol specifications, and therefore influence the operational conditions and equipment configurations to be used by the mills. Bioethanol quality differences are related to the maximum level of contaminants allowed in the product, since ethanol and water quality standards may be achieved with a single distillation column. In order to corroborate this observation, static simulations were conducted with the Aspen Plus simulator using the RADFRAC package, on three different equipment configurations. This package uses the MESH equations (Kister, 1992) for rigorously calculating distillation columns. Based on the industrial plant shown in Figure 4.1, the first column configuration simulated was composed only of sections A and B. Industrial wine (see Table 4.1) was fed into the top of section A. The phlegm was withdrawn from the top of section A and fed into the bottom of section B, without the presence of section B1. The bottom stream of section B was fed into the top of section A. Bioethanol was withdrawn from the third tray from the top (this specification was used for all three configurations). Fusel oil was withdrawn from tray 41 (top to bottom) of section B. A small stream (700 kg/h) was withdrawn as distillate of section B (second alcohol stream). In the case of the second configuration, section

B1 (13 trays) was added as a stripping section below section B. The bottom product of section B was fed into the top of section B1 and the top product of section B1 was fed into the bottom of section B. From the bottom of section B1 the flegmass stream was withdrawn. Finally, in the third configuration, sections A1 (8 trays) and D (6 trays) were added to the second configuration indicated above, acting as an enriching section of column AA1D. Wine was fed into the top of section A1 and a second alcohol stream (350 kg/h) was withdrawn as section D distillate. The second alcohol stream of section B was adjusted to maintain the total second alcohol flow rate in the three configurations (700 kg/h), and presented a value of 350 kg/h. Profiles of the congeners in section B were discussed in order to explain its influence on the industrial plant configuration. To ensure accurate comparison of the three configurations analyzed, some process parameters were kept constant in all three cases: bioethanol alcoholic graduation (93.3% in mass), bioethanol mass flow (11600 kg/h), phlegm alcoholic graduation (38.5% in mass), total second alcohol flow rate (700 kg/h) and fusel oil flow rate (500 kg/h). In addition to these specifications, it was ensured that the maximum level of ethanol in flegmass and vinasse must always be less than 0.02 % by mass. For all simulations, wine was represented by the industrial wine shown in Table 4.1.

Aiming to improve the analyses of the three equipment configurations mentioned above, a purification factor ( $F$ ) was defined to assess the purity of the bioethanol produced. The purification factor is represented in Eq. 4.1 and relates the ratios of ethanol to minor components (all components excluded ethanol and water) in the wine and bioethanol, allowing for evaluation of the efficiency of a specific configuration to purify the bioethanol produced. This factor was evaluated separately for each class of components (light, intermediate and heavy) and for the minor components as a whole.

$$F = \frac{\left( \frac{w_{ethanol}}{\sum w_{min\ comp}} \right)_{bioethanol}}{\left( \frac{w_{ethanol}}{\sum w_{min\ comp}} \right)_{wine}} \quad (4.1)$$

Where  $F$  is the purification factor and  $w$  is the mass fraction of ethanol and minor components in bioethanol and wine.

In order to investigate the influence of some constructive and operational variables on the performance of a standard bioethanol distillation plant, a series of simulations was conducted based on the third configuration described above. With the aim of reducing the complexity of the simulations and guaranteeing convergence for every set of variables, some simplifications were assumed: bioethanol was withdrawn as distillate from section B not as pasteurized alcohol, columns AA1D and BB1 were considered as two distillation columns, the pressure at the top of both columns was fixed at 1 atm and no pressure drop was considered, Murphree tray efficiency was fixed at 0.7 for all trays, the number of minor components were limited to ten and the wine composition was fixed according to values obtained in literature (see Table 4.1, especially the values under the headline Standard Wine). The wine was fed into tray 7 of column AA1D (top tray of section A1) with mass flow rate of 202542 kg/h and temperature of 94 °C. Despite the reduction in the number of minor components, those most important were considered and at least one minor component was taken into account for every organic class.

The set of simulations was conducted changing some independent variables selected according industrial observation. A first screening of variables was performed using a fractional factorial design  $2^{(11-7)}$  as well as a sensitivity test, with eleven independent variables according to the levels shown in Table 4.3. Note that most values indicated in Table 4.3 as the intermediate levels correspond to the actual levels used in the industrial practice. A second series of simulations were conducted for optimization purposes using a central composite rotational design (CCRD) for the independent variables that were statistically significant in the fractional factorial design. An alternative optimization approach was also used based on the Sequential Quadratic Programming (SQP) and on the independent variables that were statistically significant in the prior sensitivity test. The aim was to investigate the possibility of optimizing the current bioethanol production system comparing two different optimization methodologies (CCRD and SQP).

Table 4.3 - Levels for the fractional factorial design

<b>Independent Variable</b>	<b>Tag</b>	<b>-1</b>	<b>0</b>	<b>1</b>
Number of trays in section A1	TA1	2	4	6
Number of trays in section A	TA	18	22	26
Number of trays in section D	TD	3	6	9
Number of trays in section B	TB	40	45	50
Number of trays in section B1	TB1	14	18	22
Reflux ratio of section D	RRD	30	35	40
Reflux ratio of section B	RRB	3	4.5	6
Tray of fusel oil withdrawal	TFO	40	42	44
Fusel oil flow rate (kg/h)	FOF	100	200	300
Bioethanol flow rate (kg/h)	BFR	13000	14500	16000
Section D second alcohol flow rate (kg/h)	SAF	300	350	400

The SQP method is a quasi-Newton nonlinear programming algorithm that can converge tear streams, and equality and inequality constraints simultaneously with the optimization problem. Its basic principle consists of minimizing the objective function considering a set of constraints, as shown below.

$$\begin{aligned} &\text{Minimize} && F(x), \quad x \in \mathfrak{R}^n \\ &\text{Subject to} && b_l \leq \begin{Bmatrix} x \\ Ax \\ c(x) \end{Bmatrix} \leq b_u, \end{aligned}$$

Where  $c$  is a vector of nonlinear functions,  $A$  is a constant matrix that defines the linear constraints, and  $b_l$  and  $b_u$  are constant upper and lower bounds. Note that the constraints can be an array containing linear and nonlinear functions. SQP solves the optimization problem iteratively and in each step a solution is obtained by approximating the nonlinear problem in the following way: the objective function ( $F(x)$ ) is replaced by a quadratic approximation and the nonlinear constraints ( $c(x)$ ) are replaced by linear approximations. Unlike other methods that attempt to convert the problem to be optimized into a sequence of optimize subproblems without constraints, the SQP tries to solve the optimization problem iteratively where in each step the solution is obtained by the solution of an approximation of nonlinear problem where the objective function ( $F(x)$ ) is replaced by a quadratic approximation and nonlinear constraints ( $c(x)$ ) are replaced by linear approximation.

In case of the CCRD optimization, the distillation plant performance was evaluated based on the following response functions: bioethanol alcoholic

graduation (BAG), ethanol recovery (ER), absolute steam consumption (SC) and stillage/flegmass ethanol loss (EL). Optimum conditions were determined by response surface analysis and the statistical calculations were performed using the software STATISTICA 7.5 StatSoft. In the case of the SQP method, the following objective function  $F_o = \frac{Q}{D}$  was minimized, where  $Q$  is the reboiler duty in MMkcal/hr and  $D$  is the bioethanol mass flow in kg/h. The objective function so defined corresponds to the specific steam consumption (SSC). The bioethanol alcoholic graduation (BAG) and the ethanol loss (EL) were chosen as constraints. Ethanol recovery (ER) was evaluated as a further result of the optimization processes SQP optimization was solved using Aspen Plus model analysis optimization and constrains tools. The manipulated variables and their respective ranges of variation were the same for both optimization procedures and they are indicated in Table 4.4. In this way, both optimization approaches were performed on a similar basis. The results of the both methods were compared and the final optimized distillation plant was tested for the complete wine composition with 17 minor components and pasteurized bioethanol withdrawal.

Table 4.4 - CCRD 2<sup>3</sup> and SQP optimizations

		CCRD			SQP	
Objective Function		Minimize EL and SC Maximize BAG and ER <sup>1</sup>			Minimize $F_o = \frac{Q}{D}$	
Constrains		None			BAG ≥ 92.8 wt% EL ≤ 0.02%	
Manipulate Variables	Tag	-1.68	-1	0	1	+1.68
Number of trays in section B	TB	35	40	45	50	55
Reflux ratio of section B	RRB	3.5	4	4.5	5	5.5
Bioethanol flow rate (kg/h)	BFR	13600	13700	13800	13900	14000
Reflux ratio of section D <sup>2</sup>	RRD	35	Ten points			45

<sup>1</sup> ER in SQP was evaluated as a result of the optimization process.

<sup>2</sup> Only included in SQP optimization.

#### 4.2.3. Dynamic Simulations

Aiming to investigate the sensitivity of the optimized distillation unit to disturbances in process conditions, dynamic simulations were performed for a changing alcoholic graduation in the feed stream. For this purpose five samples of industrial wine, collected at the Santa Adélia mill on different days and months,

were analyzed by GC. The alcoholic graduation was quantified and the average and standard deviation values used for fixing the disturbance range. Using Aspen Dynamics, simulations were performed for evaluating the impact of wine composition on bioethanol alcoholic graduation and a PID controller was developed in order to avoid the corresponding effects. The effect of wine alcoholic graduation on ethanol losses, isoamyl content in fusel oil and volatile content (acetaldehyde) in bioethanol was also investigated, as well as performance of the PID controller evaluated in the case of these variables.

### 4.3 - Results and Discussion

In a prior work, Batista and Meirelles (2011) classified the wine minor components into the following groups: light components (acetaldehyde, acetone and ethyl acetate), intermediate volatility compounds (superior alcohols) and heavy components (acetic acid). In the present work, seven new minor components (n- and 2-butanol, amyl alcohol, 1-pentanol, 1-hexanol, methyl acetate and propionic acid) were added to the wine, requiring additional NRTL parameters for 98 binaries involving these new minor components. From the new set of binaries, parameters were readjusted for 26 binaries, presenting averages deviations in vapor phase molar fractions  $|\Delta y|$  of 0.013 and for boiling temperatures  $|\Delta T|$  of 0.72 °C.

Figure 4.2 shows the relative volatility of these components in relation to water as a function of the ethanol content in the hydro-ethanolic liquid phase. Note that in this figure only the concentrations of major components, ethanol and water, were varied along the entire range and the minor components were always kept within a diluted concentration range ( $w_{mincomp} \leq 0.0001$ ). As indicated by Figure 4.2, n- and 2-butanol, amyl alcohol, 1-pentanol, and 1-hexanol should be classified as intermediate volatility components, acting as light compounds in a water-rich environment and as heavy in the case of higher ethanol concentrations in the liquid phase. Methyl acetate can be classified as a *light component*, with a behavior very similar to acetaldehyde. On the other hand, propionic acid presented volatility values similar to those of acetic acid, being classified as a *heavy component*.

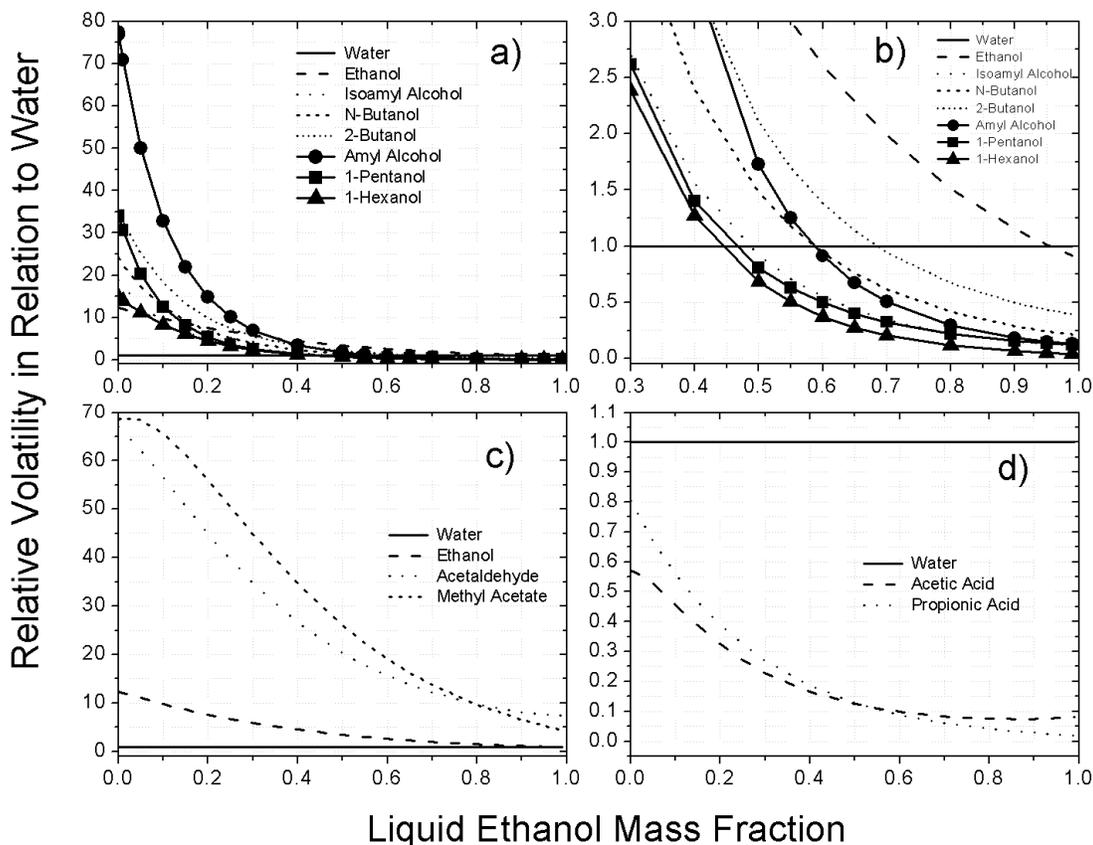


Figure 4.2 – Relative volatility in relation to water for the new congeners

#### 4.3.1. Validation of process simulation

All samples from the industrial plant were analyzed by GC. Linear calibration curves were obtained for all standards with high determination coefficients ( $R^2$ ), always greater than 0.992. Reproducibility of the calibration curves was verified through the analyses of two standard solutions with known concentrations containing water, methanol, ethanol, propanol, acetic acid, isoamyl alcohol and active amyl alcohol. The highest deviation observed between the values obtained by the GC analysis and the original composition of the above mentioned mixtures was 15 % and occurred for acetic acid. It should be noted that the selected chromatographic column was not the most appropriate for analysis of organic acids due to its relatively low polarity, but it is the most appropriate for ethanol and all other minor compounds, especially in relation to its capacity of separating isomers, such as isoamyl and active amyl alcohol. In case of other minor components the

deviations were much lower, with a maximum value of 5.5 % and an average value of 2.5 %.

Three distillation profiles were collected at the Santa Adélia mill on different days and months, analyzed and compared with the results produced by the simulations. A detailed comparison of the experimental and simulated values for profile 1 is discussed below, followed by an overview of the results for the other profiles. The comparison of the experimental and simulated profiles was performed in terms of the mass fractions of water, ethanol and minor components, calculating the absolute and relative average deviations according to Eqs. 4.2 and 4.3 below:

$$|\Delta w| = \frac{\sum_{i=1}^n |w_{exp,i} - w_{sim,i}|}{n} \quad (4.2)$$

$$|\Delta w_{rel}| = 100 \cdot \left( \frac{1}{n} \sum_{i=1}^n \frac{|w_{exp,i} - w_{sim,i}|}{w_{exp,i}} \right) \quad (4.3)$$

Where  $w_{exp,i}$  and  $w_{sim,i}$  stand for the experimental and simulated mass fractions of component  $i$ , respectively, and  $n$  represents the number of experimental results.

Figure 4.3 presents the experimental and simulated profiles of ethanol and water for columns AA1D (Figure 4.3a) and BB1 (Figure 4.3b). As shown in Figure 4.3, Aspen Plus was able to accurately reproduce the bioethanol industrial plant in terms of ethanol and water tray compositions. In fact, the experimental and simulated values were very close, with absolute and relative deviations for ethanol mass fractions in column AA1D of 0.0061 and 2.47 %, respectively, while for water the corresponding values were 0.0063 and 7.57 %, respectively. In column BB1 absolute and relative deviations of 0.0221 and 7.16 % were obtained for ethanol mass fractions and of 0.0221 and 7.16 % for water mass fractions, respectively.

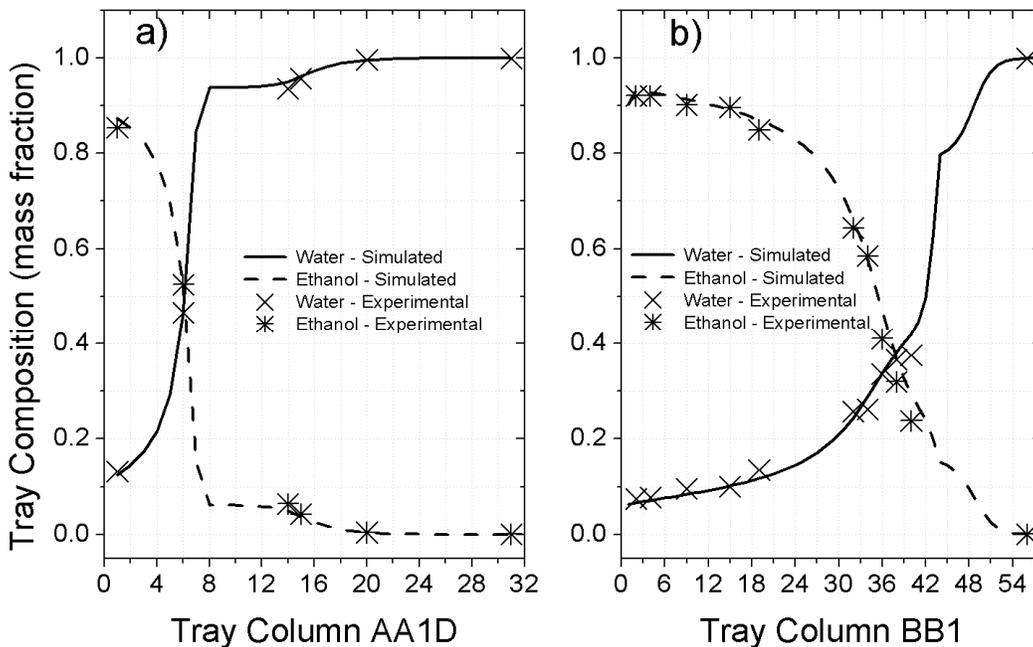


Figure 4.3 - Ethanol/Water Validation results for profile 1

Table 4.5 and Table 4.6 present the experimental and simulated mass fractions of isobutanol, isoamyl alcohol, amyl alcohol, acetaldehyde, acetic acid and the others minor compounds as a group, for columns AA1D and BB1, respectively. Table 4.5 shows that the experimental and simulated tray temperatures are very similar. In the case of minor compound composition, most experimental and simulated values have the same order of magnitude, even for the very low experimental mass fractions. Nevertheless, relative deviations are higher than 100% in some cases, for instance acetic acid in tray 20, amyl alcohol in tray 1 and isoamyl alcohol in trays 15 and 20.

The experimental and simulated tray temperatures of column BB1 were also similar (Table 4.6). In most cases the experimental and simulated composition values presented the same order of magnitude (see Table 4.6). However, high relative deviations were observed, often reaching values greater than 100%, as was the case of propanol in trays 2, 4, 9 and 15. These large deviations were obtained because of the low concentration of components at some stages, an aspect that not only increases the uncertainty of the experimental GC-analysis, but also makes the experimental composition values more sensitive to small

oscillations in equipment operation near steady state, complicating their representation by simulation with low deviations in comparison to the experimental values.

Table 4.5 - Experimental and simulated values (mass fractions) for column AA1D

		Propanol	Isobutanol	Isoamyl Alcohol	Acetaldehyde	Acetic Acid	Amyl Alcohol	Others	Temperature (°C)
T1	Exp. <sup>a</sup>	0.000328	0.000300	0.000503	0.000055	ND <sup>c</sup>	0.000136	0.001674	-
	Sim. <sup>b</sup>	0.000366	0.000064	0.000244	0.000056	Trace <sup>d</sup>	0.000039	0.002011	-
T6	Exp. <sup>a</sup>	0.000841	0.001362	0.004512	0.000019	ND <sup>c</sup>	0.001307	0.001379	-
	Sim. <sup>b</sup>	0.000819	0.000872	0.005766	0.000005	0.000039	0.000984	0.000857	-
T14	Exp. <sup>a</sup>	0.000063	0.000049	0.000139	0.000012	0.000125	0.000035	0.000054	-
	Sim. <sup>b</sup>	0.000028	0.000007	0.000313	Trace	0.000234	0.000044	0.000032	-
T15	Exp. <sup>a</sup>	0.000034	0.000014	0.000056	0.000008	0.000122	0.000022	0.000041	103.2
	Sim. <sup>b</sup>	0.000015	0.000002	0.000178	Trace	0.000237	0.000033	0.000041	102.8
T20	Exp. <sup>a</sup>	ND <sup>c</sup>	ND <sup>c</sup>	0.000010	0.000006	0.000100	ND <sup>c</sup>	0.000037	-
	Sim. <sup>b</sup>	Trace <sup>d</sup>	Trace <sup>d</sup>	0.000003	Trace <sup>d</sup>	0.000245	Trace <sup>d</sup>	0.000066	-
T30	Exp. <sup>a</sup>	ND <sup>c</sup>	ND <sup>c</sup>	ND <sup>c</sup>	ND <sup>c</sup>	0.000256	ND <sup>c</sup>	0.000064	108.2
	Sim. <sup>b</sup>	Trace <sup>d</sup>	Trace <sup>d</sup>	Trace <sup>d</sup>	Trace <sup>d</sup>	0.000247	Trace <sup>d</sup>	0.000056	109.0

<sup>a</sup> Exp – Experimental values

<sup>b</sup> Sim – Simulated Values

<sup>c</sup> ND – Not Detected by GC (<10<sup>-6</sup> mg/mg)

<sup>d</sup> Trace - 1/10<sup>-9</sup> (Aspen Technology, 2003)

On the other hand, the simulated and experimental concentration profiles of minor components show, from a qualitative point of view, similar trends in both columns AA1D and BB1. For instance, experimental and simulated profiles of propanol in column AA1D have the same trend, with maximum values at tray 6. Even in the case of components with much higher deviations between experimental and simulated results, as was observed for isobutanol, isoamyl and amyl alcohols in column AA1D, the same general trend was obtained for the experimental and simulated profiles. In general, the same behavior is observed for other profiles given in Table 4.6, including the results for light (acetaldehyde) and heavy (acetic acid) components. Furthermore, the relative deviations are lower in the trays where these minor compounds are concentrated. For instance, isoamyl alcohol in stage 40 of column BB1 (Table 4.5) or acetaldehyde in stage 1 of column AA1D, with relative deviations of 11.7 % and 1.82 %, respectively.

Table 4.7 shows the simulated and experimental results for two internal streams of the industrial equipment, the bottom product of section D and the phlegm, and all equipment output streams. In the case of ethanol and water mass fractions the relative deviations are low, especially for the bottom product of section D, with values less than 1 % (0.75 % for water and 0.68 % for ethanol). For minor components the relative deviations are much higher but most experimental and simulated values have the same order of magnitude. In the case of the main product, bioethanol, the major components are very well described by the simulation and the same occurs for minor components with low volatility (organic acids) or most of those with intermediate volatility, for which the experimental results are below the detection limit and the simulated results below trace values. However, for some light components (methanol and ethyl acetate) and some of those with intermediate volatility (propanol and 2-butanol) the obtained deviations are high. Acetaldehyde was very well described and the isopropanol simulated result corresponds to a value below the detection limit of the GC-analysis, as was also obtained for the experimental sample.

Table 4.6 - Experimental and simulated values (mass fraction) for column BB1

		Propanol	Isobutanol	Isoamyl Alcohol	Acetaldehyde	Acetic Acid	Amyl Alcohol	Others	Temperature (°C)
T2	Exp. <sup>a</sup>	0.000136	ND <sup>c</sup>	ND <sup>c</sup>	0.000018	ND <sup>c</sup>	ND <sup>c</sup>	0.003834	-
	Sim. <sup>b</sup>	0.000548	Trace <sup>d</sup>	Trace <sup>d</sup>	0.000019	Trace <sup>d</sup>	Trace <sup>d</sup>	0.002006	-
T4	Exp. <sup>a</sup>	0.000380	ND <sup>c</sup>	ND <sup>c</sup>	0.000012	ND <sup>c</sup>	ND <sup>c</sup>	0.001910	-
	Sim. <sup>b</sup>	0.000913	Trace <sup>d</sup>	Trace <sup>d</sup>	0.000001	Trace <sup>d</sup>	Trace <sup>d</sup>	0.000240	-
T9	Exp. <sup>a</sup>	0.000955	0.000072	ND <sup>c</sup>	0.000008	ND <sup>c</sup>	ND <sup>c</sup>	0.001197	-
	Sim. <sup>b</sup>	0.002597	0.000003	Trace <sup>d</sup>	Trace <sup>d</sup>	Trace <sup>d</sup>	Trace <sup>d</sup>	0.000162	-
T15	Exp. <sup>a</sup>	0.002884	0.000421	ND <sup>c</sup>	ND <sup>c</sup>	ND <sup>c</sup>	ND <sup>c</sup>	0.001442	-
	Sim. <sup>b</sup>	0.006799	0.000021	0.000015	Trace <sup>d</sup>	Trace <sup>d</sup>	Trace <sup>d</sup>	0.000348	-
T19	Exp. <sup>a</sup>	0.010429	0.003168	ND <sup>c</sup>	ND <sup>c</sup>	ND <sup>c</sup>	ND <sup>c</sup>	0.002829	-
	Sim. <sup>b</sup>	0.011812	0.000085	0.000101	Trace <sup>d</sup>	Trace <sup>d</sup>	0.000010	0.000760	-
T32	Exp. <sup>a</sup>	0.041833	0.045686	0.002740	ND <sup>c</sup>	ND <sup>c</sup>	0.001542	0.007141	-
	Sim. <sup>b</sup>	0.037348	0.005811	0.033241	Trace <sup>d</sup>	Trace <sup>d</sup>	0.004513	0.010945	-
T34	Exp. <sup>a</sup>	0.052830	0.076223	0.011087	ND <sup>c</sup>	ND <sup>c</sup>	0.005456	0.008147	-
	Sim. <sup>b</sup>	0.035202	0.009884	0.066829	Trace <sup>d</sup>	Trace <sup>d</sup>	0.009345	0.014292	-
T36	Exp. <sup>a</sup>	0.044491	0.097464	0.076945	ND <sup>c</sup>	ND <sup>c</sup>	0.028119	0.006593	-
	Sim. <sup>b</sup>	0.028293	0.015174	0.117166	Trace <sup>d</sup>	Trace <sup>d</sup>	0.016343	0.016359	-
T38	Exp. <sup>a</sup>	0.030463	0.080290	0.150671	ND <sup>c</sup>	ND <sup>c</sup>	0.048314	0.004972	-
	Sim. <sup>b</sup>	0.018919	0.020196	0.173459	Trace <sup>d</sup>	Trace <sup>d</sup>	0.022822	0.015690	-
T40	Exp. <sup>a</sup>	0.016357	0.052473	0.245347	ND <sup>c</sup>	ND <sup>c</sup>	0.068844	0.003574	101.8
	Sim. <sup>b</sup>	0.010681	0.022884	0.216526	Trace <sup>d</sup>	0.000008	0.024982	0.012606	100.4
T56	Exp. <sup>a</sup>	ND <sup>c</sup>	ND <sup>c</sup>	ND <sup>c</sup>	ND <sup>c</sup>	0.000012	ND <sup>c</sup>	ND <sup>c</sup>	108.5
	Sim. <sup>b</sup>	Trace <sup>d</sup>	Trace <sup>d</sup>	Trace <sup>d</sup>	Trace <sup>d</sup>	0.000115	Trace <sup>d</sup>	0.000042	108.6

<sup>a</sup> Exp – Experimental values, <sup>b</sup> Sim – Simulated Values, <sup>c</sup> ND – Not Detected by GC (<10<sup>-6</sup> mg/mg), <sup>d</sup> Trace - IΛ 10<sup>-9</sup> (Aspen Technology, 2003)

Note in Table 4.7 that the bioethanol alcoholic content is below that required for the biofuel. This is possible in the present case because hydrated ethanol

produced in Santa Adélia mill is dehydrated by extractive distillation with ethylene glycol and this dehydration method allows for a higher water concentration in the feed stream (Meirelles et al., 1992). In the case of vinasse and flegmass both experimental and simulated results are compatible (see Table 4.7), with most minor components below the detection limit of the chromatographic analysis and within the concentration range assumed as trace by Aspen Plus. In case of fusel oil, isoamyl alcohol should be considered as the third major component since its mass fraction has an order of magnitude similar to the ethanol mass fraction. For the major components the average relative deviation is 15.6 % and the corresponding value for isoamyl alcohol only is 11.7 %, indicating that the simulation results describe relatively well this side stream. For the other components encountered in lower concentration in fusel oil, the relative deviations are usually high.

Figure 4.4 provides a comparison of the experimental and simulated values for the three profiles in terms of ethanol and water mass fractions. The average relative deviation between experimental and simulated mass fractions was 11.4% and the determination coefficient ( $R^2$ ) of the linear correlation was 0.991, confirming that Aspen Plus was able to accurately reproduce, in terms of ethanol and water mass fractions, a typical industrial scale bioethanol distillation process.

Regarding minor compounds, the average relative deviations calculated for each component are much higher, resulting in a global average value of 92.7 %. An aspect that contributes to increasing the average deviations is the extremely low concentration of these components in specific trays along the equipment, for instance the volatile compounds (acetaldehyde, ethyl acetate, acetone, methanol and methyl acetate) in the bottom of both columns, higher alcohols and organics acids in their top and also some components with very low concentrations in the wine (1-hexanol, 1-pentanol, 2-butanol, n-butanol and isopropyl alcohol). For these reasons the relative deviations presented a large dispersion around the global average value, with a maximum close to 800 % for trays with extremely low concentrations of specific components and a minimum value of 0.38 % for the trays in which minor components reach higher concentrations, as in the region of fusel

oil withdrawal. Despite this difficulty, the determination coefficient ( $R^2$ ) of the linear correlation between the experimental and simulated values shown in Figure 4.5 is 0.821, confirming that at least from a qualitative point of view the Aspen Plus simulator was able to reproduce the industrial process in terms of minor components.

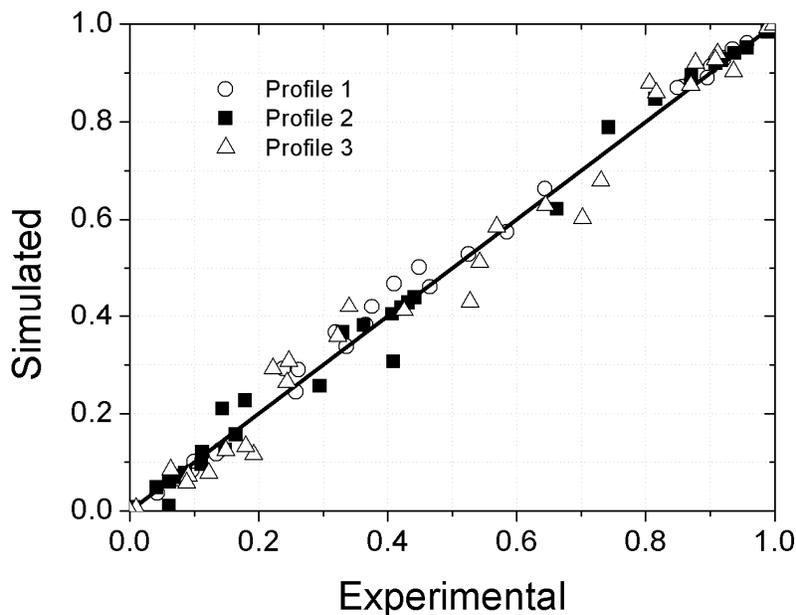


Figure 4.4 - Experimental versus simulated mass fractions of ethanol and water

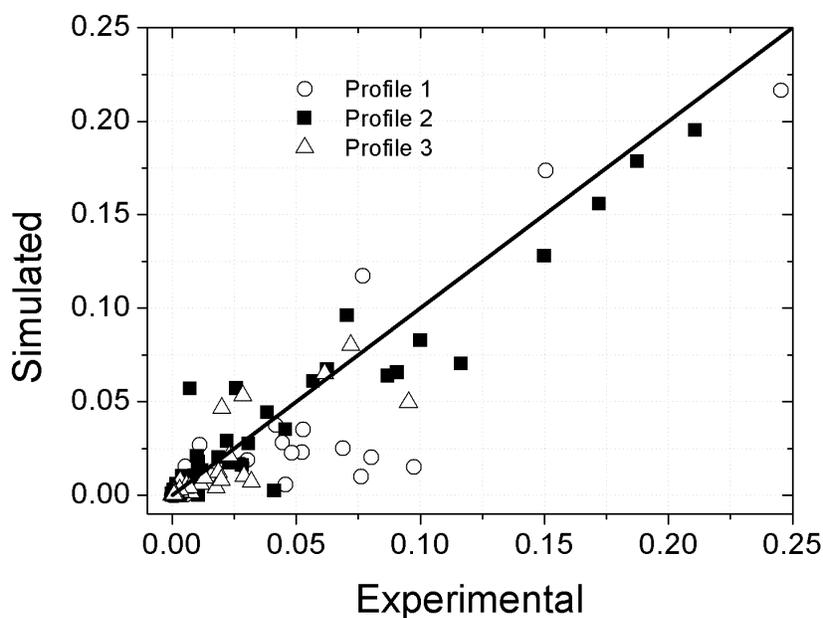


Figure 4.5 - Experimental versus simulated mass fractions of minor components.

Table 4.7 - Experimental vs simulated (w/w): phlegm, BPCD, Bioethanol, Vinasse, Flegmass and Fusel Oil

Component	Phlegm		BPCD <sup>a</sup>		Bioethanol		Vinasse		Flegmass		Fusel Oil	
	Sim.	Exp.										
Water	0.725137	0.71463	0.461957	0.465437	0.074211	0.075184	0.999676	0.999316	0.999637	0.999315	0.423698	0.375457
Ethanol	0.272717	0.283388	0.528722	0.525142	0.923126	0.920828	0.000021	0.000364	0.000219	0.000673	0.29217	0.237949
Methanol	0.00008	0.00005	0.000071	0.000565	0.000956	0.003007	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	0.000051	0.00004
Isopropanol	Trace <sup>b</sup>	ND <sup>c</sup>	Trace <sup>b</sup>	ND <sup>c</sup>	0.000009	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>
Propanol	0.000153	0.000336	0.000818	0.000842	0.000548	0.000136	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	0.010681	0.016357
Isobutanol	0.000039	0.000342	0.000872	0.001363	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	0.022884	0.052473
Isoamyl Alcohol	0.001698	0.000926	0.005766	0.004512	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	0.216526	0.245347
Ethyl Acetate	Trace <sup>b</sup>	0.000022	0.000409	0.000546	0.00035	0.000801	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	0.000004	ND <sup>c</sup>
Acetaldehyde	Trace <sup>b</sup>	ND <sup>c</sup>	0.000005	0.000019	0.000019	0.000018	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>
Acetone	Trace <sup>b</sup>	ND <sup>c</sup>	0.000002	ND <sup>c</sup>	0.000001	ND	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>
Acetic Acid	Trace <sup>b</sup>	ND <sup>c</sup>	Trace <sup>b</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	0.000247	0.000256	0.000115	0.000012	0.000008	ND <sup>c</sup>
2-Butanol	0.000019	0.000038	0.000332	0.000241	0.00078	0.000026	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	0.007155	0.001596
Amyl Alcohol	0.000152	0.000251	0.000984	0.001307	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	0.024982	0.068844
1-Pentanol	Trace <sup>b</sup>	ND <sup>c</sup>	0.000015	ND <sup>c</sup>	Trace <sup>b</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	0.000458	0.00005
1-Hexanol	Trace <sup>b</sup>	ND <sup>c</sup>	0.000009	ND <sup>c</sup>	Trace <sup>b</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	0.000458	0.000025
Methyl Acetate	Trace <sup>b</sup>	ND <sup>c</sup>	0.000009	ND <sup>c</sup>	Trace <sup>b</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>
Propionic Acid	Trace <sup>b</sup>	ND <sup>c</sup>	Trace <sup>b</sup>	ND <sup>c</sup>	Trace <sup>b</sup>	ND <sup>c</sup>	0.000056	0.000064	0.000029	ND <sup>c</sup>	0.000009	ND <sup>c</sup>
N-Butanol	0.000005	0.000017	0.000029	0.000026	Trace <sup>b</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	Trace <sup>d</sup>	ND <sup>c</sup>	0.000916	0.001862

<sup>a</sup> BPCD – Bottom product of column D, <sup>b</sup> Trace – less or equal than 10<sup>-9</sup> (Aspen Technology, 2003), <sup>c</sup> ND – Not Detected by GC (<10<sup>-6</sup> mg/mg)

In order to obtain a better insight on the significance of the deviations reported above, the relative deviations related exclusively to the phase equilibrium calculations were also evaluated. The vapor phase compositions and the corresponding deviations were calculated, in mass fraction unities, for the complete set of equilibrium data and for every binary mixture composing the alcoholic wine. The following results were obtained: for the entire concentration range of the equilibrium data the average absolute deviation is  $|\Delta w| = 0.0132$  and the corresponding relative deviation is  $|\Delta w|_{rel} = 3.14\%$ , values that confirm the good quality of the set of NRTL interaction parameters; but if one restricts the concentration range for the calculations to  $w_i < 0.25$  or to  $w_i < 0.05$ , these deviations are  $|\Delta w| = 0.0148$  and  $|\Delta w|_{rel} = 6.48\%$  or  $|\Delta w| = 0.0235$  and  $|\Delta w|_{rel} = 25.19\%$ , respectively, indicating that average deviations increase significantly for the diluted concentration range. Note that  $w_i = 0.05$  corresponds to a mass fraction hundreds of times higher than the concentration of most minor components reported in Table 4.5 to Table 4.7. Unfortunately there is not enough equilibrium data available in this dilution range in order to justify the corresponding calculation for a more restricted range of concentrations. Nevertheless, the relative deviations related to phase equilibrium calculations would surely be much higher for the diluted concentration range and probably responsible for part of the deviations observed in the profiles of minor components reported above. A further test was performed by changing the bioethanol withdrawal by  $\pm 1\%$  from its usual steady state value ( $6.8 \text{ m}^3/\text{h}$ ) and the following results were obtained: in case of increasing the product stream, the average relative deviations of the minor components increase from  $92.7\%$  to  $488\%$ , while the decrease of that stream reduces the deviation to  $87.3\%$ . These results demonstrate the relative sensibility of the minor component concentrations to changes of the bioethanol flow rate.

Taking into account the validation results, it is possible to conclude that the simulation approach was able to correctly reproduce, from a quantitative point of view, the major components' concentrations as well as the temperatures in the bioethanol distillation on an industrial scale. However, in the case of minor

components the validation results indicate that the simulation reproduces the industrial behavior from a qualitative point of view, correctly describing the general behavior of those components but generating high deviations regarding quantitative values. These deviations should be attributed to the very low concentrations of some minor components in the feed stream and also in specific parts of the distillation columns, to the higher errors involved in the phase equilibrium estimation within in the dilute concentration range and to the oscillations of the equipment operation around steady state.

#### *4.3.2. Simulation of bioethanol production*

As mentioned earlier, the complexity of the system of columns for bioethanol production is related to the quality standard desired for this alcohol, strongly influenced by the alcoholic graduation and congeners content in bioethanol. To evaluate the influence of the congeners in column setup, three different configurations were tested, together with the previously defined purification factors.

Figure 4.6 shows that the profile for ethanol/water, higher alcohols (represented by isoamyl alcohol) and methanol are very close for all configurations. On the other hand, the profiles for volatile components (represented by acetaldehyde) present a significant decrease (approximately 50%) in their concentrations in section B when the configuration AA1DBB1 is used. Acetone and ethyl acetate, not represented in Figure 4.6, also presented a decrease in their concentrations but with slightly different values than those observed for acetaldehyde.

Table 4.8 shows the purification factors for the three classes of components and the steam consumptions for all installations studied. Analyses of Figure 4.6 and Table 4.8 allows for concluding that for fuel bioethanol the complexity of the columns is not related to the specification for alcoholic graduation, since the simplest configuration (AB) was able to achieve the required values (see Table 4.2).

Table 4.8 - Purification Factor and steam consumption for the three configurations studied

Configurations	$F_{\text{volatiles}}$	$F_{\text{Intermediates}}$	$F_{\text{heavy}}$	$F_{\text{Total}}$	Steam Consumption
					(kg steam per liter of bioethanol)
AB	1.85	294.87	$> 10^{30}$	25.01	1.78
ABB1	2.10	307.83	$> 10^{30}$	28.31	1.80
AA1DBB1	2.53	309.83	$> 10^{30}$	33.85	2.17

For production of special alcohols with higher quality (H1, H2 and HN in Table 4.2) configurations AB and ABB1 are not appropriate, since these products have very strict specifications for the presence of contaminants. Figure 4.6d shows that the presence of sections A1 and especially D allows for a reduction of almost 50% in the bioethanol volatile compound concentration. This is also corroborated by the purification factor of volatiles ( $F_{\text{volatiles}}$ ) given in Table 4.8. Additional simulations showed that reduction of the volatile content in bioethanol is much more sensitive to variations in the second alcohol stream of section D than to a similar stream withdrawn from section B, indicating that this stream withdrawn from top of section D is a good way to regulate the content of volatile compounds in bioethanol.

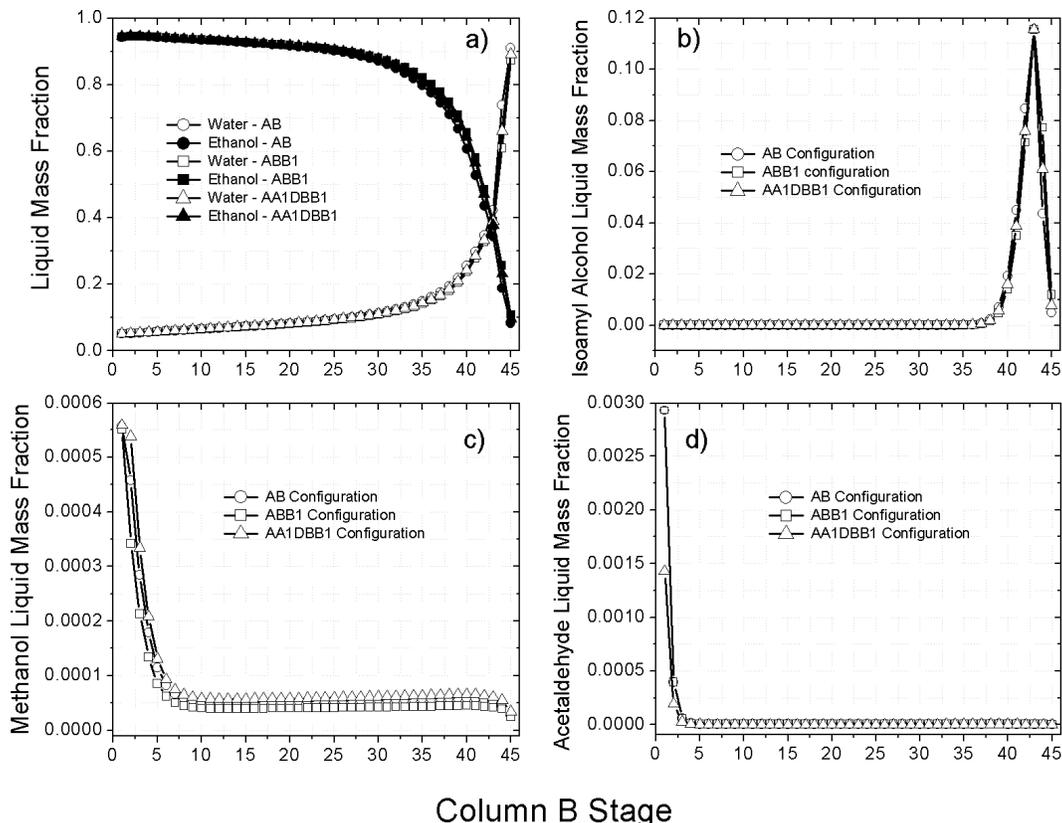


Figure 4.6 - Component profiles for configurations AB, ABB1 and AA1DBB1

Although the level of acetaldehyde is not specified for biofuel (see Table 4.2), this compound can oxidize to acetic acid during storage, contributing to an increase in acidity of bioethanol. Batista and Meirelles (2009)<sup>5</sup> discussed the problem of acetaldehyde oxidation and presented process control techniques to maintain the level of acetaldehyde in bioethanol, despite its increase in the alcoholic must.

Figure 4.6b shows that the profile of isoamyl alcohol is very similar for all the installations studied. It suggests that modifications to the industrial configurations has no influence on the bioethanol purification in respect to intermediate compounds (higher alcohols), considering that the purification factors for these components ( $F_{intermediates}$ ) are very similar in all installations (see Table 4.8). The similarity of water and ethanol compositions in the trays where the higher alcohols are concentrated in the three different configurations guarantees similar volatilities of these compounds and, consequently, similar higher alcohol profiles in all three cases. A more detailed discussion on the volatility of wine components can be found in Batista and Meirelles (2011)<sup>6</sup>.

Although higher alcohol content in bioethanol is not controlled by legislation (see Table 4.2), the presence of a side stream for their removal is essential. Their behavior as intermediate volatility components (Batista and Meirelles, 2009) causes an increase in their concentration on the trays near the bottom of section B, requiring a side stream for their withdrawal. Simulations conducted without this side stream showed that this peculiar feature of higher alcohols prevents the achievement of the required bioethanol alcoholic graduation and often prevents simulation convergence. Thus the absence of the fusel oil side stream affects the entire bioethanol production process.

Figure 4.6c shows that the profile of methanol for the three configurations studied is also very similar. Near the top of section B the relative volatility of methanol to ethanol varies little around 1.7, making their separation more difficult. With regard to bioethanol fuel, the presence of methanol does not affect the quality

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<sup>5</sup> Vide Capítulo 3

<sup>6</sup> Vide Capítulo 2, item 2.3.1

of the product because this alcohol will also be burned in combustion engines. On the other hand, for a high quality bioethanol, especially if used for potable purposes, or in the cosmetics and pharmaceutical industries (neutral alcohol), an additional column is required (demethylizer column) in order to separate ethanol from methanol (Decloux and Coustel, 2005) and prevent consumer health risks.

With respect to heavy compounds (mainly organic acids) the high purification factors ( $F_{\text{heavy}}$ ) for the three configurations shown in Table 4.8 indicate that these components are easily eliminated by the flegmass and vinasse streams.

The configuration AA1DBB1 was most efficient for producing a purer bioethanol product (H1 and H2, see Table 4.2) free of contaminants, as evidenced by the higher total purification factor ( $F_{\text{total}}$ ). On the other hand, its steam consumption is 20 % higher. The majority of Brazilian mills use the AA1DBB1 configuration (see Figure 4.1), with small variations from one mill to another, thus being able to adjust to changes in market demands for bioethanol products of different purities. Taking this into account, a series of simulations was conducted in order to investigate the influence of constructive and operational variables upon the performance of a typical Brazilian bioethanol distillation plant.

In the case of the optimization approach based on factorial techniques the first set of simulations used the fractional design  $2^{(11-7)}$  and its results show that only three independent variables (BFR, RRB and TB, see Table 4.3) have a statistically significant influence on the response functions of bioethanol alcoholic graduation (BAG), ethanol recovery (ER), absolute steam consumption (SC) and stillage/flegmass ethanol loss (EL). Using these three independent variables a central composite rotational design (CCRD)  $2^3$  was performed, according to the levels in Table 4.4. Within the range of investigated conditions ( $35 \leq TB \leq 55$ ,  $3.5 \leq RRB \leq 5.5$ ,  $13600 \text{ kg/h} \leq \text{BFR} \leq 14000 \text{ kg/h}$ ) bioethanol concentration (BAG) is influenced mainly by the value of the main product stream (BFR), which explains 99% ( $R^2$ ) of its variance. In order to guarantee the required product concentration, the main product stream should not be larger than 13700 kg/h when considering a distillation unit for processing 300 m<sup>3</sup> per day of alcoholic wine containing 8.5 GL of bioethanol. Note that for obtaining such a result the withdrawals of the second

alcohol stream and fusel oil were also considered in the simulations. As expected, the absolute steam consumption (SC) is mainly dependent on the reflux ratio (RRB), which explains 89 % of the observed variance. Ethanol recovery (ER) is significantly influenced by the value of the main product stream (BFR) and also by the reflux ratio (RRB). From a statistical point of view the ethanol loss in stillage and flegmass (EL) does not show a significant dependence on the investigated conditions. Within the range of values considered in the present investigation these conditions explain only 61% of the variance observed in the ethanol loss. However, it should be considered that in all simulations the ethanol content in the stillage and flegmass was less than 0.0002 by mass, so that the corresponding loss was always kept below the specified threshold.

Figure 4.7 and Figure 4.8 show the contour curves for the response functions of steam consumption (SC) and ethanol recovery (ER), respectively. As indicated above, steam consumption changes mainly as a consequence of reflux ratio changes, with the number of trays in section B and value of the bioethanol flow rate having a lower influence. Maximum ethanol recovery was observed near intermediate levels of the investigated range (Figure 4.8). Superposition of all response surfaces and contour curves, taking into account the objectives of minimizing the absolute steam consumption (SC) and loss of ethanol (EL), and maximizing the ethanol recovery (ER) and its alcoholic graduation (BAG), allowed for the determination of the optimal conditions.

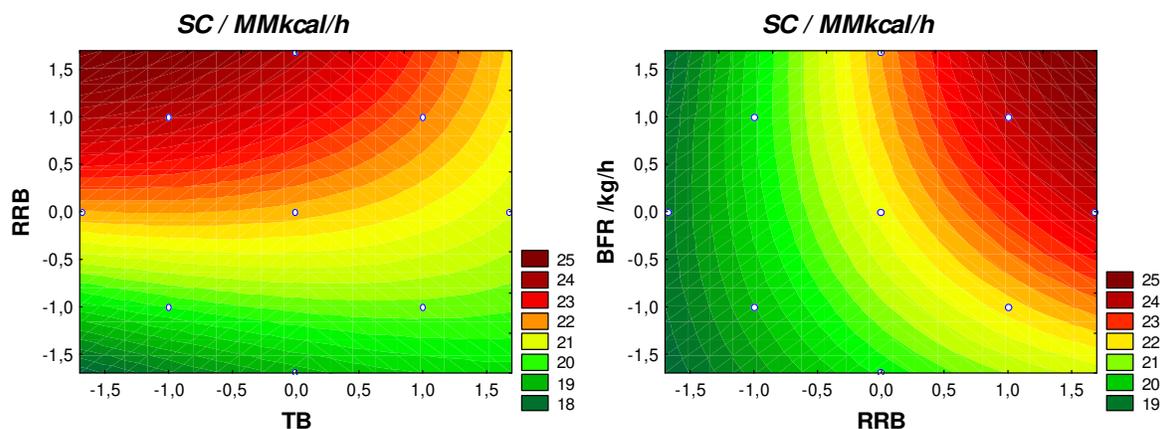


Figure 4.7 - Contour curves for the dependent variable SC

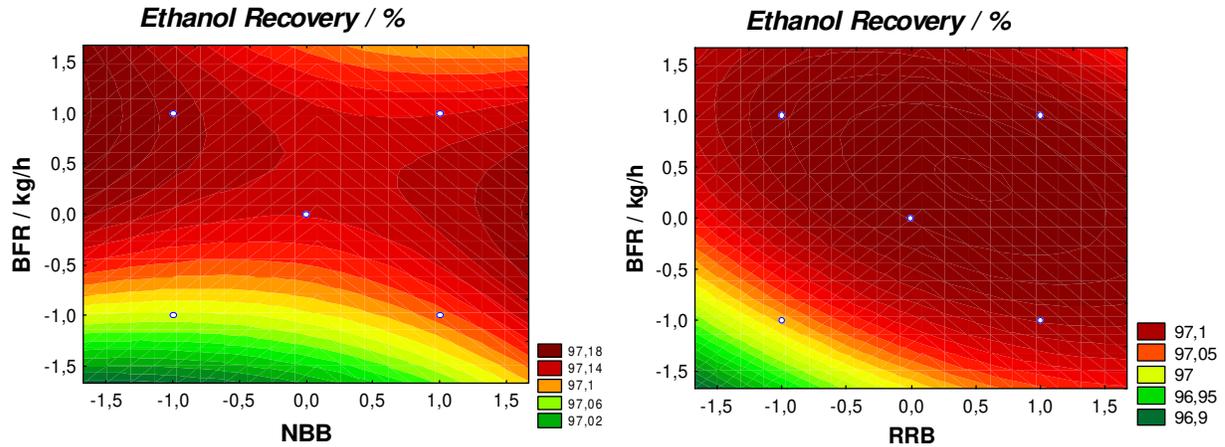


Figure 4.8 - Contour curves for the dependent variable ER

In the case of the SQP optimization approach the screening of the relevant variables was based on a sensitivity test performed using Aspen Plus. Unlike the fractional factorial design, the sensitivity test indicated four significant variables for the objective function  $F_o$  (RRD, RRB, TB and BFR). With this set of variables the SQP optimization was then performed. This technique allowed minimizing the objective function  $F_o$  with the independent variables simultaneously subject to the restrictions shown in Table 4.4, while the determination of the optimal conditions by the CCRD method requires the analysis of all response surfaces and contour curves for each response function. The optimal conditions obtained according to both methods are shown in Table 4.9.

Table 4.9 - Optimum operational and constructive conditions of the AA1DBB1 configuration for distilling 300 m<sup>3</sup>/day of alcoholic wine – CCRD and SQP optimization.

<i>Independent Variable</i>	<i>Tag</i>	<i>Value</i>	
		CCRD	SQP
Number of trays in section A1 <sup>1</sup>	TA1	4	4
Number of trays in section A <sup>1</sup>	TA	22	22
Number of trays in section D <sup>1</sup>	TD	6	6
Number of trays in section B	TB	45	47
Number of trays in section B1 <sup>1</sup>	TB1	18	18
Reflux ratio of section D <sup>2</sup>	RRD	35	35
Reflux ratio of section B	RRB	4	3.92
Tray of fusel oil withdrawal <sup>1</sup>	TFO	42	42
Fusel oil flow rate (kg/h) <sup>1</sup>	FOF	200	200
Bioethanol flow rate (kg/h)	BFR	13600	13600
Flow rate of second alcohol in section D (kg/h) <sup>1</sup>	SAF	350	350

<sup>1</sup> - Variable not significant in fractional design - Fixed at center point for CCRD and SQP.

<sup>2</sup> - Significant only for sensitivity test - Fixed at center point for CCRD and included in SQP optimization

The differences are circumscribed to two variables, the number of trays and reflux ratio of section B, and they are small in both cases. Such a result seems to suggest that both methods can be used for determining the optimal conditions of complex processes as the industrial distillation of bioethanol. In fact, both optimization methods were applied in the improvement of edible oils, spirit, biofuel and chemical distillation processes with good accuracy (Kiss and Suszwalak, 2012; Wang et al., 2012; Figueiredo et al., 2011; Noshadi et al., 2011; Diaz-Tovar et al., 2010; Lachenmeier et al., 2006).

With the set of optimal conditions determined by both methods two simulations were performed using the complete wine composition (17 minor components, see Table 4.1) and pasteurized bioethanol withdrawn. For the CCRD optimal conditions, the results showed an ethanol loss of 46 mg per kg of total stillage, ethanol concentration in the main product of 93.1% by mass, steam consumption of 2.12 kg per liter of bioethanol produced and an ethanol recovery of 97% as the main product. Taking into account the byproduct streams (second alcohol and fusel oil) the ethanol recovery increases to 99.8%. The total purification factor ( $F_{total}$ ) is 64.0, indicating a good removal of congeners from bioethanol, probably due to its withdrawal as a pasteurized stream. This purification is mainly related to the reduction in concentration of volatile compounds, since the corresponding purification factor ( $F_{volatile}$ ) was 3.87, larger than the values presented in Table 4.8. For the intermediate and heavy components the purification factors do not have significant differences in comparison to the prior values (Table 4.8). In case of SQP optimal conditions the results are a total ethanol loss from stillage and flegmass of 44.2 mg per kg, bioethanol alcoholic graduation of 93.2 wt%, specific steam consumption (objective function -  $F_o$ ) of 2.05 kg of steam per liter of bioethanol, an ethanol recovery of 97.3% as the main product and a total purification factor ( $F_{total}$ ) of 62.8. Although both sets of results are very similar, the specific steam consumption is slightly lower in case of the SQP optimization technique.

Table 4.10 shows the bioethanol compositions according to both sets of optimal conditions. Both alcoholic products obtained according to the optimal

conditions given in Table 4.9 meet the requirements of the Brazilian National Petrol Agency (ANP). In relation to minor components both products also meet the requirements of Copersucar H1 (see Table 4.2). In order to meet the requirements of the H2 standard, some changes in the operational modifications are required: the contamination with acetaldehyde can be diminished by an increase in second alcohol streams (Sections D and B top product) and/or in the degassing stream and the decrease of contamination with higher alcohols requires an increase in fusel oil withdrawal. In the case of HN alcohol (neutral alcohol), changes in the entire installation are required. According to Decloux and Coustel (2005) three additional columns should be considered: an *extractive distillation column* using water as purifying agent and almost 50 trays in order to decrease contamination with light and intermediate volatility contaminants, a *rectifier column* with almost 80 trays for re-concentrating the diluted ethanol stream from the bottom of the extractive column, and a *demethylizer column* with approximately 50 trays to remove methanol from the concentrated ethanol stream.

Table 4.10 - Results for simulation in optimum conditions

Characteristics	Unity		According CCRD			According SQP		
			Bioeth. <sup>1</sup>	SASD <sup>2</sup>	SASB <sup>3</sup>	Bioeth. <sup>1</sup>	SASD <sup>2</sup>	SASB <sup>3</sup>
Flow rate (kg/h)	-		13600	430	400	13600	430	400
Alcoholic graduation (°INPM 20°C)	%	min	93.1	86.8	93.3	93.2	86.7	93.4
Alcoholic graduation (°GL 20°C)	m/m	min						
	%	min	94.7	89.2	94.9	94.8	89.2	94.9
Total acidity (Acetic Acid)	mg/L	máx	Trace	Trace	Trace	Trace	Trace	Trace
Acetaldehyde	mg/L	máx	14.08	5814.12	442.75	14.12	5814.12	440.27
Methanol	mg/L	máx	33.43	56.75	66.47	34.58	56.75	65.72
Acetone	mg/L	máx	46.24	4571.94	341.94	46.85	4571.94	340.98
Ethyl Acetate	mg/L	máx	18.49	2619.52	64.37	18.49	2619.52	64.37
Isopropyl alcohol	mg/L	máx	11.74	52.64	9.54	12.27	52.64	9.12
N-Propanol	mg/L	máx	2.93	89.38	1.43	3.19	89.38	1.27
N-Butanol	mg/L	máx	Trace	0.30	Trace	Trace	0.30	Trace
Isobutanol	mg/L	máx	Trace	69.44	Trace	Trace	69.44	Trace
Isoamyl Alcohol	mg/L	máx	Trace	7.81	Trace	Trace	7.81	Trace
Superiors Alcohols	mg/L	máx	14.68	226.16	10.97	15.46	226.16	10.39

<sup>1</sup> Bioethanol

<sup>2</sup> Second Alcohol Section D

<sup>3</sup> Second Alcohol Section B

A further simulation study was conducted in order to evaluate the influence of the feed tray of the internal streams, PFD and Phlegm, on the specific steam consumption (objective function  $F_o$ ), considering the same constraints (BAG and

EL) indicated above. The study was conducted with the SQP method and the feed tray was varied along the entire section B. The specified conditions used in these simulations were those given in Table 4.9 and bioethanol was withdrawn as pasteurized alcohol. The results showed that the feed position of the phlegm and PFD streams were already in best plate, tray 45 of section B.

#### *4.3.3. Dynamic simulations*

Analyses of the industrial wines collected from the Santa Adélia Mill presented an average of 5.92% by mass in ethanol (7.3 °GL) and a standard deviation of 0.6%. This means that for the dynamic study the ethanol content in the wine was varied from 5.32% (6.6 °GL) to 6.52% (8.1 °GL). This variation was performed in two steps. The first step (time 0) included an increase in wine ethanol content from the average to the upper value. After operation of the PID controller and the consequent stabilization of the bioethanol alcoholic graduation, a second pulse (time 5 hours) decreased the wine ethanol content from the higher to the lower value. Static simulations showed that this change in the wine alcoholic content could cause a variation in bioethanol alcoholic graduation from 83.7% (lower limit) to 94.1% (upper limit) by mass, so that in both cases the product would be out of the required range (Table 4.2). Two control possibilities for stabilizing the bioethanol alcoholic graduation (controlled variable) were tested and are shown in Figure 4.9. In the first case (Figure 4.9a) control was performed via manipulation of the wine flow rate through an inverse relationship with the controlled variable. This means that a reduction in the ethanol content of the product is compensated for an increase in wine flow rate until the alcoholic graduation of the product is restored, observing the opposite when the ethanol content is increased. In the second case (Figure 4.9b) control was based on manipulation of the bioethanol flow rate in a direct relationship with the controlled variable. As can be observed in Figure 4.9, the control based on manipulation of bioethanol flow rate is more sensitive, stabilizing the bioethanol alcoholic graduation in almost 2.5 hours after the perturbation compared to a time of 4 hours for the controller based on the wine flow rate manipulation. However, the two control systems are efficient since in both

cases the maximum and minimum overshootings were not sufficient to cause production of bioethanol outside the required concentration limits. Although the control based on manipulation of wine flow rate is less efficient than the manipulation of bioethanol flow rate, in the industrial practice there is a preference for the first control type since it can be performed without changing the bioethanol production. However, a large decrease in the bioethanol concentration requires a high wine flow rate that can cause flooding of section A of the first column.

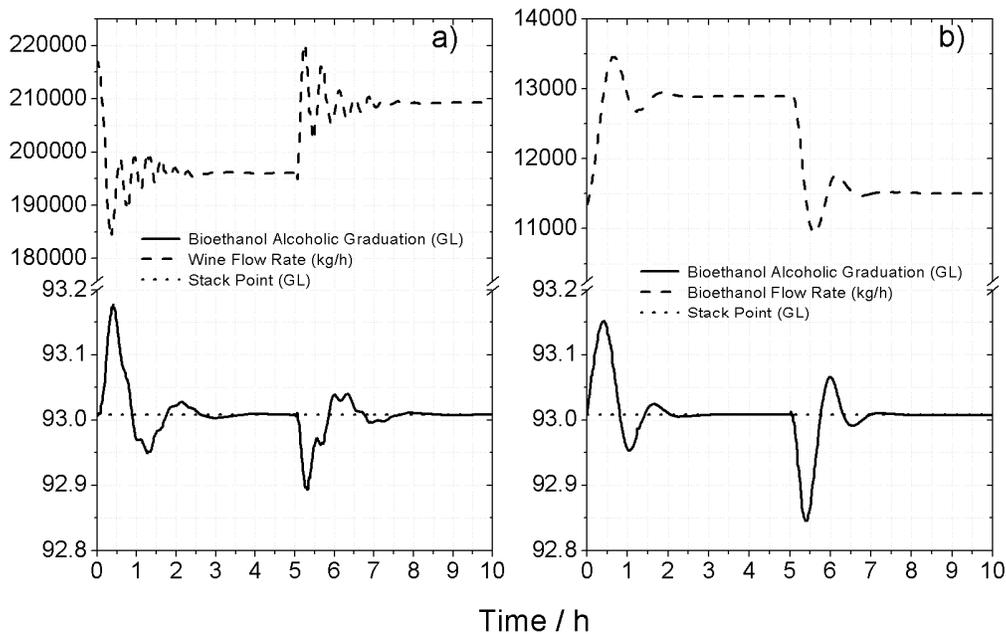


Figure 4.9 – Actuation of PID controllers

The absence of a control system to compensate for small fluctuations in the alcohol content of the wine can cause serious difficulties in the production process. Static simulations were performed with alcohol content at the maximum and minimum values previously presented and the impacts on the volatile content in bioethanol, loss of ethanol in the vinasse and flegmass streams and on the fusel oil concentration in the selected trays (represented by isoamyl alcohol) were studied, as well as the impact on the alcohol content of bioethanol, already discussed. The results showed that the variations in wine alcohol content in the range considered does not cause significant impacts on the bioethanol volatile content or on the loss of ethanol via vinasse that, in the worst case, reaches values of approximately

14.00 kg/h which represents a concentration of 82 mg/kg and is still within the limits acceptable by the sugar mills. On the other hand, the impact on the ethanol loss in flegmass and on the fusel oil concentration is quite significant. Increasing the wine alcohol content causes a substantial increase in the loss of ethanol by flegmass, reaching values of 770.00 kg/h with a concentration of 40,000 mg/kg. As a consequence of this greater ethanol loss, the fusel oil profile in the column is shifted down so that these components are concentrated near the bottom of section B1. The opposite is observed when the wine alcohol content is reduced. This reduction minimizes ethanol loss in flegmass (0.003 kg/h and 0.193 mg/kg) causing the displacement of higher alcohols (fusel oil) to the trays near the top of the column, contaminating the bioethanol produced and preventing acquisition of the required alcohol content.

Figure 4.10 shows the effect of the PID controller based on the manipulation of the wine flow rate on the higher alcohols withdrawal and ethanol losses in the flegmass stream. The PID controller was able to maintain ethanol losses in the flegmass stream within a very restricted range even before stabilization and is capable of bringing the isoamyl alcohol stream to a steady state level after approximately 4 hours. This additional effect of the PID controller is especially important because it prevents economic losses associated to high ethanol content in the flegmass stream as well as buffers the fluctuation of the higher alcohols profile along the column, keeping the region of their highest concentration on the trays from where fusel oil is usually removed. The results showed that the industrial PID controller accurately compensates for changes in the alcoholic graduation of the wine, guaranteeing that bioethanol is produced according to the required standard. This type of controller can be especially efficient for mills that work with batch fermentation, a situation in which the variation of ethanol content in the wine is more likely to occur. However, the controller is less efficient when wine with very low alcohol content is fed to the process. This occurs because in order to compensate for the low alcohol content in wine, the controller increases the flow rate fed to the distillation unit. In some cases the flow of wine may be so high that it causes flooding of trays, especially in section A. Problems related to column

flooding can also occur when the second control type is used (manipulation of bioethanol flow rate). Wines with high ethanol content increase the bioethanol alcoholic graduation to values higher than those required. In this case, the controller acts to increase the bioethanol flow rate in order to reduce its alcohol content, and flooding may occur in section B depending on the required final flow rate.

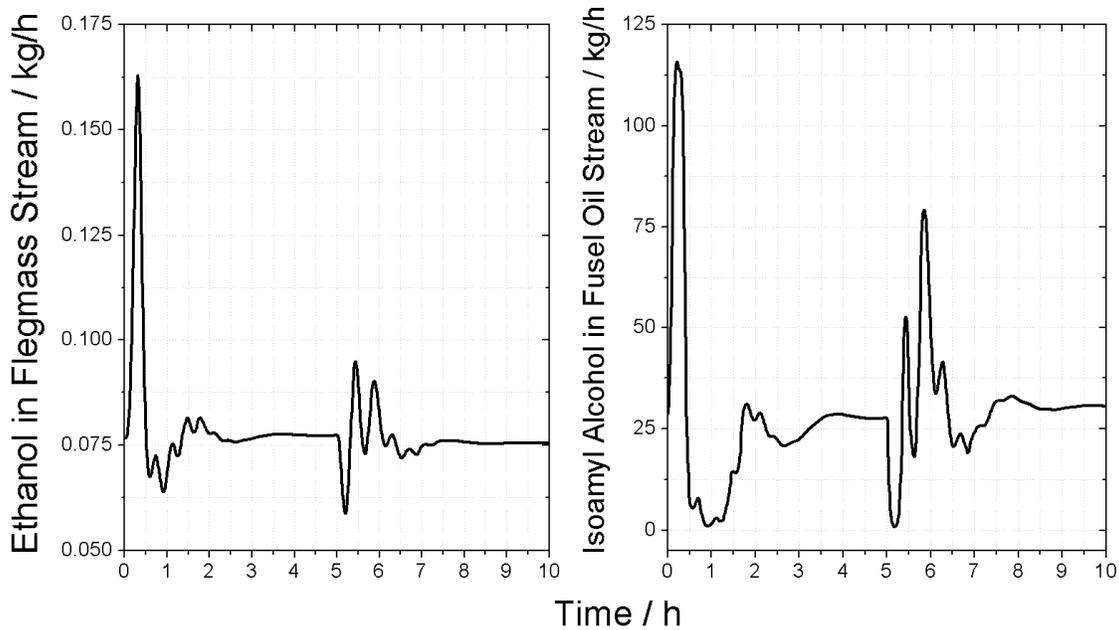


Figure 4.10 – Effect of the industrial PID controller on flegmass ethanol losses (a) and higher alcohol in fusel oil (b)

#### 4.4 - Conclusions

In the present work bioethanol distillation was investigated by simulation, taking into account the industrial equipment configurations and 17 minor components present in real sugar cane wines. Simulation results were validated against experimental values obtained in an industrial distillation unit. Deviations in concentration were very low for the major components, but the corresponding values were much higher in the case of minor components. This latter result can probably be attributed to the difficulty of accurately describing the vapor-liquid equilibrium in very low concentrations. Despite this fact the simulation results were able to qualitatively describe the behavior of the minor components observed in the industrial plant. In contrast to the more simplified equipment configurations, the

complete configuration AA1DBB1 guarantees a higher purification factor of bioethanol, especially in relation to volatile contaminants. The influence of operational and constructive variables on the performance of the industrial plant was investigated using the fractional design technique and sensitivity tests. On the basis of the prior investigation the distillation plant was optimized by the CCRD and SQP techniques and the optimal conditions obtained by both methods were very similar. Bioethanol composition, obtained by simulation at the optimal conditions, was compared with the specifications for fuel bioethanol and for other ethanolic products of higher purity. Finally a PID control loop was suggested in order to ensure the concentration of ethanol after a disturbance in the wine's alcohol content and this control loop was also able to prevent loss of ethanol in flegmass and allow an appropriate withdrawal of higher alcohols.

The simulation approach adopted in the present work was able to represent the bioethanol distillation in an industrial scale, including the complexity of the alcoholic wine and the real configuration of the industrial equipments. Despite the higher deviations observed for the minor components, the distillation behavior was well described from a qualitative point of view, so that this simulation approach gives a reliable basis for investigating and developing new configurations for bioethanol distillation, be this product used as fuel or as raw material for the industrial production based on the alcohol-chemistry. Alternative plant configurations for producing bioethanol of higher purity will be investigated in a future work.

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## Capítulo 5

# A new distillation plant for neutral alcohol production <sup>7</sup>

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## **Abstract**

The wide variety of commercial products that can be produced based on the alcohol chemistry (plastics, fuels, alcohol, solvents, etc.) and the related concept of biorefinery, a new type of industrial sector in which most of the biomass obtained from different carbohydrate sources is used with high efficiency and low environmental impact, is leading the sugar mills and distilleries to improve their production processes. In fact, the use of ethanol as a raw material for a variety of bioproducts requires higher standards of product quality in order to avoid loss of efficiency in its conversion or damage to catalysts due to the presence of contaminants. Taking this into account this work aims to investigate industrial plants for neutral alcohol production, a special kind of hydrated alcohol with low concentration of contaminants widely used in the fine chemical, pharmaceutical and beverage industries. For this purpose, a series of operational and constructive changes in a typical fuel bioethanol distillation plant were investigated by computational simulation. The wine was represented by a standard solution containing water, ethanol and 17 congeners. The results were compared with an industrial plant for neutral alcohol reported in the literature and with a typical Brazilian industrial plant for neutral alcohol distillation. The new suggested installation is more efficient than the prior one reported in the literature and the Brazilian industrial plant, since the steam consumption was, respectively, 48.5% and 40.0 % lower, the ethanol recovery as neutral alcohol was 5.0 % and 1.7 % higher and the number of trays required for purifying bioethanol is also lower. Furthermore, the second alcohol and fusel oil streams, generated as byproducts from the neutral alcohol distillation, were used for producing fuel bioethanol according to the specifications of the Brazilian legislation. A second version of the new plant was proposed to work with wine with high isopropanol contamination, congener only specified in Brazilian standard quality for neutral alcohol.

*Keywords: Fuel ethanol, bioethanol, neutral alcohol, alcohol chemistry, biorefinery, Aspen Plus.*

## 5.1 - Introduction

International benchmark in the use of bioethanol as automotive fuel, Brazil has the most successful experience of replacing fossil fuels with a cleaner source of renewable energy. Ethanol from sugar cane along with the use of their bagasse for power generation accounted for about 18% of Brazil's energy supply in 2010, so that sugar cane is the second largest source of energy in the national matrix (UNICA, 2011). The vast Brazilian experience in bioethanol production, with competitive prices in relation to oil and its derivatives at least along the last twelve years, is creating a promising scenario for the diversification of its use, especially as a raw material for the production of other products of higher market value. In fact, bioethanol is nowadays not only a source of energy, but it is becoming more and more a basis for the production of various other chemicals such as acetic acid (Voss et al., 2011), acetone (Bussia et al., 1998), ethane (Kamalkumar et al., 2001), ethyl acetate (Santacesaria et al., 2011) and ethylene (Lippits and Nieuwenhuys, 2010; Bi et al., 2010; Bedia et al., 2011; Kamm and Kamm, 2004; Hamelinck et al., 2005). The conversion to ethylene is doubtless one of the most important since it provides the basis for the production of bioplastics.

In fact, the use of bioethanol as a feedstock is allowing the development of an industrial sector based on the alcohol chemistry (Arruda, 2011), which will eventually encourage the transformation of the existing sugar mills to biorefineries. National and multinational companies (Braskem, Dow Chemical, Solvay Indupa, Rhodia, Coca-Cola) are developing industrial projects based on the alcohol chemistry and are increasing their domestic demand for ethanol of better quality, so that neutral alcohol should represent something between 5% to 10% of the total production of ethanol in 2011 (UNICA, 2011).

The biorefinery concept is widely discussed in the current scientific literature. It involves a set of unit operations for the total conversion of biomass and works in a way similar to an oil refinery, so that multiple products, such as fuels, energy and chemicals, can be produced with maximum efficiency and low environmental cost (Rabelo et al., 2011; Zondervan et al., 2011; Alvarado-Morales et al., 2009; Fernando et al., 2006, Cherubini, 2010; Luo et al., 2011). The steps

involved in its operation include biomass pretreatment, hydrolysis, fermentation and distillation to ethanol recover (Margeot et al., 2009). The integration of the current production of ethanol based on sugar juice extraction, fermentation and distillation, with the second-generation bioethanol seems entirely possible since the residual biomass of the first process provides the raw material for producing the second generation biofuel.

In this context alcoholic products of better quality, in particular neutral alcohol, emerge as an important feedstock with a large potential market in the growing industrial sector based on ethanol chemistry. This type of alcohol can be defined as a hydrated (mainly) or anhydrous alcohol with very low level of contaminants that is used as raw material for the pharmaceutical, chemical, food and beverage industries (Decloux and Coustel, 2005). In the chemical industry it can be used for the manufacture of paints, solvents, detergents and as a basis for the production of other chemicals. In the food industry it is used as a precipitating agent or, alternatively, as solvent in separation processes. It is also used to correct the ethanol content in alcoholic beverages or directly in the production of specific spirits, for instance, liqueurs. In the pharmaceutical and cosmetics industries neutral alcohol is applied in the extraction of natural compounds and in the manufacture of vaccines and other medicines, perfumes, deodorants and beauty creams.

Despite this broad spectrum of applications, there is no universal standard of neutral alcohol that secures the quality of this product. In Brazil and the U.S. this lack of a definite standard implies that each producer is required to set its own product specification. On the other hand, countries in the European Union and South Africa have specifications set by legislation and their standards are slightly different from those established by the sugar mills and distilleries in Brazil and US, as can be seen in Table 5.1.

In Brazil fuel bioethanol is the raw material used for producing neutral alcohol. Fuel bioethanol is produced by fermentation of sugar cane juice or a must composed of cane juice and molasses. The fermentation broth is deyeasted by

centrifugation and the obtained alcoholic wine, with a composition similar to that shown in Table 5.2 , is fed into the distillation plant.

Table 5.1 - Alcohol standards

Characteristics	Unity		Neutral Alcohol					Bioethanol	
			Countries					Brazil <sup>6</sup>	
			Brazil <sup>1</sup>	USA <sup>2</sup>	EU <sup>3</sup>	South Africa <sup>4</sup>	France <sup>5</sup>	Hydrated	Anhydrous
<b>Alcoholic Graduation</b>	mass%	Min.	94.0	-	-	-	-	92.6-93.8	99.3
	vol%	Min.	96.1	96.1	96	96.4	96.0	-	-
<b>Acidity (Acetic Acid)</b>	mg/L	Max.	10	12	15	10	10	30	30
<b>Acetaldehyde</b>	mg/L	Max.	5	2	5	5	5	-	-
<b>Methanol</b>	mg/L	Max.	5	5	50	50	25	-	-
<b>Ethyl Acetate</b>	mg/L	Max.	5	-	13	30	13	-	-
<b>Acetone</b>	mg/L	Max.	1	-	-	-	-	-	-
<b>Isopropanol</b>	mg/L	Max.	2	-	-	-	-	-	-
<b>n-Propanol</b>	mg/L	Max.	8	2	-	-	-	-	-
<b>n-Butanol</b>	mg/L	Max.	0.5	-	-	-	-	-	-
<b>Isobutanol</b>	mg/L	Max.	2	2	-	-	-	-	-
<b>Isoamyl Alcohol</b>	mg/L	Max.	3	2	-	-	-	-	-
<b>Total Superiors Alcohols</b>	mg/L	Max.	15	10	5	5	5	-	-

<sup>1</sup> – Coopersucar standard - [http://www.copersucar.com.br/produtos/ing/alcool\\_etilico.asp](http://www.copersucar.com.br/produtos/ing/alcool_etilico.asp)

<sup>2</sup> – Archer Daniels Midland (A.D.M.) neutral spirit standard - <http://www.distill.com/specs/ADM.html>

<sup>3</sup> – Neutral alcohol standard in accordance of Council Regulation N° 1576/1989 and N°. 1623/2000

<sup>4</sup> – [http://www.distill.com/specs/South\\_Africa-Illovo.html](http://www.distill.com/specs/South_Africa-Illovo.html)

<sup>5</sup> – Reported by Decloux and Coustel (2005)

<sup>6</sup> - National Petrol Agency (ANP – Brazil) - Resolution N° 36, of 12/06/2005 – DOU 7.12.2005

The exact configuration of the distillation unit used to produce fuel bioethanol depends on the quality standard required (see Table 5.1 for standards of Brazilian fuel bioethanol) and on the usual range of variations of the alcoholic wine obtained by fermentation, but the typical industrial plant is that presented in Figure 5.1. This industrial plant is composed of two distillations columns (AA1D and BB1) containing a total of approximately 90 trays. The wine is fed into the first tray of section A1 with an alcoholic graduation between 6 and 10 °GL, being concentrated to approximately 94 °GL (92.8% in mass) in the bioethanol stream with a ethanol recovery of more than 99%. A complete and detailed description of this industrial plant was reported in a previous work (Batista et al., 2012)<sup>8</sup>.

<sup>8</sup> Artigo reportado no Capítulo 4 desta tese

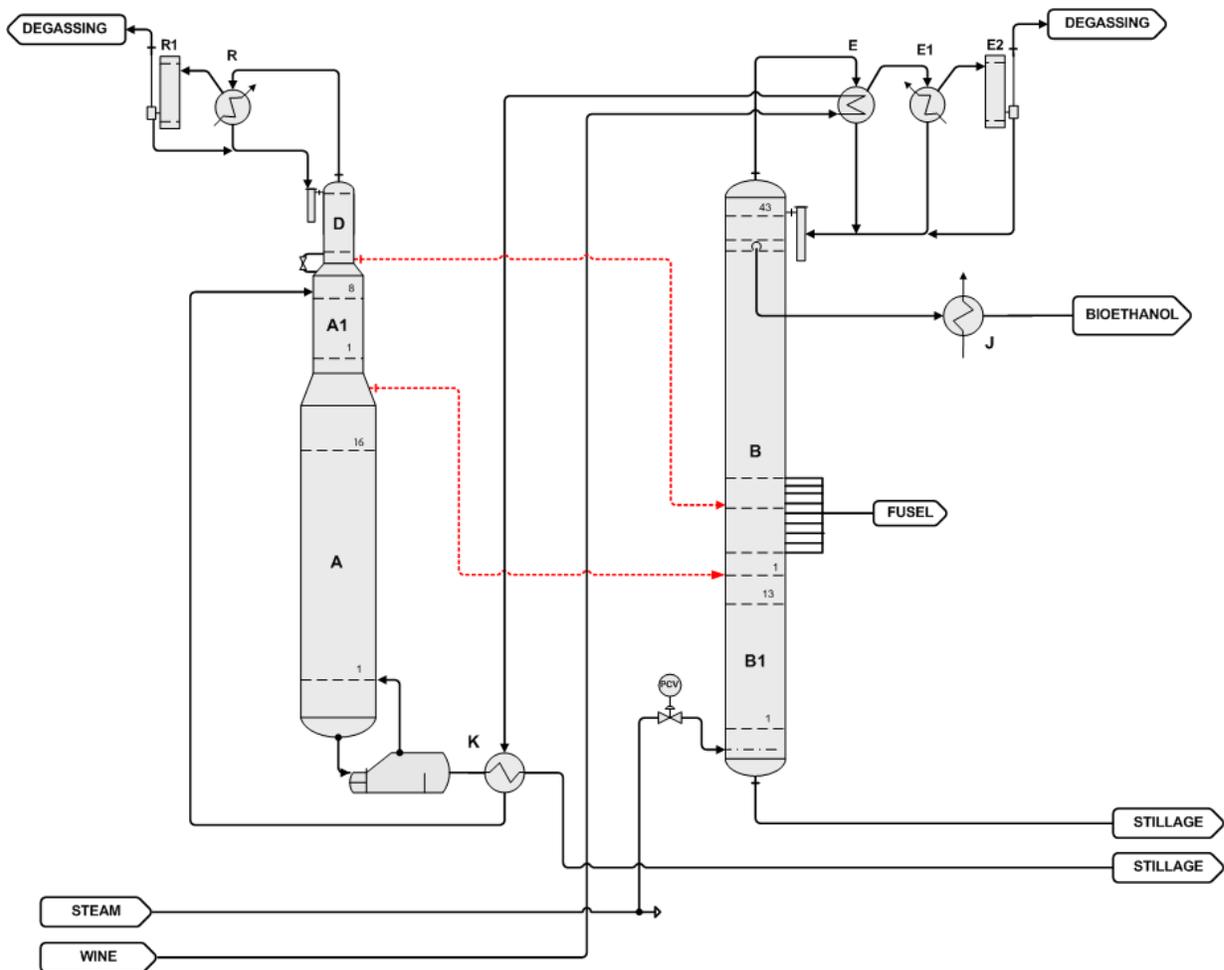


Figure 5.1 - Typical bioethanol industrial plant

According Decloux and Coustel (2005) and information collected in Brazilian sugar mills and equipment companies, the traditional way to produce neutral alcohol is the purification of fuel bioethanol in three additional distillation columns, as shown in Figure 5.2. Fuel bioethanol is fed into a *Hydroselection column* composed of around 51 trays (20 trays above and 30 under the feed tray). A stream of potable water is fed into the column top and dilutes the superior alcohols content in the liquid phase. In a water-rich environment, superior alcohols have very high activity coefficients, increasing significantly their volatilities, so that they can be concentrated in the column top and withdrawn mostly by the distillate stream (Batista and Meirelles, 2011)<sup>9</sup>. A diluted and purified bioethanol stream (10

<sup>9</sup> Artigo reportado no Capítulo 2 desta tese

<sup>o</sup>GL) is recovered in the bottom of the column being subsequently fed into the *Rectifier Column*.

Table 5.2 - Typical industrial wine composition

Component	Wine (w/w)		
	Industrial <sup>1</sup>	Decloux and Coustel(2005)	Max wine
Water	0.9319	0.919	-
Ethanol	$6.627 \cdot 10^{-02}$	$8.023 \cdot 10^{-02}$	$6.627 \cdot 10^{-02}$
Methanol	$1.212 \cdot 10^{-05}$	$4.058 \cdot 10^{-05}$	$6.200 \cdot 10^{-05}$
Isopropanol	$2.000 \cdot 10^{-07}$	-	$2.000 \cdot 10^{-07}$
Propanol	$5.300 \cdot 10^{-05}$	$1.015 \cdot 10^{-04}$	$8.320 \cdot 10^{-04}$
Isobutanol	$4.695 \cdot 10^{-05}$	$1.017 \cdot 10^{-04}$	$2.750 \cdot 10^{-03}$
N-Butanol	$1.250 \cdot 10^{-06}$	-	$6.000 \cdot 10^{-04}$
2-Butanol	$5.760 \cdot 10^{-06}$	-	-
Isoamyl alcohol	$1.845 \cdot 10^{-04}$	$2.466 \cdot 10^{-04}$	$1.660 \cdot 10^{-03}$
2-Methyl-1-Butanol <sup>2</sup>	$4.326 \cdot 10^{-05}$	-	-
1-Pentanol	$1.000 \cdot 10^{-06}$	-	-
1-Hexanol	$1.000 \cdot 10^{-06}$	-	-
Methyl Acetate	$1.000 \cdot 10^{-06}$	-	-
Ethyl Acetate	$1.976 \cdot 10^{-05}$	$1.209 \cdot 10^{-05}$	$5.250 \cdot 10^{-03}$
Acetaldehyde	$1.740 \cdot 10^{-05}$	$4.882 \cdot 10^{-05}$	$1.740 \cdot 10^{-02}$
Acetone	$1.000 \cdot 10^{-06}$	-	$1.000 \cdot 10^{-02}$
Acetic Acid	$2.574 \cdot 10^{-04}$	-	-
Propionic Acid	$7.470 \cdot 10^{-05}$	-	-
CO <sub>2</sub> <sup>3</sup>	$1.100 \cdot 10^{-03}$	-	-

<sup>1</sup> – Values obtained by analyzing five industrial wine samples collected from Santa Adelia mill, located in Jaboticabal, SP, Brazil.

<sup>2</sup> – Amyl alcohol

<sup>3</sup> – Estimated in accordance with Dalmolin et al. (2007). For details see Batista et al. (2012).

The *Rectifier Column* is comprised of about 80 trays (66 trays in the case of Decloux and Coustel, 2005), with 49 plates above the feed tray and 30 below. This column aims to concentrate ethanol to about 94 wt% and complete the removal of volatile compounds (acetate, acetaldehyde, ethanol, and acetone) and fusel oil. Volatiles are removed by the distillate, as head product of the column, and a fusel oil stream is necessary to further reduce contamination with superior alcohols. Concentrated bioethanol is withdrawn from a tray located two or three trays below the column top via a stream usually named pasteurized alcohol. Pasteurized alcohol is fed into the *Demethylizer Column* composed of around 50 trays (19 trays above and 30 below the feed plate) aiming to eliminate the methanol contamination from neutral alcohol. The relative volatility of the methanol/ethanol mixture has a value relatively close to one, which means that a column with large number of trays and operating at high reflux ratios is required for decreasing methanol

contamination. A methanol-rich stream is withdrawn as distillate and neutral alcohol is obtained as the column bottom product.

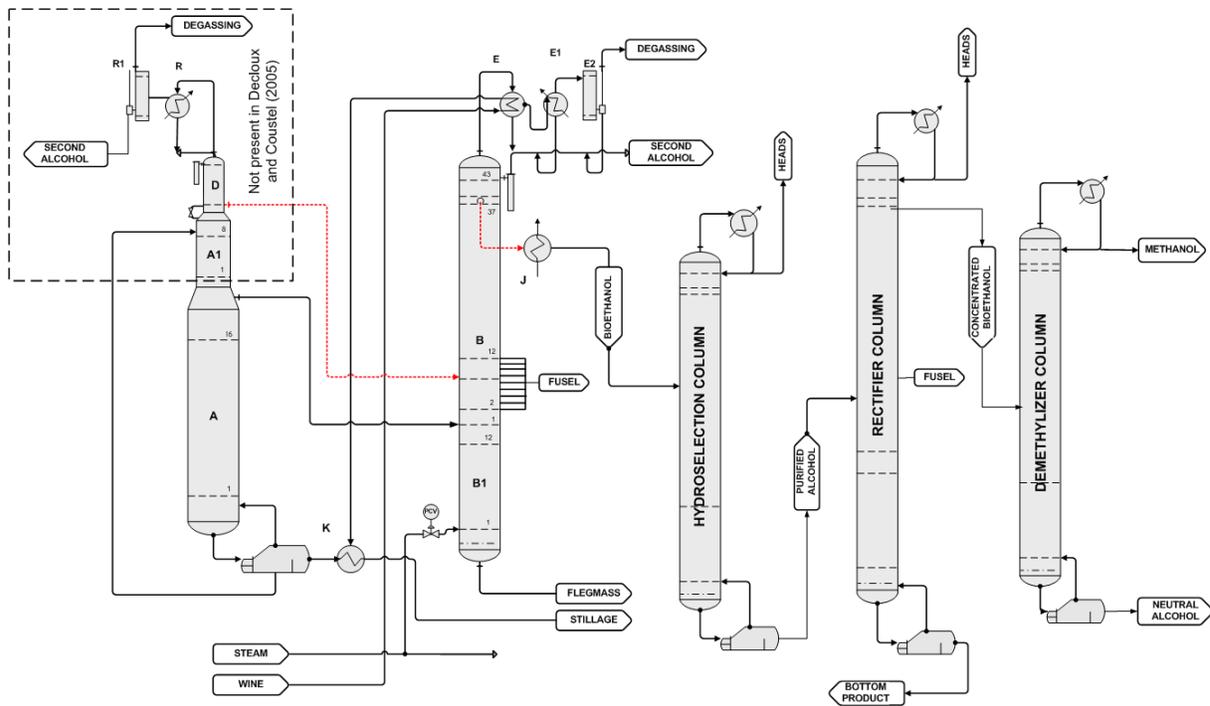


Figure 5.2 - Brazilian neutral alcohol industrial plant

Taking into account the growing demand for bioethanol with better quality and the experience of the authors with distillation processes applied to different areas of the chemical and food industries (Batista and Meirelles, 2011, Batista and Meirelles, 2009, Haypek et al, 2000; Meirelles et al, 2008; Ceriani et al, 2008; Ceriani and Meirelles, 2006; Ceriani and Meirelles, 2007, Scanavini et al., 2010, Scanavini et al., 2011), this paper aims to investigate, by computer simulation, the production of neutral alcohol and to develop a new equipment configurations for distilling this high-purity product.

## 5.2 - Methodology

### 5.2.1. Vapor-Liquid Equilibrium

The complexity of the fermented must, especially due to its multicomponent character and low concentration of congeners, makes it difficult to predict the

vapor-liquid equilibrium with accuracy and this can be considered a major source of errors in the simulation of distillation processes for bioethanol production (Faúndez and Valderrama, 2004). On the other hand, the availability of vapor-equilibrium data for several binary mixtures containing wine components allows the selection of appropriate thermodynamic models and the corresponding interaction parameters for a reliable representation of the fermented must, helping to minimize the errors involved in process simulation. Batista and Meirelles (2011) and Batista et al. (2012)<sup>10</sup> assumed that the typical alcoholic wine can be well represented by a mixture composed of 10 to 17 minor components in addition to ethanol and water. They then selected the NRTL model for the calculation of activity coefficients and the Virial equation with the Hayden-O'Connell model (Hayden and O'Connell, 1975) for the fugacity coefficients. Using the ASPEN data bank as initial estimates for NRTL parameters and experimental data collected from literature and DECHEMA data bank, they readjusted several binary interaction parameters in order to improve the equilibrium description. They also classified the congeners (minor components) into light components, intermediate volatility compounds and heavy components according to their volatilities in relation to ethanol and water. This classification helps to understand the behavior of congeners along the distillation columns as well as to find ways to improve the configuration of the equipments used nowadays. Details on the modeling of the vapor-liquid equilibrium of the alcoholic wine can be found in Batista and Meirelles (2011) and Batista et al. (2012).

### *5.2.2. Validation of the Process Simulation*

In order to check the reliability of the simulation results using the new set of NRTL parameters Batista and Meirelles (2011) and Batista et al. (2012)<sup>11</sup> validated the entire simulation procedure by comparing the results obtained by simulation with a comprehensive set of information collected from a bioethanol industrial plant. The first part of this validation was focused on section A of the distillation unit

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<sup>10</sup> Artigos reportados respectivamente nos Capítulos 2 e 4 desta tese

<sup>11</sup> Artigos reportados respectivamente nos Capítulos 2 e 4 desta tese

shown in Figure 5.1, a part of the equipment whose output stream (phlegm) has composition similar to an alcoholic spirit, such as *Rum* or *Cachaça* (see Batista and Meirelles, 2011). In the second part the entire distillation unit was considered, including the main product bioethanol. In both cases operational data and experimental samples were collected from an industrial plant that produces 300 m<sup>3</sup> of bioethanol per day and belongs to Santa Adélia Mill, a sugar and bioethanol company located in the city of Jaboticabal, state of São Paulo, Brazil. This information was taken along different days of the last sugar cane season and the samples, collected from feed, intermediate and output streams as well as from selected trays, were analyzed by gas chromatography (GC). Feed stream composition, operational conditions (pressures, values of input and output streams, etc.) and information on the equipment configuration, especially number of trays in each section, were used as input data and the simulation results generated by Aspen Plus (compositions and temperatures of the selected trays and from the intermediate and output streams) were compared with the experimental values obtained in the industrial unit. Deviations in temperature and concentrations of the major components were very low, but in the case of minor components the corresponding values were significantly higher. It should be considered that for the majority of the minor components concentrations in the feed stream were within the range  $(2 \text{ to } 9000) \cdot 10^{-7} \text{ g} \cdot \text{g}^{-1}$  (see Table 5.2), intermediate and output streams as well as in the selected trays, so that even small absolute deviations generate high relative errors. Nevertheless, the simulation procedure was able to describe correctly the behavior observed in the industrial plant. In case of minor components the industrial behavior was reliably described at least from a qualitative point of view. Further details about the results of the validation process and the methodology used for chromatographic analysis can be found in Batista and Meirelles (2011) and Batista et al. (2012)<sup>12</sup>.

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<sup>12</sup> Artigos reportados respectivamente nos Capítulos 2 e 4 desta tese

### *5.2.3. Simulation of Neutral Alcohol Production*

The first step of this work was to reproduce the simulations of neutral alcohol production reported by Decloux and Coustel (2005), considering the same wine composition indicated by the authors, a model solution containing water, ethanol and 6 representative congeners (acetaldehyde, ethyl acetate, propanol, isobutanol, isoamyl alcohol and acetic acid). Decloux and Coustel (2005) used ProSim Plus for simulating an installation with seven columns, the first two, for the production of hydrated alcohol, very similar to hydrated fuel bioethanol, the following three columns (Extractive distillation column, rectifier column and demethylizer column) for the additional purification steps and production of neutral alcohol and further two columns (congeners concentration column and stripping column) for the concentration of minor components and ethanol recovery. The vapor-liquid equilibrium was calculated using the UNIFAC model and ideal gas behavior in the vapor phase. The first column is similar to column A and the second column is similar to column BB1 of the fuel bioethanol Brazilian industrial plant (see Figure 5.1). Thus, in order to use a uniform nomenclature, column 1 will be called column A and column 2 as column BB1. Moreover, the equipment named by Decloux and Coustel as Extractive distillation column corresponds to the above mentioned Hydroselection column, which is the name used in the Brazilian industrial practice.

In order to reproduce this previous simulation work all specifications of the distillation unit were taken from Decloux and Coustel (2005). The first set of simulations was carried out using the same approach for calculating vapor-liquid equilibrium, UNIFAC model with ideal vapor phase. Afterwards the simulations were repeated with identical specifications but using NRTL parameters and the Virial equation with the Hayden-O'Connell model, as suggested by Batista and Meirelles (2011) and Batista et al. (2012). The package RADFRAC of Aspen Plus was selected and it employs methods based on the MESH equations (Kister, 1992) for the rigorous calculation of distillation columns. The different simulation results were compared in terms of ethanol recovery obtained in the intermediate and output streams, following the approach used by the Decloux and Coustel (2005).

According to information collected in the Brazilian companies the industrial plant for neutral alcohol production (see Figure 5.2) is slightly different from the process presented by Decloux and Coustel (2005). The main differences are the number of trays in the rectifier column, 66 according to Decloux and Coustel (2005) and 80 in the Brazilian plant, and the absence of a column for concentration of minor components in the Brazilian case. The Brazilian plant was simulated having as feed hydrated ethanol according to Decloux and Coustel's specification but using NRTL parameters and the Virial equation with the Hayden-O'Connell model. The specifications for the distillation plant are shown in Table 5.3. The output streams and reflux ratios were adjusted in order to reach the purity standard specified for neutral alcohol. The results were compared with the Decloux and Coustel's installation in terms of steam consumption, ethanol recovery in neutral alcohol, neutral alcohol composition and the purification factors calculated by Eq. 5.1.

$$F = \frac{\left( \frac{w_{ethanol}}{\sum w_{congeners}} \right)_{product}}{\left( \frac{w_{ethanol}}{\sum w_{congeners}} \right)_{feed}} \quad \text{Eq. 5.1}$$

Where  $F$  is the purification factor and  $w$  stands for the mass fraction of ethanol and congeners in the product and feed streams.

The three purification columns (hydroselection, rectifier and demethylizer) used in both neutral alcohol installations cover concentration ranges of ethanol, water and minor components very similar to those observed in the industrial plant for fuel bioethanol production (see Figure 5.1). For instance, in the hydroselection column ethanol is diluted from a concentration of 93% in mass to almost 10 °GL, a graduation close to that of the alcoholic wine, and then reconcentrated in the rectifier column. The dilution with potable water generates a liquid phase environment that increases the volatility of higher alcohols and makes it possible to withdraw most of these compounds by means of a small distillate stream. However, the hydroselection column also generates the additional requirement of a distillation step to remove the added amount of water. Note that a liquid phase rich

in water is also present at the bottom of sections A and B1 of the installation for production of fuel bioethanol (see Figure 5.1) and, for this reason, fusel oil is removed from a tray located at the bottom of section B (see Figure 5.1). In the case of fuel ethanol this sidestream is removed with the sole purpose of allowing that the necessary concentration of hydrous ethanol (93% by weight) is achieved. Taking these aspects into account, improvements and modifications of the distillation unit shown in Figure 5.1 could allow the production of neutral alcohol with a lower number of columns. The final part of this work is then focused on the investigation of alternative configurations for the neutral alcohol distillation unit and the required conditions for its appropriate operation.

Table 5.3 - Specifications of the Brazilian industrial plant for neutral alcohol production

	<b>Hydroselection</b>	<b>Rectifier</b>	<b>Demethylizer</b>
<b>Configuration</b>	<ul style="list-style-type: none"> <li>- Total condenser</li> <li>- 50 trays (20 above and 29 below the feed tray)</li> <li>- Tray efficiency = 70%</li> <li>- <math>P_{top} = 1.013</math> bar</li> <li>- <math>\Delta P = 0.2</math> bar</li> </ul>	<ul style="list-style-type: none"> <li>- Total condenser</li> <li>- 80 trays (60 above and 19 below the feed tray)</li> <li>- Tray efficiency = 70%</li> <li>- <math>P_{top} = 1.013</math> bar</li> <li>- <math>\Delta P = 0.264</math> bar</li> </ul>	<ul style="list-style-type: none"> <li>- Total condenser</li> <li>- 50 trays (20 above and 29 below the feed tray)</li> <li>- Tray efficiency 70%</li> <li>- <math>P_{top} = 1.013</math> bar</li> <li>- <math>\Delta P = 0.2</math> bar</li> </ul>
<b>In</b>	- Intermediate product or hydrated bioethanol	- Purified bioethanol	- Pasteurized alcohol
<b>Out</b>	<ul style="list-style-type: none"> <li>- Distillate</li> <li>- Purified bioethanol from the bottom</li> </ul>	<ul style="list-style-type: none"> <li>- Distillate</li> <li>- Pasteurized alcohol on tray 4</li> <li>- Fusel oil on tray 58</li> <li>- Bottom product (spent wash)</li> </ul>	<ul style="list-style-type: none"> <li>- Distillate</li> <li>- Neutral alcohol from bottom</li> </ul>
<b>Specifications</b>	<ul style="list-style-type: none"> <li>- 1 kg of steam per liter of ethanol fed into the column</li> <li>- The ethanol in distillate should not exceed 2% of the total amount of ethanol fed into column</li> <li>- The purified bioethanol must have an alcoholic content around 10 °GL</li> </ul>	<ul style="list-style-type: none"> <li>- 2 kg of steam per liter of ethanol fed into the column</li> <li>- The ethanol in distillate should not exceed 1% of the ethanol fed into column</li> <li>- The ethanol in fusel oil stream should not exceed 1% of the ethanol fed into column</li> <li>- The pasteurized ethanol must have an alcoholic content higher than 94 mass %.</li> </ul>	<ul style="list-style-type: none"> <li>- 1 kg of steam per liter of ethanol fed into the column</li> <li>- The ethanol in distillate should not exceed 1% of the ethanol fed into column</li> <li>- The neutral alcohol must have an alcoholic content higher than 94 mass %.</li> </ul>

The following strategy was used for developing alternative configurations for neutral alcohol production. As a first step, simulations of the biofuel distillation plant (Figure 5.1) were performed in order to evaluate the influence of operational and constructive conditions on bioethanol contamination with light components. The conditions were varied according to the experimental design technique using a fractional factorial design  $2^{(5-2)}$  (Box, 1978) with five independent variables, as shown in Table 5.4. Aiming to reduce the complexity of the simulations and to

guarantee convergence for every simulated condition, a simplified wine containing only some light contaminants (methanol, acetaldehyde, ethyl acetate and acetone) was considered. The concentrations of ethanol and of light contaminants were the same shown under the tag “industrial wine” in Table 5.2, being the water content adjusted to replace the disregarded contaminants. Except for section B, the configurations of the equipment sections (A, A1, D, and B1) were the same reported by Batista et al. (2012). For the entire set of simulations the alcoholic graduation of bioethanol produced was fixed in 94 mass%, a value in accordance with the neutral alcohol specification (HN) shown in Table 5.1. The simulation results were evaluated in terms of bioethanol purification factor, taking into account only the selected light components.

Table 5.4 - Levels for the fractional design factorial

<b><i>Independent Variable</i></b>	<b><i>Tag</i></b>	<b><i>-1</i></b>	<b><i>0</i></b>	<b><i>1</i></b>
Number of trays above bioethanol sidestream in section B	TB	2	21	40
Reflux ratio of column D	RRD	30	100	170
Reflux ratio of column B	RRB	300	800	1300
Column D second alcohol flow rate (% of wine flow rate)*	SAD	0.20	0.45	0.70
Column B second alcohol flow rate (% of wine flow rate)*	SAB	0.20	0.45	0.70

\* Wine flow rate = 202357 kg/h

In order to evaluate the influence of the variables reported in Table 5.4 upon the concentration profiles of superior alcohols and heavy components, a second set of simulations were performed with a wine containing only components with intermediate volatility (isoamyl alcohol, isobutanol, propanol) and one heavy compound (acetic acid). As indicated in the prior case, the concentrations of ethanol and of the selected contaminants were the same shown under the tag “industrial wine” in Table 5.2, being the water content adjusted to replace the disregarded contaminants. The second set of simulations was then complemented by a sensitivity analysis performed by changing the sidestream and flow rate of fusel oil and evaluating its effect on the purity of ethanol.

With a better insight on the influence of operational and constructive conditions upon the purification of fuel bioethanol, the investigation was then directed to the production of ethanol according to the neutral alcohol specification. A new sensitivity analysis was carried out with the complete wine composition and

the variables shown in Table 5.4 aiming at bioethanol purity within the neutral alcohol specification and at the best performance in terms of steam consumption and number of trays. Since bioethanol contamination with methanol was above the required level in all simulation cases, the configuration of the distillation unit must be complemented by using a demethylizer column, as in the traditional installations. Likewise, the difficulty in separating isopropanol from ethanol in the absence of hydroselection column motivated the introduction of additional changes in the new plant, enabling the production of neutral alcohol within the standards required even in the case of using a wine with higher isopropanol concentration. The performance of the suggested installations were then compared with the distillation unit reported by Decloux and Coustel (2005) and the Brazilian plant (see Figure 5.2), considering the steam consumption, the recovery of ethanol in the neutral alcohol stream, neutral alcohol purity and the purification factors of the main product.

The suggested installation does not include the hydroselection and rectifier columns, but its use in an industrial scale must guarantee resilience to changes in concentration of the contaminants present in the alcoholic wine. In order to check its resilience and to identify the maximum permissible concentration of each congener, an additional sensitivity analysis was conducted by manipulating the level of each contaminant in the feed stream. In a way similar to the one indicated above, two simplified wines were considered in this analysis, the first one containing light congeners and the second wine with the components of intermediate volatility and the heavy ones. The initial concentrations of the components were always equal to the values given in Table 5.2, being the water content adjusted to replace the disregarded contaminants. For each type of wine a set of simulations was performed increasing the content of each congener individually until its concentration in the neutral alcohol reaches values above specification. In the case of components with intermediate volatility this analysis was carried out individually for each component and also for the entire class of components, since the total concentration of superior alcohols is an additional requirement in some national and international specifications of neutral alcohol.

The new plant was able to produce neutral alcohol from an alcoholic wine containing higher levels of contamination of all minor components, with the unique exception of isopropanol. As indicated in Table 5.1, maximum levels for isopropanol, acetone and n-butanol are specified only in the case of Brazilian neutral alcohol. Taking this into consideration, a modified new plant was also developed in order to avoid the contamination with isopropanol in case of an alcoholic wine containing higher levels of this component since the others compounds (acetone and n-butanol) are easily eliminated in the new plant by the columns head products (acetone) and by the section B fusel oil stream (n-butanol).

The production of a neutral alcohol usually involves the generation of significant amounts of byproducts (second alcohol and fusel oil streams), so that at least 8% of ethanol fed into the plant is not recovered in the main product. In the Brazilian sugar mills at least part of these streams is recycled to distillation units used specifically for producing fuel bioethanol. In the present investigation the suggested approach is to mix all byproduct streams and distill this composed feed in an equipment named *fuel bioethanol column* in order to produce the biofuel in a unique additional distillation column. The top product of this new column was then mixed with the demethylizer column distillate to produce the final fuel bioethanol. The appropriate configuration of this *fuel bioethanol column* was investigated by simulation.

### **5.3 – Results and Discussion**

Our previous studies have focused on improving the simulation of the industrial distillation of ethanol to be used as biofuel or as alcoholic beverage (Batista and Meirelles, 2011; Batista et al., 2012)<sup>13</sup>. This included the consideration of the actual configuration of large scale equipments, of the multicomponent wine used as feed stream and a better representation of the corresponding phase equilibrium. In the present work the focus was placed on the investigation of industrial plants for distilling high purity ethanol to be used as raw material in the production of bio-based products.

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<sup>13</sup> Artigos reportados respectivamente nos Capítulos 2 e 4 desta tese.

As a first step, the simulation of the neutral alcohol distillation reported by Decloux and Coustel (2005) was reproduced. Figure 5.6 shows the ethanol recovery in the main output streams of columns A (column 1) and BB1 (column 2) that produce hydrated ethanol (see Figure 5.2), the raw material used for neutral alcohol distillation. The values reported by Decloux and Coustel (2005) and those obtained in this study are close, with average absolute deviation (AAD) of 2.2 and 3.5 % for the phase equilibria calculated according to the UNIFAC or NRTL models, respectively. The corresponding average relative deviations (ARD) were 23.64 and 30.51 %, respectively. In case of Table 5.6, that shows the ethanol recovery in the main streams of the hydroselection, rectifier and demethylizer columns, the AAD was 1.3 and 3.8 % for UNIFAC and NRTL models, respectively, and the ARD had values of 6.5 % and 10.4 % for the same thermodynamic models. Some components had large deviation in of the case of specific streams, as isoamyl alcohol in the intermediate product stream. These larger deviations between simulation results should be probably attributed to differences in the way of calculating vapor-liquid equilibrium. Although the reproduction of the work has been performed taking into account the exact specifications reported by Decloux and Coustel (2005), the authors did not indicated the version of the UNIFAC model used in their work. In the present work all the variations of the UNIFAC model available in the ASPEN PLUS library were tested. The lower deviations were obtained with the modified Dortmund UNIFAC model (Weidlich and Gmehling, 1987) and the corresponding recoveries are shown in Table 5.5 (column 1 and 2) and Table 5.6 (hydroselection, rectifier and demethylizer columns).

The results presented in Table 5.5 and Table 5.6 indicate that both ethanol recovery profiles, calculated by Aspen or ProSim, are very similar when the vapor-liquid equilibrium is calculated using the UNIFAC model. On the other hand, when the NRTL model was considered differences appear mainly in relation to superior alcohols. These components have intermediate volatility and tend to concentrate in the bottom of section B (column 2), being withdrawn through the fusel oil stream.

Note that in case of isobutanol, its recovery via the fusel oil stream (see Table 5.5) is very low when the UNIFAC model is considered, independent of the

simulator chosen, being around 65 % lower than the recovery estimated with the NRTL model. In this case, the NRTL model seems to generate results that agree better with the expected behavior. Furthermore, the careful study of vapor-liquid equilibrium of mixtures involving wine components reported by Batista and Meirelles (2011) and Batista et al. (2012) justifies the option for the NRTL model with the Virial and Hayden and O'Connell equations (NRTL-HOC) as the best approach for the phase equilibrium calculation in the subsequent simulations.

As mentioned above the industrial plant for neutral alcohol distillation used in the Brazilian sugar mills is slightly different from that reported by Decloux and Coustel (2005), particularly in relation to the number of trays in the rectifier column and to the absence of a specific column for the concentration of congeners and recovery of ethanol present in the byproduct streams. In the Brazilian case these streams are usually recycled to the distillation plant for producing fuel bioethanol. Aiming to evaluate the performance of the Brazilian neutral alcohol plant, simulations were carried out for the set of columns shown in Figure 5.2 fed with hydrated ethanol according to the specifications for this input stream reported by Decloux and Coustel (2005). The detailed specifications of the hydroselection, rectifier and demethylizer columns are shown in Table 5.3.

Table 5.5 - Recovery of components in % of the input flow in each column (1 and 2)

Components	Heads of column A			Stillage			Hydrated bioethanol		
	ProSim <sup>1</sup> (UNIFAC)	Aspen (UNIFAC)	Aspen <sup>2</sup> (NRTL)	ProSim <sup>1</sup> (UNIFAC)	Aspen (UNIFAC)	Aspen <sup>2</sup> (NRTL)	ProSim <sup>1</sup> (UNIFAC)	Aspen (UNIFAC)	Aspen <sup>2</sup> (NRTL)
Ethanol	0.36	0.36	0.36	0.00	0.01	0.00	97.99	98.40	98.43
Acetaldehyde	3.49	2.94	8.38	0.02	0.00	0.00	44.35	52.92	46.33
Ethyl acetate	29.51	29.43	44.51	0.00	0.00	0.00	68.30	96.81	96.91
Methanol	0.26	0.25	0.24	1.47	2.83	1.98	96.78	98.51	98.28
Propanol	0.43	0.44	0.58	0.24	0.00	0.00	90.49	93.12	94.48
Isobutanol	0.81	0.83	0.66	0.14	0.00	0.00	79.61	86.57	46.89
Isoamyl alcohol	0.77	0.82	0.41	0.13	0.00	0.00	11.98	26.29	20.67

Components	Heads of column BB1			Fusel oil			Spent wash		
	ProSim <sup>1</sup> (UNIFAC)	Aspen (UNIFAC)	Aspen <sup>2</sup> (NRTL)	ProSim <sup>1</sup> (UNIFAC)	Aspen (UNIFAC)	Aspen <sup>2</sup> (NRTL)	ProSim <sup>1</sup> (UNIFAC)	Aspen (UNIFAC)	Aspen <sup>2</sup> (NRTL)
Ethanol	0.18	0.18	0.18	1.47	1.42	1.39	0.00	0.00	0.00
Acetaldehyde	52.04	46.95	53.56	0.12	0.13	0.11	0.00	0.00	0.00
Ethyl acetate	2.06	3.01	2.91	0.13	0.17	0.18	0.00	0.00	0.00
Methanol	0.78	0.76	0.80	0.71	0.73	0.92	0.00	0.00	0.00
Propanol	0.03	0.03	0.04	9.05	6.85	5.48	0.00	0.00	0.00
Isobutanol	0.01	0.02	0.01	19.57	13.41	53.10	0.00	0.00	0.00
Isoamyl alcohol	0.00	0.00	0.00	87.26	73.71	79.33	0.00	0.00	0.00

<sup>1</sup> Reported by Decloux and Coustel (2005), <sup>2</sup> NRTL with Virial equation and Hayden and O'Connell model

Table 5.6 – Components recovery in % of the input flow in each column

Components	<i>Hydroselction column</i>			<i>Rectifier column</i>			<i>Demethylizer column</i>					
	Bottom - Purified alcohol			Heads			Pasteurized alcohol			Neutral		
	ProSim <sup>1</sup> (UNIFAC)	Aspen (UNIFAC)	Aspen <sup>2</sup> (NRTL)									
<b>Ethanol</b>	93.75	93.05	93.50	1.08	1.11	1.10	88.50	90.51	89.77	96.35	96.35	96.34
<b>Acetaldehyde</b>	0.00	0.00	0.00	-	-	0.00	-	-	0.00	-	-	-
<b>Ethyl acetate</b>	0.00	0.00	0.00	-	-	0.00	-	-	0.00	-	-	-
<b>Methanol</b>	99.68	99.79	99.93	7.34	4.95	4.73	89.95	92.55	92.08	2.49	0.82	1.08
<b>Propanol</b>	86.25	83.26	67.44	0.00	0.00	0.00	0.00	0.00	0.00	99.76	100.00	100.00
<b>Isobutanol</b>	45.86	38.16	70.85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Isoamyl Alcohol</b>	56.21	48.18	87.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

<sup>1</sup> Reported by Decloux and Coustel (2005), <sup>2</sup> NRTL with Hayden and O'Connell state equation

Table 5.7 shows the recovery of components in each column of the Brazilian industrial plant. Volatile compounds, such as acetaldehyde and ethyl acetate, are fully eliminated via the head product of the hydroselction column (see Figure 5.3f). Around 30 % of propanol and isobutanol and 10 % of isoamyl alcohol are also withdrawn through that stream, being the rest of them eliminated with the fusel stream in the rectifier column. The volatility of superior alcohols is increased by the water-rich environment available in the liquid phase of both columns, so that they concentrated in the head product of the hydroselction column, just above the potable water feed stream, and in the intermediate region of the rectifier column, where the liquid phase changes from a water-rich solution to a ethanol-rich one. As explained elsewhere (Batista and Meirelles, 2011; Batista et al., 2012), the activity coefficients of higher alcohols and, consequently, their volatilities are much larger in an environment rich in water, being this effect the main reason suggested by the industrial engineers for the hydroselction step used in the purification of neutral alcohol. Indeed Figure 5.3e clearly shows that the superior alcohols tend to concentrate at the top of the hydroselction column. The amount of methanol remains almost constant in the main product streams of the hydroselction and rectifier columns, bottom product and pasteurized alcohol respectively, and is, for practical purposes, entirely recovered in the head product of the demethylizer column. This recovery reach values higher than 99 % in the last column, but demands very high reflux ratios in order to be achieved. Concerning the recovery of congeners in the byproduct streams and the remaining contamination in the neutral alcohol, the results obtained in the present case are similar to those reported by Decloux and Coustel (2005), with the main exception observed for methanol. In fact, its concentration in the neutral alcohol is much lower (see Table 5.8) and its recovery in the head product of the demethylizer column is higher, suggesting a better efficiency of the installation shown in Figure 5.2.

Table 5.8 compares the performances of the plant reported by Decloux and Coustel (2005) and the Brazilian installation. The Brazilian plant decreases by about 16 % the steam consumption per liter of neutral alcohol, a decrease related mainly to the smaller number of distillation columns, and it increases in 3 % the

ethanol recovery in the main product. In relation to the neutral alcohol quality only the contamination with propanol is slightly higher in the Brazilian plant, while the methanol concentration is significantly lower. Nevertheless, both products are in accordance with the required standards (see Table 5.1). The total purification factor ( $F_{total}$ ) for the Brazilian plant is about five times higher, mainly due to its better performance in reducing contamination with methanol (see  $F_{methanol}$ ) and other volatile components (see  $F_{volatiles}$ ).

Table 5.7 - Recovery of components as a percentage of the input flow in each column for the Brazilian neutral alcohol plant

Components	Hidroselection		Rectifier			Demethylizer		
	Heads	Bottom	Heads	Pasteurized alcohol	Fusel	Bottom	Heads	Neutral Alcohol
<b>Ethanol</b>	1.00	99.00	1.01	98.12	0.87	0.00	1.01	98.99
<b>Acetaldehyde</b>	100.00	0.00	0.00	0.00	0.00	0.00	-	-
<b>Ethyl acetate</b>	100.00	0.00	0.00	0.00	0.00	0.00	-	-
<b>Methanol</b>	0.00	100.00	2.87	95.60	0.42	1.11	99.94	0.06
<b>Propanol</b>	29.90	70.10	0.00	0.10	99.90	0.00	0.00	100.00
<b>Isobutanol</b>	36.17	63.83	0.00	0.00	100.00	0.00	0.00	100.00
<b>Isoamyl Alcohol</b>	10.65	89.35	0.00	0.00	100.00	0.00	0.00	0.00

Figure 5.3 shows the concentration profiles for ethanol in hydroselection (a) and rectifier columns (b), superior alcohols in the rectifier column (c), methanol in the demethylizer column (d), superior alcohols (e) and volatile compounds (f) in hydroselection column. The potable water stream fed into the top of the hydroselection column dilutes the hydrated bioethanol from an alcoholic graduation around 92.8% to approximately 8% in mass (10 °GL). This dilution is responsible for the above mentioned effect upon the activity coefficients and volatilities of superior alcohols, making possible the extraction of an expressive amount of these components, together with most of the volatile components, through the top of this column. The diluted and purified alcohol (bottom product of the hydroselection column) is fed to the rectifier column and concentrated to around 94 wt% (see Figure 5.3b). Likewise, the higher alcohols remaining in the diluted ethanol feed stream are concentrated in the fusel oil and withdrawn as a sidestream, as shown in Figure 5.3c. Finally, the pasteurized alcohol stream is fed into the demethylizer column whose main function is to eliminate the methanol contamination. High

number of trays and large reflux ratios are required to concentrate methanol in the top product up until 4 mass% (see stage 1 in Figure 5.3d), with a recovery of approximately 86 % of the total mass of methanol present in the wine and a concentration that becomes 1,000 times higher in comparison to its value in the wine (see Decloux and Coustel wine composition in Table 5.2).

The range of concentrations covered by the two major wine components, ethanol and water, along the hydroselection and rectifier columns (see Figure 5.3a and 5.3b) is similar to the range observed in the installations for fuel bioethanol distillation (Batista et al., 2012). In fact the trays located in the bottom region of section B and in the top regions of sections A and B1 (see Figure 5.1) contain a liquid phase with ethanol concentrations within the same range shown in Figure 5.3a and the rectifier column has a ethanol profile equal to that observed in column BB1. Taking into account that the volatilities of the minor components is mainly influenced by the changes in the concentrations of the two major components, most of the ethanol contamination with congeners can potentially be decreased to the levels specified for neutral alcohol by appropriate changes in the configuration and operational conditions of the industrial plants used for fuel bioethanol distillation. On the other hand, methanol contamination is more difficult to be eliminated, as suggested by the profile shown in Figure 5.3d. In fact, the reduction of this contamination requires a combination of high reflux ratios and large number of trays due to the low relative volatility methanol to ethanol. Although the range of ethanol concentrations found in the demethylizer column is similar to the range observed in the top trays of section B of the industrial plants used for fuel bioethanol distillation, the elimination of methanol contamination through the top product of that section can potentially require a extremely large number of stages above the bioethanol sidestream (see Figure 5.1), a solution that is difficult to be implemented because of the high total pressure drop along such a column.

Based on the above considerations our investigation was then focused on improving the configurational and operational conditions of industrial plants used for fuel bioethanol distillation with the aim of producing bioethanol according to the neutral alcohol standard. A fractional experimental design was performed with the

independent variables and levels shown in Table 5.4 in order to identify what conditions influence bioethanol purification in terms of volatile compounds and methanol. The results showed that for the purification factor of volatile compounds  $F_v$ , only the number of trays in section B, TB, was statistically significant, while for the purification factor of methanol  $F_m$ , TB and the reflux ratio of section B, RRB, are both significant.

Table 5.8 – Main differences between Brazilian and French industrial plant considering the wine composition reported by Decloux and Coustel, 2005.

Specifications	Decloux and Coustel (2005)	Brazilian plant	New plant
<b>Steam Consumption</b>			
(kg of steam / L neutral alcohol)	6.10	5.12	3.75
$F_{total}$	1166.28	5997.41	655.40
$F_{intermediate}$	8126.64	6405.34	1274.65
$F_{volatiles}$	243.22	4677.47	207.89
$F_{methanol}$	97.26	1870.34	83.13
<b>Ethanol recovery in neutral alcohol (%)</b>	87.17	90.25	92.53
<b>Neutral alcohol composition</b>			
<b>Ethanol (%v/v)</b>	97.3	97.2	97.2
<b>Acetaldehyde (mg / L)</b>	0.00	0.00	0.00
<b>Ethyl acetate (mg / L)</b>	0.00	0.00	0.00
<b>Methanol (mg / L)</b>	4.09	0.22	4.06
<b>Propanol (mg / L)</b>	0.54	0.70	2.95
<b>Isobutanol (mg / L)</b>	0.00	0.00	0.00
<b>Isoamyl alcohol (mg / L)</b>	0.00	0.00	0.00

Considering the results of the fractional experimental design presented before, a first attempt to develop a new industrial plant was performed by increasing the number of trays and reflux ratio in section B. Wine, with the composition given in Table 5.2 under the tag “industrial wine”, was fed into column AA1 at a flow rate of 202357 kg/h and a temperature of 94 °C. A large number of trays in the region located above bioethanol sidestream and a high reflux ratio were required, as well as a large second alcohol stream in top of section B, in order to avoid methanol contamination in neutral alcohol. Sections AA1, D and B1 are identical to the corresponding sections used for fuel bioethanol distillation (Batista et al., 2012), except for a second alcohol stream withdrawn from the top of section D. This stream is necessary in order to eliminate part of the volatile

components and methanol, contributing to an additional purification of neutral alcohol. The byproducts generated in the top of sections B and D were mixed to produce fuel bioethanol. As indicated above, besides the additional second alcohol stream in section D, the modifications are concentrated in section B, involving TB = 40 trays, RRB = 600 and a second alcohol stream approximately equal to 12% of the neutral alcohol flow rate. These results indicate that, despite the increase in the number of trays and in the reflux ratio, the flow rate of the second alcohol byproduct should also be larger in order to reduce the contamination with volatile components to the values specified for neutral alcohol.

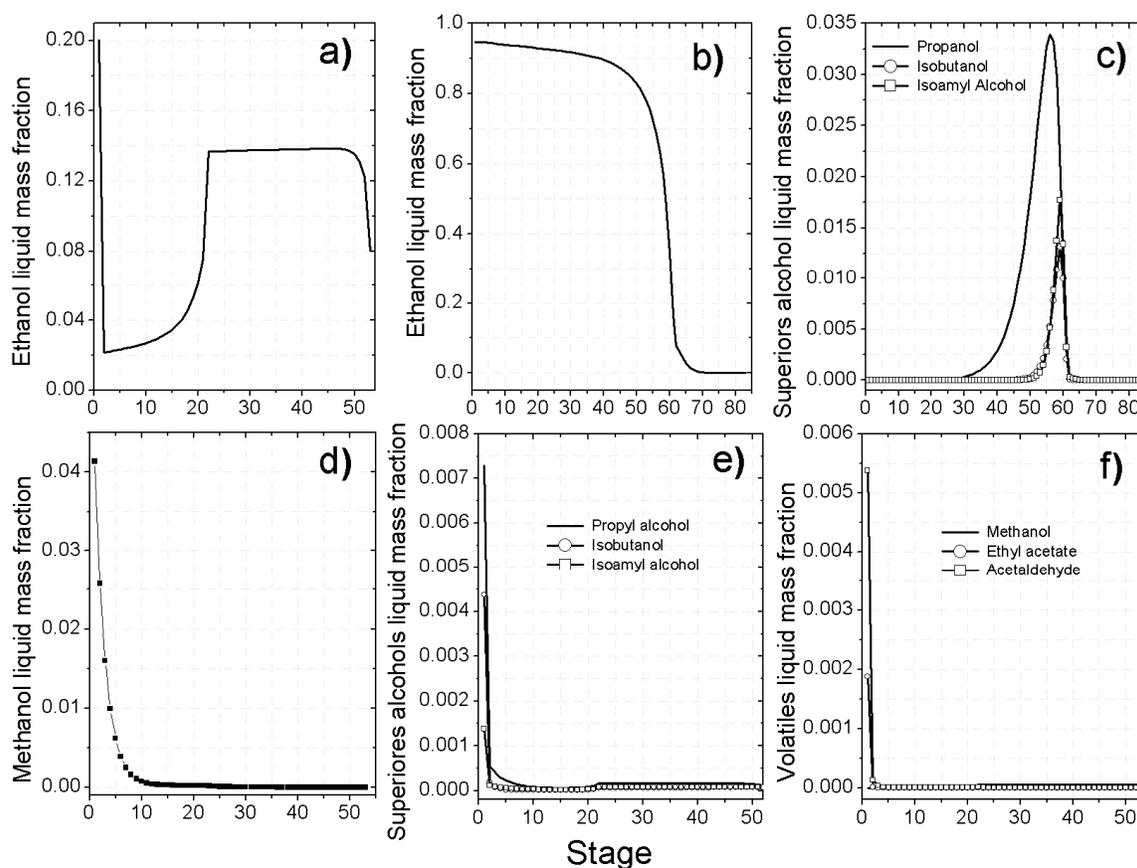


Figure 5.3 – Ethanol profile in hydroselection column (a), rectifier column (b), superior alcohols profile in rectifier column (c) and methanol profile in demethylizer column (d), superior alcohols profile in hydroselection column (e), volatile profile in hydroselection column (f).

Moreover, contamination of ethanol with higher alcohols was reduced to the values required for the neutral alcohol standard by increasing the fusel oil sidestream up to 800 kg/h, an amount corresponding to 6 % of the neutral alcohol

production and therefore much greater than the stream of fusel oil usually removed during the production of fuel ethanol (around 0.1 % to 0.3 % of fuel ethanol flow rate). Figure 5.4 shows the change in bioethanol contamination with superior alcohols as a function of the fusel oil side stream. Note that the best purification is around 500 kg/h of fusel oil flow rate (3.8 % of bioethanol flow rate). However, a flow rate of fusel oil less than 600 kg / h spreads the different higher alcohols over the trays near the section B bottom, so that more than one side stream is required for an efficient removal of these compounds. On the other hand, flow rates greater than 1000 kg/h cause significant variations in the alcoholic concentration of bioethanol, preventing their use. A flow rate of 800 kg/h (6.16 % of bioethanol flow rate) makes possible the concentration of superior alcohols around one specific tray, allowing the removal of most of these components via a unique sidestream and, for this reason, this value was choosed in the first version of the new plant. The complete flowsheet and specification for the new plant are presented in Figure 5.5 and annex 1, respectively.

Although the suggested modifications allow the production of neutral alcohol in a distillation plant similar to the installation used for fuel bioethanol, they exhibit the following disadvantages: the excessive increase in the number of trays of section B causes a high pressure drop, requiring the use of heating steam with a higher pressure and increasing the operational cost; the combination of a high reflux ratio and a large second alcohol flow rate increases the steam consumption to 22 kg of steam per liter of neutral alcohol, a value more than three times the normal energy consumption required in neutral alcohol distillation; and they also imply a lower recovery of ethanol in the main product stream when compared with the Brazilian industrial plant for neutral alcohol distillation.

Taking into account the low relative volatility of methanol to ethanol, these disadvantages are mostly caused by the attempt of eliminating methanol contamination together with the other volatile components. Therefore, a second alternative configuration was tested focused on eliminating only the volatile components other than methanol in section B of the industrial plant for fuel ethanol,

with the decrease of methanol contamination being carried out in a separate demethylizer column.

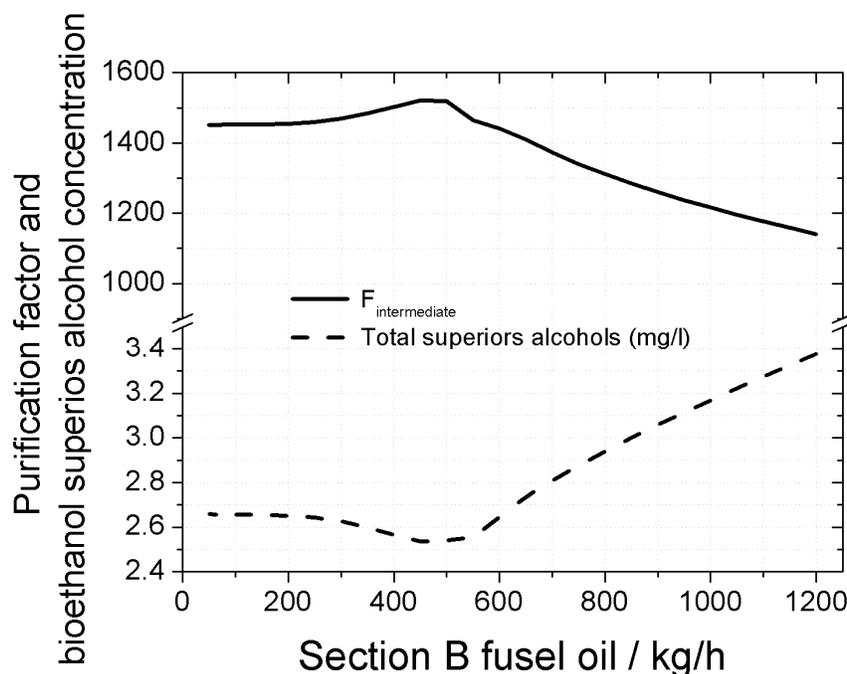


Figure 5.4 – Bioethanol superior alcohols as a function of fusel oil stream

As indicated by Figure 5.6a, most volatile contaminants have higher concentrations only in the 5 to 10 trays near the top of section B, so that the number of trays located between the distillate (second alcohol stream) and the bioethanol sidestream does not need to be much higher than those values in order to decrease the contamination with acetaldehyde, acetone and ethyl acetate to the range required for neutral alcohol. A sequence of simulations were performed in order to select an appropriate combination of TB, RRB and second alcohol stream able to reduce the volatile contamination other than methanol to a value below the required level (see column BB1 specification in annex 2). As a side effect of the selected values for TB, RRB and second alcohol stream, the methanol contamination of bioethanol is also partially decreased, so that the additional decontamination to be performed in the demethylizer column can be lower than the required in the industrial plant reported by Decloux and Coustel (2005) and in the Brazilian installation. In this column, methanol is removed in the distillate and

reaches concentrations of 1.1 % by mass, a value corresponding to an enrichment of 900 times compared to its concentration in the wine. The relatively high concentration of methanol causes a slight decrease of the ethanol content in the distillate (see Figure 5.6b), but anyway this stream can be directly mixed with the distillate from the fuel bioethanol column to produce a biofuel in accordance with the legislation.

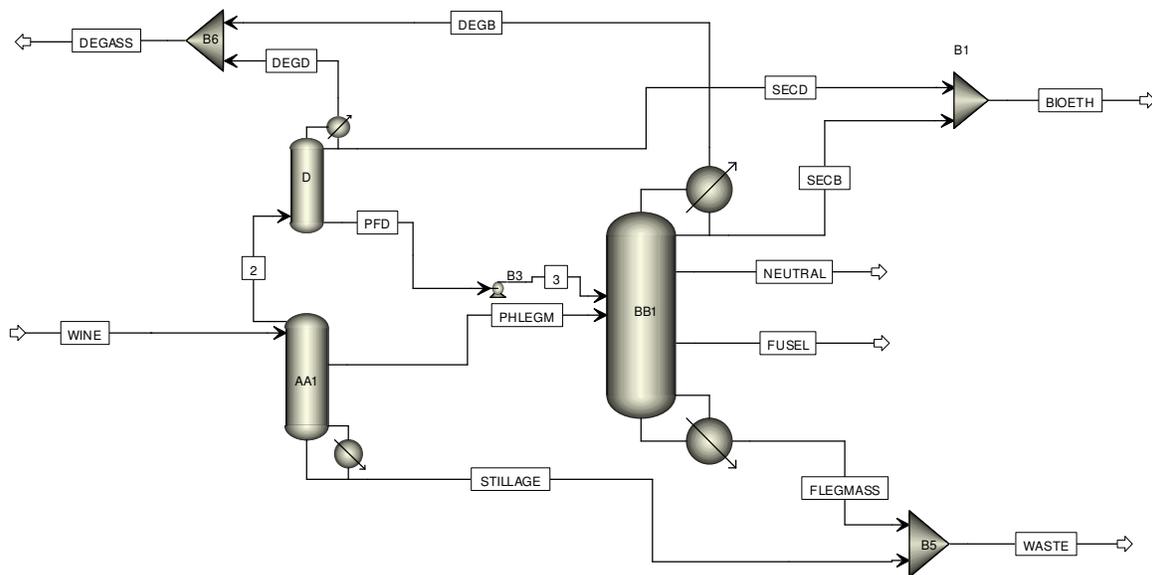


Figure 5.5 - Modified Brazilian bioethanol industrial plant for neutral alcohol production – First configuration

The decrease of methanol content in bioethanol reached in column BB1 can reduce the reflux ratio that should be used in the demethylizer column for eliminating methanol contamination, as is indicated by the results of the sensitivity analysis shown in Figure 5.7. Different combinations of number of trays above bioethanol withdrawn in section B (TB) and reflux ratio in the demethylizer column allow the production of neutral alcohol with a methanol content below the most stringent requirement established by Brazilian and American sugar mills (5 mg/L, see Table 5.1), a level indicated in Figure 5.7a by the dashed-dotted line. This means that for different TB-values it is possible to produce neutral alcohol provided the correct reflux ratio is selected in the demethylizer column and that a higher reflux ratio does not cause a substantial increase in the steam consumption (see

Figure 5.7b) because the distillate stream has a low value. The steam consumption has, in the worst case, a value of 3.6 kg of steam per liter of neutral alcohol, about 40% lower than the consumption presented by the Brazilian industrial plants and by the plant reported by Decloux and Coustel (2005). According to Figure 5.7a a number of trays TB above 30 does not cause any additional decrease in the reflux ratio of the demethylizer column. Taking into account these results a combination of 15 trays for TB and 600 for the reflux ratio in the demethylizer column was selected (see annex 2).

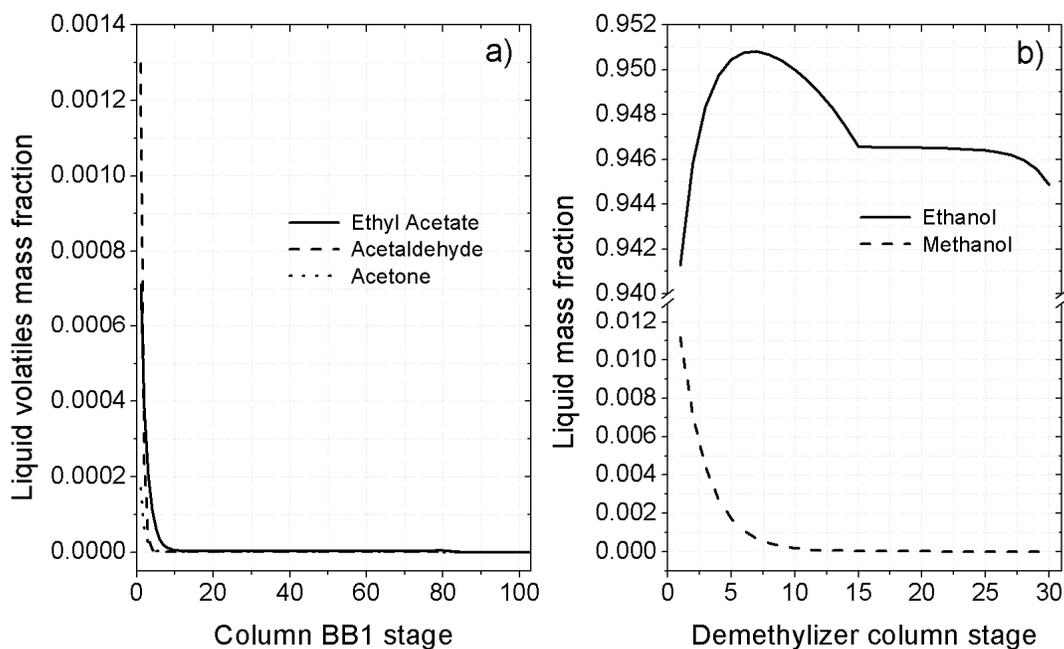


Figure 5.6 - Volatile profiles in column BB1 (a) and Ethanol/Methanol profiles in demethylizer column (b)

Table 5.9 and Table 5.10 shows a summary of the products compositions obtained with the suggested new distillation plant for neutral alcohol. As can be seen, the ethanol produced by the proposed configuration meets all the requirements to be classified as neutral alcohol, according to the Brazilian standard and other national or international standards (see Table 5.1), This result was obtained with a specific steam consumption 35-45% lower than the Brazilian plant and the installation reported by Decloux Coustel (2005). Furthermore, the steam

consumption of this new installation for neutral alcohol production is only 1.5 times higher than that required to produce fuel hydrated bioethanol (Batista et al., 2011).

Purification factors were evaluated for each one of the configurations and for both wine compositions, the industrial wine with 17 components (Table 5.10) and the simplified wine with 8 components (Table 5.8). In both cases the same trend was observed: the purification factors for the new installation are lower than those obtained for the traditional Brazilian plant and for the equipment reported by Decloux and Coustel (2005). However, the neutral alcohol specifications were attained in all plants, including the suggested new configuration, which has the advantages of lower steam consumption and lower number of columns.

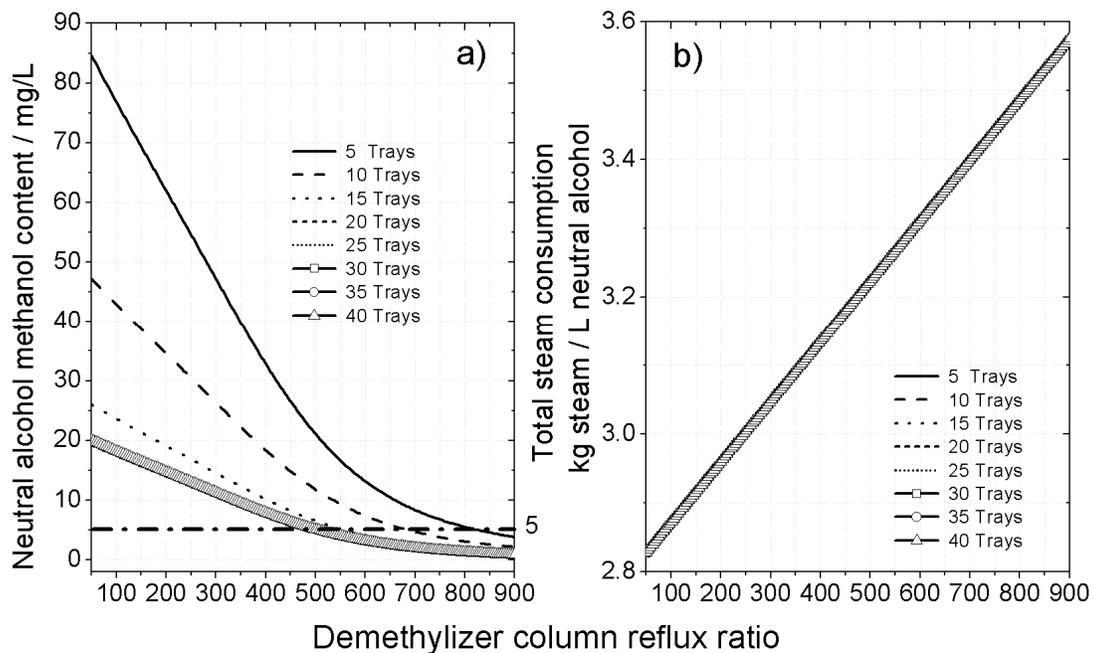


Figure 5.7 - Sensitivity analysis result: methanol concentration in neutral alcohol (a) and total steam consumption (b) as a function of reflux ratio in the demethylizer column and number of trays above bioethanol withdrawn.

On the other hand, the ethanol recovery as main product was also somewhat higher in the new configuration than the values obtained in the other plants. In order to increase the ethanol recovery all byproducts, second alcohol streams withdrawn from the top of sections D and B and the fusel oil sidestream, were mixed and distilled to produce hydrated bioethanol in a fourth column named *fuel bioethanol column*. This column has about 20 trays and generates a bottom

product that concentrates the major part of the higher alcohols present in wine and is also almost ethanol-free. After cooling, this stream can be separated in a liquid-liquid decanter, producing a waste stream rich in water and commercial fusel oil (Table 5.9). As top product, this column produces hydrated ethanol in accordance with the Brazilian fuel legislation. This stream can be mixed with the top product of the demethylizer column and the obtained blend still fulfills the specifications of fuel bioethanol (Table 5.9). Therefore, the proposed plant is able to produce three economically viable products (neutral alcohol, hydrated ethanol and fusel oil) in a single process with low steam consumption. Taking into account the products neutral and hydrated alcohols, the total ethanol recovery reaches the value of 99.3%, increasing to 99.9%, if the amount of ethanol contained in the third product, fusel oil, is considered. This amount of ethanol is distributed, according to the production volume of the major products, in 91.0% of neutral alcohol, 8.6% of hydrated alcohol and 0.4% of fusel oil. The complete flowsheet and specifications of all columns for the new industrial plant are presented in Figure 5.8 and annex 2, respectively.

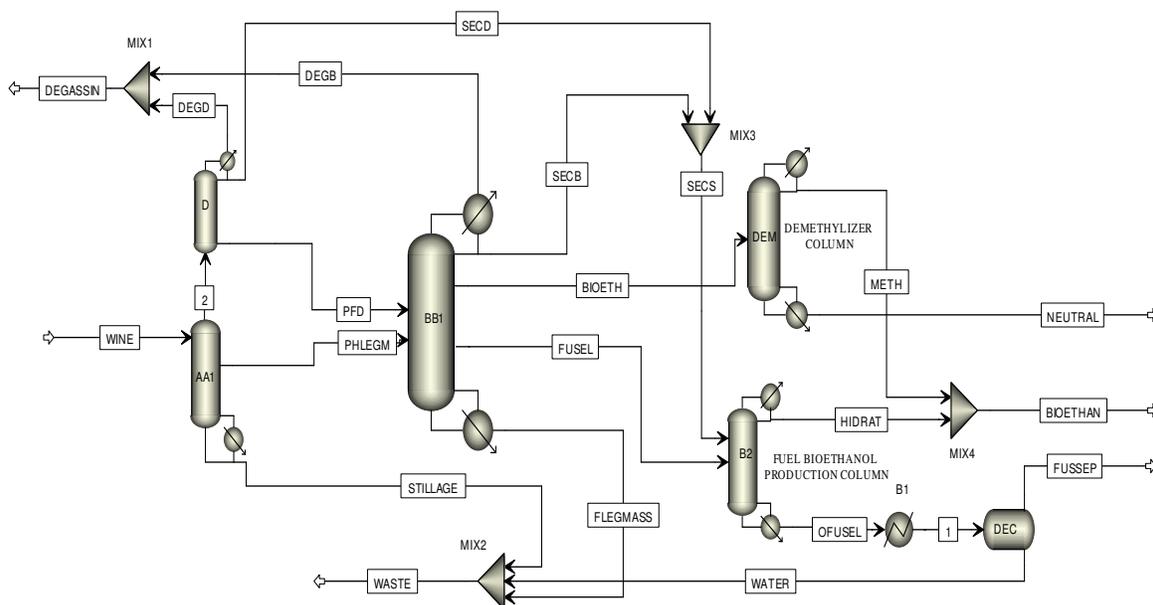


Figure 5.8 – New industrial plant for neutral alcohol production

Table 5.9 - Fuel bioethanol and Fusel oil composition for the new industrial plants

	Unity	New plant		New plant max purification		Modified new plant	
		Fuel Bioethanol <sup>1</sup>	Fusel oil	Fuel Bioethanol <sup>1</sup>	Fusel oil	Fuel Bioethanol <sup>1</sup>	Fusel oil
<b>Alcoholic graduation</b>	mass%	93.10	9.30	93.40	31.80	93.0	1.90
<b>Acidity (acetic acid)</b>	mg/L	-	2.36	-	15.90	-	13.20
<b>Acetaldehyde</b>	mass%	0.300	-	0.200	-	0.048	-
<b>Ethyl Acetate</b>	mass%	0.300	-	0.300	-	0.053	-
<b>Acetone</b>	mass%	0.016	-	0.015	-	0.003	-
<b>Methanol</b>	mass%	0.200	-	0.200	-	0.032	-
<b>Isopropanol</b>	mass%	-	-	-	-	0.004	-
<b>Propanol</b>	mass%	0.012	9.50	0.004	4.18	0.061	7.40
<b>Isobutanol</b>	mass%	-	9.20	-	3.82	-	12.60
<b>Butanol</b>	mass%	-	0.30	-	0.11	-	0.33
<b>2-Butanol</b>	mass%	-	1.10	-	0.46	-	1.51
<b>Isoamyl Alcohol</b>	mass%	-	43.40	-	17.82	-	49.17
<b>Amyl Alcohol</b>	mass%	-	10.20	-	4.17	-	12.86
<b>1-Pentanol</b>	mass%	-	0.20	-	0.10	-	0.29
<b>1-Hexanol</b>	mass%	-	0.30	-	0.11	-	0.29
<b>Others compounds</b>	mass%	6.072	16.5	5.881	37.43	6.799	13.65

<sup>1</sup> – Top product of fuel bioethanol column plus top product of demethylizer column

The specific steam consumption informed in Table 5.10 refers only to the neutral alcohol production, i.e. to the total heating steam used in columns AA1D, BB1 and demethylizer divided by the amount of neutral alcohol, resulting in 3.31 kg of steam per liter of bioethanol. The fourth column used for recovering ethanol as biofuel demands an additional amount of steam corresponding to 1.81 kg of steam per liter of fuel alcohol, a value 15% lower than the consumption reported by Batista et al. (2012) for the biofuel production. The manner in which the steam consumption is assigned to each specific product or byproduct of the proposed new plant may be subject to some discussion, but even in the case of assigning the total consumption of steam, including the steam amount used in the fuel bioethanol column, to the main product, the specific value increases only to 3.48 kg of steam per liter of neutral alcohol, a performance still much better than the obtained in the traditional installations for neutral alcohol distillation. In order to improve the purification factors obtained by the new plant, the reflux ratios or the byproducts streams must be further increased, with corresponding impacts on the steam consumption and on the ethanol recovery in the main product. Assuming that the traditional Brazilian plant sets limits for a maximum value that is admissible for the specific steam consumption and a minimum value for the ethanol recovery, Table 5.10 (see “New Plant Max Purification” column) shows the improvement that

can be obtained by changing those operational conditions without crossing the limits fixed by the traditional plant. In fact, increasing the second alcohol stream withdrawn and reflux ratio in section D from 300 to 500 kg/h and from 30 to 50 respectively, decreasing the fusel oil stream in section B from 800 to 650 kg/hr, and, at last, increasing the distillate produced in the demethylizer column and its reflux ratio from 40 to 150 kg/h and from 600 to 800, respectively, guarantees much better purification factors, but the specific steam consumption must be increased to 5.22 kg of steam per liter of neutral alcohol.

Table 5.10 - Comparison between French, Brazilian and New Plant for neutral alcohol production considering the industrial wine composition

Specifications	Decloux and Coustel (2005)	Brazilian	New Plant	New Plant Max Purification	Modified New Plant
<b>Steam Consumption (kg of steam / L neutral alcohol)</b>	6.20	5.22	3.31	5.22	5.22
$F_{total}$	7804.63	8249.65	1091.47	2605.82	8803.61
$F_{intermediate}$	10782.06	3951.39	1309.36	1229.12	4228.67
$F_{volatiles}$	840.12	25834.04	127.39	24357.60	24582.90
$F_{methanol}$	198.16	6093.41	34.07	5745.82	5798.32
<b>Ethanol recovery as neutral alcohol (%)</b>	88.25	90.41	91.15	91.15	47.81
<b>Ethanol recovery as hydrated bioethanol (%)</b>	-	-	8.67	8.12	52.13
<b>Fuel bioethanol alcoholic graduation (%wt)</b>	-	-	93.0	93.2	93.0
<b>Neutral alcohol composition</b>					
<b>Ethanol (%v/v - %wt)</b>	96.2 - 94.8	96.1 - 94.7	96.0 - 94.4	96.0 - 94.5	96.1 - 94.7
<b>Acetaldehyde (mg/L)</b>	0.00	0.00	0.00	0.00	0.00
<b>Ethyl acetate (mg/L)</b>	0.00	0.00	0.01	0.00	0.00
<b>Methanol (mg/L)</b>	0.70	0.02	4.00	0.03	0.02
<b>Propanol (mg/L)</b>	0.04	0.18	0.84	0.80	0.20
<b>Isopropanol (mg/L)</b>	0.35	0.69	1.97	1.98	0.64
<b>Isobutanol (mg/L)</b>	0.00	0.00	0.00	0.00	0.00
<b>Isoamyl alcohol (mg/L)</b>	0.00	0.00	0.00	0.00	0.00
<b>Total superiors alcohol (mg/L)</b>	0.39	0.87	2.81	2.78	0.84

However, although there has been a substantial increase in the total purification factor ( $F_{total}$ ) after the operational changes in new plant, this variable is still well below the value obtained in the traditional Brazilian plant (see columns "Brazilian", "New plant" and "new plant max purification" in Table 5.10), mainly because of the low value of the  $F_{intermediate}$ . This difference is related mainly due to the difficult in the separation of isopropanol from ethanol in the new plant.

Figure 5.9 shows the relative volatility of methanol, isopropanol, propanol and isobutanol in relation to ethanol in hydroalcoholic solutions with different ethanol concentrations. It is possible to observe that, for a range of concentrations of ethanol found in hydrated alcohol production ( $2 \cdot 10^{-4}$  in the bottom of section A and 0.93 - 0.94 in the top of section B, in mass fraction) the relative volatility of isopropanol vary from approximately 2.0, in the bottom of section A, to 0.85 in top of section B and in the tray of hydrated alcohol withdrawn. In the same range of ethanol concentration, the relative volatility of methanol vary from 0.6 to 1.5. Note that methanol and isopropanol have antagonistic behavior in alcoholic solutions. It means that, in the bottom of the columns, a region very diluted in ethanol, the methanol tends to be concentrated in the liquid phase and isopropanol in the vapor phase. This behavior indicates that isopropanol can not be withdrawn via the bottom products of the distillation columns. On the other hand, in the top of the columns, a region concentrated in ethanol, although the relative volatilities are close to unity, methanol is more volatile than ethanol and the opposite is observed for isopropanol. The behavior of the components in the top of the columns indicates that only methanol can be withdrawn as a top product, though a high energy consumption (substantial increase in the reflux ratio) or even a specific column is required for such process, as discussed before. In case of isopropanol, the increase of the reflux ratio and/or the increase of the top product flow rate has no effect on the separation of this component since its volatility is lower than ethanol in this column part. For this reason, this component tends to be extracted together with the bioethanol stream contaminating the neutral alcohol produced.

Even though the volatility of the propanol and isopropanol are close the behavior described above for isopropanol. Thus, propanol can be considered as a kind of key component dividing the higher alcohols that tends to be concentrated in the fusel oil stream (propanol, isobutanol, butanol, 2-butanol, isoamyl alcohol, amyl alcohol, 1-hexanol, 1-pentanol, etc) from that higher alcohol (isopropanol) that tends to be withdrawn with the bioethanol stream.

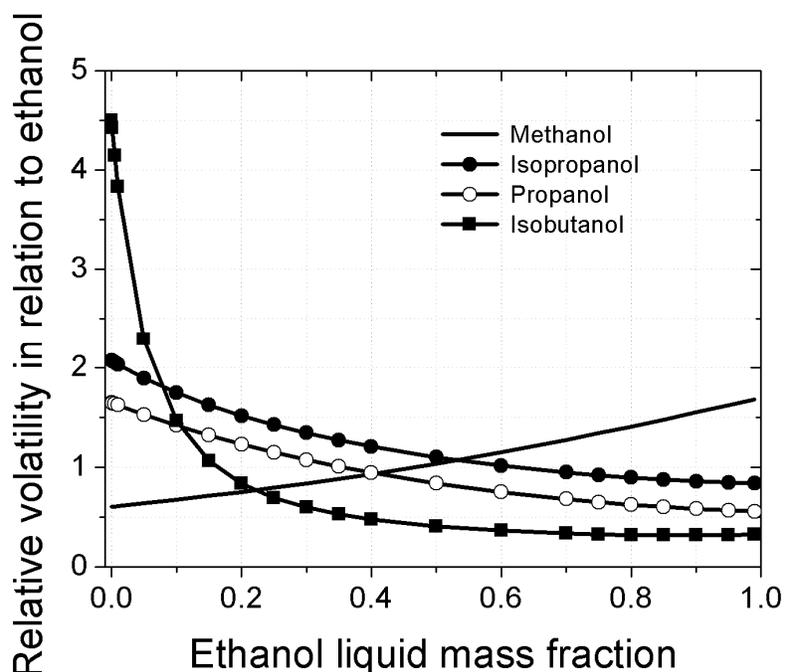


Figure 5.9 - Relative volatility of ethanol in relation to methanol and isopropanol

The behavior described for isopropanol is a consequence of the absence of the hydrosselection and rectifier columns in the new plant. As discussed before, the operating principle of the hydrosselection column is based on the dilution of the hydrated ethanol coming from the section B with posterior reconcentration of this decontaminated alcohol in the rectifier column. Therefore, the activity coefficient of isopropanol increases allowing its extraction from the top of the hydrosselection column. This extraction is highly efficient and can reach, in the Brazilian plant, values higher than 90% of all isopropanol contained in the wine. Thus, although isopropanol has not been detected in any sample of sugar cane industrial wines analyzed in prior works (see Batista et al., 2012), the possibility of working with other raw materials (cellulose hydrolyzed, sweet sorghum, corn, beet, etc.) does not guarantee the absence, or low levels, of isopropanol in every wine, making necessary the search for alternative routes for extracting isopropanol in the new proposed industrial plant. Taking into account higher levels of isopropanol in the wine, a modified version of the new plant was proposed. The main objective of the modifications was to find an alternative way to withdrawn the isopropanol without

diluting the bioethanol with water and, for consequence, maintaining the standard proposed for the new plant (absence of hydroselction and rectifier columns).

After a series of simulation tests and analyses of concentrations profiles, the following alternative configuration was selected for removing isopropanol without using a hydroselction column: a larger part of the phlegm stream was directed to column D and from this column fed into the fuel bioethanol column, so that the amount of fuel bioethanol produced by the entire installation increases at the cost of decreasing the amount of bioethanol produced as neutral alcohol. The vapor stream withdrawn from the top of section A1 and fed in the bottom of column D was increased from 4000 kg/h to 15000 kg/h and the phlegm stream withdrawn from the first tray of section A and pumped to column BB1 was decreased in the same proportion aiming to keep constant the steam consumption in the column AA1D. In consequence of this change, the largest part of isopropanol contamination present in the wine was transferred to column D. A phlegm in vapor phase was withdrawn from the third tray of column D and fed into the fuel bioethanol column. For a correct extraction of isopropanol, the flow rate of this phlegm stream need to be set at least as 70% of the flow rate of the vapor stream fed into the bottom of column D. As this phlegm stream is fed into the fuel bioethanol column, the amount of biofuel produce increases. In the same way used in the prior configuration, the bottom product of the column D was fed into the column BB1 to produce neutral alcohol.

On the other hand, the prior fusel oil stream extracted from section B was, in the new modified configuration, divided in two streams (high fusel oil and low fusel oil) aiming to increase the  $F_{intermediate}$ . The total flow rate of fusel oil was decreased to 200 kg/h, being 40 kg/h as high fusel oil and 160 kg/h as low fusel oil. This modification was necessary to improve the propanol extraction. The composition profile of this component in section B presents a peak concentration in trays next to the other higher alcohols. However, this component has a tail of concentration on trays above the low fusel oil withdrawal that contaminates the hydrated ethanol with propanol residues, contributing to the decrease of the purification factor of the intermediate compounds on neutral alcohol. Thus, a small high fusel oil extraction

(4 trays above the low fusel oil extraction) was necessary to avoid this contamination.

The changes in the amount and the composition of the streams fed into the fuel bioethanol column required an increase in the number of trays, from 20 to 50, and in the steam consumption, from 1.81 to 2.00 kg of vapor per liter of bioethanol, a value still lower than that reported by Batista and Meirelles (2011).

The product distribution in the modified new plant for distilling wine with high contamination of isopropanol was 47.0 % of neutral alcohol, 52.6 % of fuel bioethanol and 0.4 % of fusel, with 0.1 % of total ethanol loss. The flowsheet of the modified new plant and the corresponding specifications are shown in Figure 5.10 and Annex 3, respectively.

Table 5.10 shows the results obtained for the modified new industrial plant fed with an industrial wine according to the composition shown in Table 5.2 under the tag “industrial wine”. It is possible to see that, for the same steam consumption, the total purification factor ( $F_{total}$ ) was higher than the corresponding values for the other industrial plants. In the case of purification factors for the different component classes the values were very similar. However, the concentration of isopropanol in the neutral alcohol presented a value lower than the Brazilian industrial plant, indicating a higher efficiency of this modified new plant since it does not require hydrosselection column, as the Brazilian and Decloux and Coustel plants for neutral alcohol production.

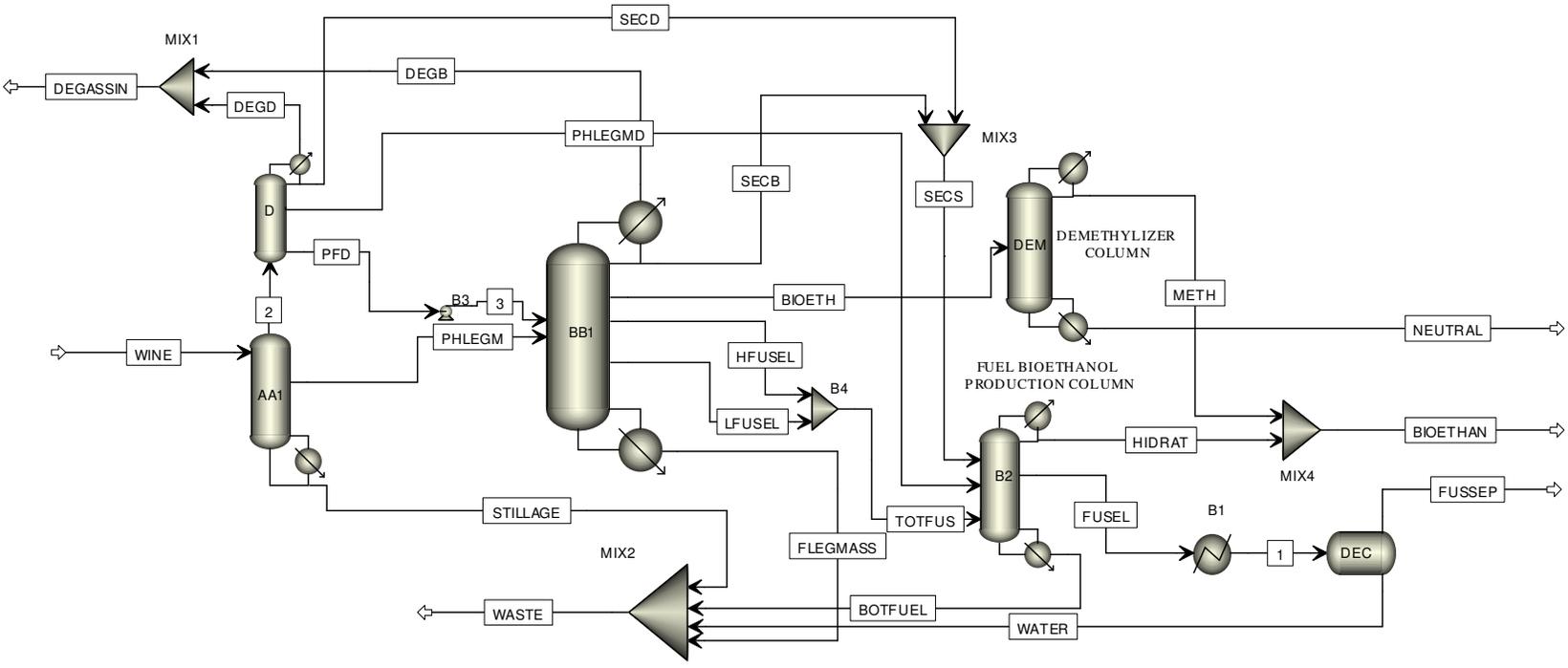


Figure 5.10 - Modified new plant for high isopropanol content in the wine

A final aspect to be considered in developing a new distillation plant for producing ethanol of high purity is its ability to prevent the generation of off-specification products due to changes in the concentration of the contaminants found in the alcoholic wine. The development of the suggested industrial plant (see Figure 5.8) was based on a wine with average composition (see “industrial wine”, Table 5.2). However, variations in wine composition must be considered, especially in sugar mills that use batch fermentation systems. If these wine changes occur mainly in the alcoholic graduation, simple adjustments in operational conditions (reflux ratio, products flow rate) can guarantee products’ specifications. On the other hand, if the concentrations of some congeners are high, the neutral alcohol specifications can be eventually not reached. Taking this into account, a sensitivity test was performed to identify the maximum concentration of selected congeners that does not prevent from reaching the neutral alcohol specifications. The chosen congeners were those directly involved in the neutral alcohol specifications (see Table 5.1). The maximum concentration values are given in Table 5.2 under the headline “Max wine”. Note that “Max wine” corresponds not to a wine composition, but to the maximum admissible concentration of each congener in order to prevent an off-specification product, given the operational and constructive conditions of the industrial plant. Table 5.2 indicates that, with the exception of isopropanol, the concentration of the selected congeners can be increased from a minimum of 5.2 times, in case of methanol, to a maximum of  $10^4$  times, in case of acetone, without compromising the final product purity.

In case of wine with high level of isopropanol the best way is to work with the modified new industrial plant (see Figure 5.10) that, according to the sensitive analysis, can work with wine until  $2.1 \cdot 10^{-5}$  in mass fraction of isopropanol. For concentrations above this level, the modified new industrial plant is able to produce neutral alcohol inside the levels required for isopropanol provided the flow rate of the vapor stream withdrawn from the top of column A1 and fed in the bottom of column D is increased, together with the increase of the extraction of the second phlegm stream in column D. As a consequence, the percentage of the products will be altered, further reducing the amount of neutral alcohol produced.

Especially in relation to methanol, the maximum value shown in Table 5.2 considered that there would be no change in the operational conditions in the new plant. Nevertheless, this maximum value could be much higher if the reflux ratio and, consequently, the steam consumption in the demethylizer column can be increased.

#### **5.4 - Conclusions**

In this work, the process for the production of neutral alcohol was investigated by computer simulation using Aspen Plus. Two typical industrial plants, the Brazilian distillation unit and the unit reported by Decloux and Coustel (2005), were simulated and the results showed a superior performance of the Brazilian plant, mainly due to lower steam consumption, lower total number of trays and highest purification factors, this latter result being directly related to the better quality of the neutral alcohol produced. However, the high steam consumption of both plants, which is caused mainly by the dilution and redistilling of fuel bioethanol, motivated the development of a new plant able to concentrate and purify the alcoholic wine according to the strictest requirements specified for neutral alcohol. A careful study of the profiles of minor components observed in the Brazilian plants indicated that changes in operational and constructive variables of the fuel ethanol distillation units could allow the production of neutral alcohol without the dilution and redistilling steps. The required changes in constructive and operational conditions were investigated using factorial design techniques and the obtained results indicate that the new plant decreases the steam consumption in approximately 40% and the total number of trays in approximately 48% in comparison with the corresponding values required by the existing plants for neutral alcohol production. The byproducts of the new distillation unit were used for producing fuel ethanol, improving its economic performance and total recovery of bioethanol. Although the new installation produces bioethanol with purification factors lower than those obtained in the traditional industrial units, it still produces neutral alcohol according to the strictest specifications and has the advantages of consuming less steam and of requiring a lower number of columns. Some changes

in the operational conditions of the new industrial plant have improved the purification factors. However, the purification factor for the intermediate volatility components was still relatively low, mainly due to difficulty of eliminating contamination with isopropanol. A modified version of the new industrial plant with higher purification factors was developed. This unity can produce a lower amount of neutral alcohol with a very high purification factor, but it still keeps the lower number of columns and the same steam consumption. In this way, it decreases the operational and investment costs related to this alcoholic product of high purity, a product that will, probably, play a very important role among the goods produced by the future biorefineries.

### **Acknowledgments**

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## Annex 1

### Columns specifications for the previous new industrial plant

	<b>Column D</b>	<b>Column AA1</b>	<b>Column BB1</b>
<b>Column</b>	<ul style="list-style-type: none"> <li>• Partial condenser</li> <li>• 6 trays (0.7 Murphree efficiency, 1.6 meter of diameter)</li> <li>• Ptop = 1 atm</li> <li>• Condenser pressure drop = 0.15 atm</li> <li>• Stage pressure drop = 70 mm-water</li> </ul>	<ul style="list-style-type: none"> <li>• No condenser</li> <li>• 22 trays (0.7 Murphree efficiency)</li> <li>• 2.0 meter of diameter – tray 1 to 8.</li> <li>• 2.5 meter of diameter – tray 9 to 22.</li> <li>• Ptop = 1.22 atm</li> <li>• Stage pressure drop = 60 mm-water</li> </ul>	<ul style="list-style-type: none"> <li>• Partial condenser</li> <li>• 102 trays (0.7 Murphree efficiency and 2.6 meters of diameter)</li> <li>• 83 trays above the feed (section B) and 18 trays under feed (section B1)</li> <li>• Ptop = 1 atm</li> <li>• Condenser pressure drop = 0.15 atm</li> <li>• Stage pressure drop = 50 mm-water</li> </ul>
<b>In</b>	<ul style="list-style-type: none"> <li>• Vapor from column AA1 at bottom.</li> </ul>	<ul style="list-style-type: none"> <li>• Wine</li> </ul>	<ul style="list-style-type: none"> <li>• PFD at tray 83</li> <li>• Phlegm at tray 83</li> </ul>
<b>Out</b>	<ul style="list-style-type: none"> <li>• Distillate (second alcohol stream)</li> <li>• Degassing stream from partial condenser</li> <li>• Bottom product (PFD)</li> </ul>	<ul style="list-style-type: none"> <li>• Vapor from top to column D (stream 2)</li> <li>• Vapor phlegm at tray 9</li> <li>• Stillage from bottom</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate (second alcohol stream)</li> <li>• Degassing stream from partial condenser</li> <li>• Neutral alcohol from tray 41</li> <li>• Fusel oil from tray 80</li> <li>• Flegmass from bottom</li> </ul>
<b>Simulation Parameters</b>	<ul style="list-style-type: none"> <li>• Distillate = 300 kg/h</li> <li>• Degassing stream = 0.8 % of distillate</li> <li>• Mass reflux ratio = 30</li> </ul>	<ul style="list-style-type: none"> <li>• Stream 2 = 4000 kg/h</li> <li>• Phlegm = 32137 kg/h</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate = 1500 kg/h</li> <li>• Degassing stream = 0.8% of distillate</li> <li>• Mass reflux ratio = 600</li> <li>• Drawn at tray 41 = 12278 kg/h</li> <li>• Drawn at tray 80 = 800 kg/h</li> </ul>
<b>Specifications</b>	None	Ethanol loss in stillage < 200 ppm in mass fraction	Ethanol loss in Flegmass < 200 ppm in mass fraction

## Annex 2

### Columns specifications for the final new industrial plant

	Column BB1	Demethylizer column	Fuel bioethanol column
<b>Column</b>	<ul style="list-style-type: none"> <li>• Partial condenser</li> <li>• 77 trays (0.7 Murphree efficiency and 2.6 meters of diameter)</li> <li>• 58 trays above the feed (section B) and 18 trays under feed (section B1)</li> <li>• Ptop = 1 atm</li> <li>• Condenser pressure drop = 0.15 atm</li> <li>• Stage pressure drop = 50 mm-water</li> </ul>	<ul style="list-style-type: none"> <li>• Total condenser</li> <li>• 29 trays – 14 above and under feed.</li> <li>• Ptop = 1 atm</li> <li>• Condenser pressure drop = 0.15 atm</li> <li>• Stage pressure drop = 50 mm-water</li> </ul>	<ul style="list-style-type: none"> <li>• Total condenser</li> <li>• 18 trays</li> <li>• Ptop = 1 atm</li> <li>• Condenser pressure drop = 0.15 atm</li> <li>• Stage pressure drop = 60 mm-water</li> </ul>
<b>In</b>	<ul style="list-style-type: none"> <li>• PFD at tray 58</li> <li>• Phlegm at tray 58</li> </ul>	<ul style="list-style-type: none"> <li>• Bioethanol stream from column BB1</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate of column D in tray 1</li> <li>• Distillate of column BB1 in tray 1</li> <li>• Fusel oil stream from column BB1 in tray 9</li> </ul>
<b>Out</b>	<ul style="list-style-type: none"> <li>• Distillate (second alcohol stream)</li> <li>• Degassing stream from partial condenser</li> <li>• Bioethanol from tray 16</li> <li>• Fusel oil from tray 55</li> <li>• Flegmass from bottom</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate</li> <li>• Neutral alcohol from bottom</li> </ul>	<ul style="list-style-type: none"> <li>• Fuel hydrated bioethanol as a distillate</li> <li>• Fusel oil as bottom product</li> </ul>
<b>Simulation Parameters</b>	<ul style="list-style-type: none"> <li>• Distillate = 500 kg/h</li> <li>• Degassing stream = 0.8% of distillate</li> <li>• Mass reflux ratio = 200</li> <li>• Drawn at tray 16 = 12977 kg/h</li> <li>• Drawn at tray 55 = 800 kg/h</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate = 40 kg/h</li> <li>• Mass reflux ratio = 600</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate = 1200 kg/h</li> <li>• Mass reflux ratio = 8</li> </ul>
<b>Specifications</b>	Ethanol loss in Flegmass < 200 ppm in mass fraction	<ul style="list-style-type: none"> <li>• Ethanol in distillate &lt; 1% of total ethanol fed into the column</li> <li>• Steam consumption less or equal than 1 kg of steam per liter of ethanol fed into the column</li> </ul>	

- Column D and AA1 has the same specification presented in Annex 1.

## Annex 3

### Columns specifications for the modified new industrial plant

	Column AA1	Column D	Column BB1
<b>Column</b>	<ul style="list-style-type: none"> <li>• No condenser</li> <li>• 22 trays (0.7 Murphree efficiency and 2 meters of diameter – tray 1 to 8 – and 2.5 meters – tray 9 to 22)</li> <li>• P<sub>top</sub> = 1.22 atm</li> <li>• Stage pressure drop = 60 mm-water</li> </ul>	<ul style="list-style-type: none"> <li>• Partial condenser</li> <li>• 7 trays.</li> <li>• P<sub>top</sub> = 1 atm</li> <li>• Condenser pressure drop = 0.15 atm</li> <li>• Stage pressure drop = 70 mm-water</li> </ul>	<ul style="list-style-type: none"> <li>• Partial condenser</li> <li>• 77 trays (0.7 Murphree efficiency and 2.6 meters of diameter)</li> <li>• 58 trays above the feed (section B) and 18 trays under feed (section B1)</li> <li>• P<sub>top</sub> = 1 atm</li> <li>• Condenser pressure drop = 0.15 atm</li> <li>• Stage pressure drop = 50 mm-water</li> </ul>
<b>In</b>	<ul style="list-style-type: none"> <li>• Wine at tray 1</li> </ul>	<ul style="list-style-type: none"> <li>• Top product of column AA1.</li> </ul>	<ul style="list-style-type: none"> <li>• PFD at tray 58</li> <li>• Phlegm at tray 58</li> </ul>
<b>Out</b>	<ul style="list-style-type: none"> <li>• Top product.</li> <li>• Phlegm stream at tray 9.</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate (second alcohol)</li> <li>• Degassing stream at condenser.</li> <li>• Second phlegm stream at tray 3.</li> <li>• Bottom product</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate (second alcohol stream)</li> <li>• Degassing stream from partial condenser</li> <li>• Bioethanol from tray 16</li> <li>• Higher Fusel oil from tray 53.</li> <li>• Lower Fusel oil from tray 55.</li> <li>• Flegmass from bottom</li> </ul>
<b>Simulation Parameters</b>	<ul style="list-style-type: none"> <li>• Top product (vapor) = 15000 kg/h.</li> <li>• Phelgm = 19137 kg/h.</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate = 250 kg/h</li> <li>• Mass reflux ratio = 30</li> <li>• Degassing stream = 0.8 % of distillate</li> <li>• Second phlegm stream = 9000 kg/h (vapor stream)</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate = 400 kg/h</li> <li>• Degassing stream = 0.8% of distillate</li> <li>• Mass reflux ratio = 200</li> <li>• Bioethanol at tray 16 = 6977 kg/h</li> <li>• Higher fusel oil = 40 kg/h</li> <li>• Lower fusel oil = 150 kg/h</li> </ul>
<b>Specifications</b>	Ethanol loss in Stillage < 200 ppm in mass fraction	<ul style="list-style-type: none"> <li>• Higher than 90% of the mass of isopropanol present in the wine need to be in second phlegm stream.</li> </ul>	Ethanol loss in Flegmass < 200 ppm in mass fraction

	<b>Demethylizer column</b>	<b>Fuel bioethanol column</b>
<b>Column</b>	<ul style="list-style-type: none"> <li>• Total condenser</li> <li>• 29 trays – 14 above and under feed.</li> <li>• Ptop = 1 atm</li> <li>• Condenser pressure drop = 0.15 atm</li> <li>• Stage pressure drop = 50 mm-water</li> </ul>	<ul style="list-style-type: none"> <li>• Total condenser</li> <li>• 48 trays (34 trays above and 13 below the feed)</li> <li>• Ptop = 1 atm</li> <li>• Condenser pressure drop = 0.15 atm</li> <li>• Stage pressure drop = 60 mm-water</li> </ul>
<b>In</b>	<ul style="list-style-type: none"> <li>• Bioethanol stream from column BB1.</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate of column D in tray 35</li> <li>• Distillate of column BB1 in tray 35</li> <li>• Higher Fusel oil stream from column BB1 in tray 35.</li> <li>• Lower fusel oil stream from column BB1 in tray 35.</li> <li>• Second Phlegm stream from column D at tray 35.</li> </ul>
<b>Out</b>	<ul style="list-style-type: none"> <li>• Distillate</li> <li>• Neutral alcohol from bottom</li> </ul>	<ul style="list-style-type: none"> <li>• Fuel hydrated bioethanol as a distillate</li> <li>• Fusel oil at tray 47.</li> <li>• Bottom product.</li> </ul>
<b>Simulation Parameters</b>	<ul style="list-style-type: none"> <li>• Distillate = 210 kg/h</li> <li>• Mass reflux ratio = 320</li> </ul>	<ul style="list-style-type: none"> <li>• Distillate = 7300 kg/h</li> <li>• Mass reflux ratio = 2.5.</li> <li>• Fusel oil = 200 kg/h.</li> </ul>
<b>Specifications</b>		<ul style="list-style-type: none"> <li>• Ethanol loss in bottom product &lt; 200 ppm in mass fraction</li> </ul>

- The fusel oil withdrawn in fuel bioethanol column is fed in a liquid-liquid decanter to separate the organic phase from the aqueous phase. The organic phase is storage in fusel oil vat and the aqueous phase is discarded as waste.

## Capítulo 6

### 6.1 – Conclusões Gerais

A grande experiência nacional na produção de etanol combustível sugeriria um processo produtivo plenamente consolidado sem grandes lacunas para sua melhoria ou desenvolvimento de novos processos. No entanto esse presente trabalho deixou evidente que, principalmente em termos de bioetanol de qualidade superior, ainda existe espaço para muita discussão científica. Através do uso de ferramentas de simulação computacional foi possível reproduzir um sistema industrial típico de produção de bioetanol combustível considerando etanol, água e 17 outros componentes minoritários. Um cuidadoso estudo do equilíbrio de fase dos diversos binários formados com os componentes considerados foi realizado. O objetivo desse estudo foi à melhoria da predição do equilíbrio pelo simulador Aspen Plus e o estudo do comportamento dos componentes em soluções com diferentes teores de etanol, através da análise de suas volatilidades, permitindo assim inferir sobre os locais de concentração desses componentes ao longo das colunas e então determinar pontos de retirada dos contaminantes do bioetanol a ser produzido. Amostras industriais foram coletadas em uma planta industrial típica brasileira para a produção de bioetanol hidratado combustível sendo posteriormente analisadas por cromatografia gasosa permitindo a quantificação desses componentes nas diferentes correntes e bandejas das colunas de destilação, possibilitando a determinação de um perfil real de concentração, posteriormente utilizado para a validação do simulador Aspen Plus. Uma tentativa de otimização do processo foi realizada levando-se em conta 11 variáveis independentes e 4 dependentes. Com o simulador Aspen Dynamics foi possível estudar sistemas de controle típicos aplicados pelas usinas no controle de qualidade do bioetanol combustível produzido, apresentando as principais vantagens e desvantagens de cada um. Finalmente, após um cuidadoso estudo de perfis de concentração e do processo como um todo, uma nova planta

industrial, capaz de produzir álcool neutro e álcool hidratado combustível num único processo, foi proposta.

Os resultados apresentados no Capítulo 2 permitiram concluir que as diversas classes de compostos presentes no vinho apresentam comportamento extremamente distintos entre si, quando da análise de suas volatilidades, possibilitando sua classificação em três grandes grupos: *compostos leves*, que apresentam volatilidades sempre maiores do que o etanol e a água sendo facilmente eliminados pelo topo das colunas de destilação; *compostos pesados*, de comportamento contrário aos compostos leves, são sempre menos voláteis do que a água e o etanol sendo facilmente eliminados do processo pelo produto de fundo das colunas; *compostos de volatilidade intermediária*, que apresentam inversão de volatilidade dependendo do teor de etanol da mistura, ora sendo mais voláteis do que o etanol (soluções diluídas), ora tendo volatilidade intermediária entre o etanol e a água e ora sendo menos voláteis do que a água (soluções concentradas). Esses compostos tendem a se concentrar em regiões intermediárias das colunas sendo retirados por processo por extrações laterais nas colunas de destilação.

Essa classificação dos compostos foi determinante para uma tentativa de otimização de uma planta industrial típica para produção de etanol hidratado combustível, apresentada no Capítulo 4. Os resultados mostraram que em termos das variáveis dependentes consideradas, ou seja, graduação alcoólica do etanol combustível, recuperação de etanol como produto principal, consumo de vapor e perda de etanol pela vinhaça e flegmaça, o sistema já está muito próximo do seu ponto ótimo de trabalho, uma vez que o resultado da otimização apresentou as variáveis independentes idênticas, ou muito próximas, do ponto central cujos valores foram fixados de acordo com informações industriais. Essa eficiência industrial na produção de álcool hidratado deve-se basicamente a longa experiência adquirida pelo Brasil na produção deste biocombustível. No entanto, quando o assunto são alcoóis especiais, os resultados apresentados no Capítulo 5 evidenciam que as plantas industriais utilizadas hoje em dia estão muito longe de seu ponto ótimo de trabalho.

A diferença básica dos alcoóis especiais para o álcool combustível esta na concentração máxima admitida de contaminantes que, por consequência, determinam uma aplicação mais fina para esses alcoóis especiais. Um estudo criterioso dos perfis reais de concentração (Capítulo 4 e 5) indicou possibilidades de modificação no processo produtivo tradicional de bioetanol combustível visando à produção de alcoóis de qualidade superior, especialmente o álcool neutro. Tradicionalmente a produção desse álcool é baseada na purificação do álcool hidratado combustível em três colunas (coluna de hidrosseleção, retificação e demetilação), no caso brasileiro, e em cinco colunas no caso francês, perfazendo um total de, no mínimo, 170 bandejas a mais, do que aquelas necessárias para a produção de álcool combustível, para se obter o álcool neutro, com um consumo de, no mínimo, aproximadamente 5,3 kg de vapor por litro de álcool neutro produzido. Assim, toda discussão em torno do estudo das plantas brasileira e francesa para a produção de álcool neutro apresentada no Capítulo 5, permitiu concluir que modificações no número de bandejas da seção B do sistema tradicional de produção de álcool hidratado e o acréscimo de uma coluna demetiladora de menor tamanho (30 bandejas contra 50 bandejas nas plantas brasileira e francesa) tornaram possível a produção de álcool neutro utilizando-se apenas 45 bandejas a mais do que o necessário para se produzir álcool hidratado (economia de 73% com relação a planta brasileira de produção de álcool neutro), com um consumo de 3,31 kg de vapor por litro de álcool neutro, 37% menor do que o consumo na planta tradicional. Uma segunda coluna adicional foi acrescentada ao processo contendo 20 bandejas para a produção de álcool hidratado combustível como subproduto da produção de álcool neutro, consumindo 1,81 kg de vapor por litro de álcool hidratado produzido, 15% menor do que na planta tradicional para produção de álcool hidratado. No entanto, as análises dos fatores de purificação apontaram grandes diferenças entre a nova planta industrial e planta tradicional brasileira para produção de álcool neutro, com ampla vantagem para a planta brasileira. Essas diferenças se deveram basicamente a dificuldade da nova planta em separar o isopropanol do etanol fazendo com que o fator de purificação dos compostos intermediários ficasse

extremamente baixo contribuindo para uma redução no fator de purificação global. Como solução para o caso optou-se pelo aumento da vazão da corrente de vapor do topo da coluna A1, que é alimentada à base da coluna D, com redução da vazão de Flegma na mesma proporção. Assim, a grande maioria do isopropanol é transferido para a coluna D sendo retirada por uma segunda corrente de flegma em fase vapor na coluna D. Essa corrente foi então alimentada diretamente a coluna adicional para produção de álcool hidratado. Como consequência dessa modificação, o consumo de vapor para a produção de álcool neutro foi elevado para 5,3 kg por litro de álcool neutro, valor idêntico ao consumo na planta tradicional brasileira. Da mesma forma, a coluna adicional para produção de álcool hidratado teve seu número de bandejas elevado de 20 para 50 e seu consumo de vapor elevado para 2 kg de vapor por litro de álcool hidratado. Outra consequência importante foi a modificação na proporção dos produtos produzidos pela nova planta industrial, decorrente da diminuição da vazão da corrente de Flegma da coluna A. Na primeira versão da nova planta, a produção estava distribuída em 91,0 % de álcool neutro, 8,6 % de álcool hidratado e 0,4% de óleo fúsel. Com as modificações para melhorar a separação do isopropanol, os produtos ficaram distribuídos em 52% de álcool hidratado, 47,6% de álcool neutro e 0,4% de óleo fúsel.

Ainda que essas alterações tenham provocado aumento no consumo de vapor para a produção de álcool neutro e álcool hidratado, o aumento no fator de purificação, tornando-se maior do que na planta brasileira e francesa, e a ausência das colunas de hidrosseleção e retificação garante uma substancial vantagem da nova planta industrial para produção de álcool neutro com relação à planta tradicional brasileira. Outra vantagem da nova planta industrial proposta está na possibilidade de se produzir conjuntamente álcool neutro e álcool hidratado combustível, aumentando o valor econômico da nova planta industrial além de praticamente reduzir as perdas de etanol a valores muito mais baixos do que as plantas tradicionais. Assim, esta tese cumpriu seus objetivos iniciais apresentando uma nova planta industrial para a produção de álcool neutro com menor custo e maior valor econômico agregado, tendo como possibilidade, através do acréscimo

de algumas retiradas laterais na coluna demetiladora, a produção de alcoóis de padrão de qualidade intermediários entre o álcool hidratado combustível e o álcool neutro (álcool H1 e H2).

## **6.2 – Sugestões de trabalhos futuros**

Ainda que o processo produtivo para a produção de álcool já tenha sido amplamente explorado é possível apresentar sugestões para trabalhos futuros, principalmente baseados nos novos conceitos de produção surgidos atualmente, como os indicados a seguir.

- Estudo dinâmico da nova planta industrial com conseqüente desenvolvimento de malhas de controle e estudo da estabilidade do sistema.
- Estudo da robustez da nova planta industrial no que se refere à produção de bioetanol de segunda geração.
- Inclusão de novos componentes ao sistema, principalmente sólidos solúveis e insolúveis, açúcares e gases responsáveis pela acidez volátil, e verificação da influência dos mesmos sobre o processo produtivo.
- Estudo experimental do sistema através da construção de um modelo reduzido em escala laboratorial.