



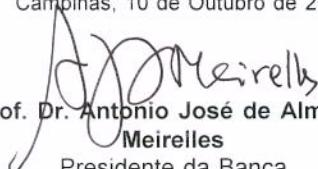
UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ENGENHARIA DE ALIMENTOS
DEPARTAMENTO DE ENGENHARIA DE ALIMENTOS

**DESACIDIFICAÇÃO DE ÓLEOS VEGETAIS POR EXTRAÇÃO LÍQUIDO-
LÍQUIDO: EQUILÍBRIO DE FASES E SIMULAÇÃO DO PROCESSO**

PARECER

Este exemplar corresponde à redação final da tese defendida por **Eduardo Augusto Caldas Batista**, aprovada pela Comissão Julgadora em 10 de outubro de 2002.

Campinas, 10 de Outubro de 2002.


Prof. Dr. Antonio José de Almeida
Meirelles
Presidente da Banca

Eduardo Augusto Caldas Batista

Engenheiro de Alimentos

Mestre em Engenharia de Alimentos

Prof. Dr. Antonio José de Almeida Meirelles

Orientador

Profa. Dra. Maria Regina Wolf Maciel

Co-orientador

Tese apresentada à Faculdade de Engenharia de Alimentos da Universidade Estadual de Campinas para obtenção do título de Doutor em Engenharia de Alimentos.

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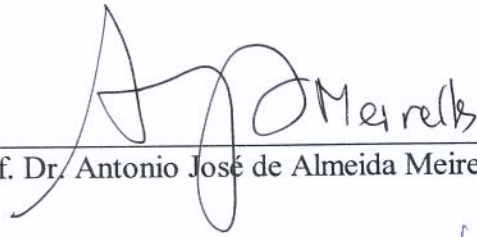
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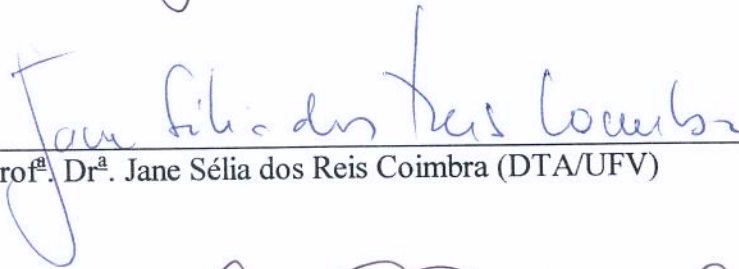
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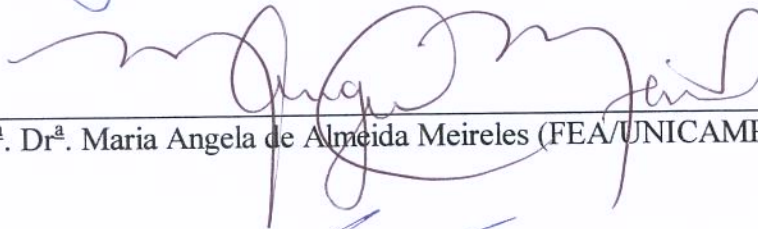
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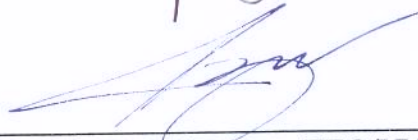
Prof. Dr. Antonio José de Almeida Meirelles (FEA/UNICAMP)



Prof.ª Dr.ª Jane Sélia dos Reis Coimbra (DTA/UFV)



Prof.ª Dr.ª Maria Angela de Almeida Meireles (FEA/UNICAMP)



Prof. Dr. Martin Aznar (FEQ/UNICAMP)

Dr.ª Rosemar Antoniassi (CTAA/EMBRAPA)



Prof. Dr. Fernando Antonio Cabral (FEA/UNICAMP)

Prof.ª Dr.ª Maria Alvina Krahenbühl (FEQ/UNICAMP)

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RESUMO

Óleos vegetais podem ser desacidificados através de processos convencionais como refino químico e físico. O refino químico, aplicado à maioria das matérias-primas, pode causar grandes perdas de óleos neutros. Para óleos de alta acidez, o refino físico também é possível, mas pode provocar alterações indesejáveis na cor e redução da estabilidade oxidativa. Uma alternativa é a desacidificação por extração líquido-líquido, processo conduzido à temperatura ambiente e pressão atmosférica. O conhecimento do equilíbrio de fases de sistemas óleos vegetais, ácidos graxos, solventes é importante para o projeto de equipamentos adequados à implementação da extração líquido-líquido. No presente trabalho, os modelos NRTL e UNIQUAC foram ajustados a dados experimentais dos sistemas óleo de canola, ácido oléico, álcoois de cadeia curta. Alguns dos parâmetros de interação binária dos modelos de contribuição de grupos UNIFAC e ASOG também foram ajustados a dados experimentais ternários, permitindo a predição do equilíbrio de fases de sistemas multicomponentes com sucesso. A transferência de diglicerídeos e a perda de óleo neutro para a fase extrato foram calculadas e apresentaram pequenos desvios quando comparadas a dados experimentais. O algoritmo desenvolvido por Naphtali e Sandholm foi adaptado para a simulação de colunas de extração líquido-líquido. Os resultados indicaram as melhores condições para a desacidificação de óleos vegetais por extração líquido-líquido. A relação solvente/óleo bruto, número de estágios, porcentagem de água no etanol puderam ser selecionados para garantir uma redução de ácidos graxos livres com um mínimo de perda de óleo neutro. Planejamento fatorial e análise de superfície de resposta foram utilizados como potente ferramenta na otimização do processo de desacidificação por extração líquido-líquido.

SUMMARY

Vegetable oils can be deacidified by conventional process such as alkaline and physical refining. Alkaline refining is applicable for all raw materials, however, it can result in great losses of neutral oil. For high acidity oils, physical refining is also a possibility, but can cause undesirable alterations in color and reduction of stability to oxidation. Another possibility is the deacidification through liquid-liquid extraction, process carried out at room temperature and atmospheric pressure. A knowledge of the liquid-liquid equilibrium of vegetable oils, fatty acids and solvents is important for the design of adequate equipments for the implementation of the liquid-liquid extraction. In the present work, NRTL and UNIQUAC models were adjusted to experimental data for systems of canola oil, oleic acid and short chain alcohols. Some UNIFAC and ASOG group interaction parameters were also adjusted to ternary experimental data and these parameters allowed a quite successful prediction of liquid-liquid equilibrium for multicomponent systems. The diglyceride transfer and loss of triglycerides to the extract phase were calculated and presented a good agreement with the experimental data. The algorithm developed by Naphtali and Sandholm was adapted to liquid-liquid extraction. The results obtained indicate the best conditions for deacidification by solvent extraction. The solvent to crude oil ratio, the number of stages and the water percent in ethanol could be selected to reach the free fatty acids content lower than 0.3 % in the refined oil with minimum losses of neutral oil. Factorial design and surface analysis response were used as a powerful tool in the optimization of the liquid-liquid extraction.

INTRODUÇÃO

Óleos vegetais brutos contêm impurezas prejudiciais à sua qualidade e estabilidade oxidativa que devem ser eliminadas durante o seu processamento. Tradicionalmente, tais impurezas são removidas por refino químico e físico.

O refino químico, por ser um processo bastante conhecido, versátil e aplicado a qualquer matéria-prima, é o mais usado, mas também ocasiona grandes perdas de óleo neutro na centrifugação para óleos de alta acidez. O refino físico é um processo aplicado, principalmente, a óleos de alta acidez e pode causar alterações indesejáveis na cor e redução da estabilidade oxidativa.

Um processo alternativo seria a desacidificação de óleos vegetais por extração líquido-líquido. É um processo conduzido à temperatura ambiente e pressão atmosférica e baseia-se na diferença de solubilidade de ácidos graxos livres e triglicerídeos no solvente.

Com o avanço computacional, tornou-se viável o estudo de processos pouco conhecidos por simulação. Para a simulação de colunas de extração líquido-líquido, o conhecimento do equilíbrio de fases ou a disponibilidade de dados experimentais de equilíbrio líquido-líquido para os sistemas de interesse é fundamental. A literatura apresenta modelos semi-empíricos descritivos, como NRTL e UNIQUAC, que possuem parâmetros ajustáveis a dados experimentais. Outra alternativa é a predição do equilíbrio de fases através de métodos de contribuição de grupos (UNIFAC e ASOG), mas sua capacidade preditiva do equilíbrio de fases para os sistemas estudados deve ser investigada.

Outro problema em estudos por simulação é o grande número de variáveis e o efeito destas variáveis na resposta que, muitas vezes, torna trabalhosa a análise, conclusões e obtenção de regiões ótimas operacionais. Uma técnica muito utilizada na otimização de experimentos e que pode ser utilizada como ferramenta em estudos por simulação é o planejamento fatorial e a análise de superfície de resposta. Esta técnica reduz o número de simulações, garante a possibilidade de obter informações dos efeitos das variáveis sobre a resposta e gera modelos que podem ser analisados por superfície de resposta.

O trabalho apresentado a seguir reúne artigos escritos e submetidos a revistas científicas e congressos durante o desenvolvimento desta pesquisa. Os assuntos abordados em cada capítulo estão resumidos a seguir:

Capítulo 1: Revisão Bibliográfica

Capítulo 2: Aplicação de planejamento fatorial e análise de superfície de resposta na simulação de um processo conhecido, com o intuito de testar a eficiência desta técnica a estudos de otimização de processos por simulação.

Capítulo 3: Modelagem do equilíbrio líquido-líquido para sistemas óleo de canola, ácidos oléico, álcoois de cadeia curta. Os parâmetros binários dos modelos NRTL e UNIQUAC foram ajustados aos dados experimentais para a descrição do equilíbrio de fases destes sistemas.

Capítulo 4: Predição do equilíbrio líquido-líquido para sistemas óleos vegetais, ácidos graxos, etanol. Os parâmetros de interação binária dos modelos de contribuição de grupos UNIFAC e ASOG foram ajustados a dados ternários e posteriormente testados na capacidade preditiva do equilíbrio líquido-líquido de sistemas óleo, ácidos graxos, etanol.

Capítulo 5: Simulação da desacidificação do óleo de canola usando extração líquido-líquido. Foi aplicada a técnica de planejamento experimental e análise de superfície de resposta na busca de condições ótimas do processo.

Capítulo 6: Predição do equilíbrio líquido-líquido para sistemas de óleo de milho, diglicerídeos, ácidos graxos e etanol. Os parâmetros de interação binária do modelo de contribuição de grupos UNIFAC foram testados na capacidade preditiva do equilíbrio líquido-líquido de sistemas óleo de milho, diglicerídeos, ácidos graxos, etanol. A transferência de diglicerídeos do óleo bruto e a perda de triglicerídeos para a fase alcoólica foram preditas e comparadas a dados experimentais também.

Capítulo 7: Simulação da desacidificação do óleo de milho por extração líquido-líquido. Neste caso, considerou-se a presença de diglicerídeos na alimentação do extrator e testou-se a adição de água ao solvente com o objetivo de aumentar a sua seletividade.

OBJETIVOS

1. Testar a eficiência do planejamento fatorial e análise de superfície de resposta na otimização de processos estudados por simulação;
2. Modelar os dados de equilíbrio de fases óleo de canola/ácido oléico/ álcoois de cadeia curta utilizando os modelos NRTL e UNIQUAC;
3. Analisar a capacidade preditiva dos modelos de contribuição de grupos UNIFAC e ASOG no equilíbrio líquido-líquido de sistemas óleo vegetal/ácidos graxos/etanol. Caso seja necessário, reajustar parâmetros de interação de grupos.
4. Desenvolver um programa computacional que permita a simulação de colunas de extração líquido-líquido e analisar as condições operacionais do processo.

JUSTIFICATIVA

A extração líquido-líquido apresenta-se como uma alternativa promissora na desacidificação de óleos vegetais. É um processo conduzido à temperatura ambiente e pressão atmosférica e portanto oferece condições mais brandas que o refino físico, onde temperaturas elevadas e pressões abaixo da atmosférica são necessárias para garantir a volatilidade dos ácidos graxos livres. Em relação ao refino químico, pode apresentar menor perda de óleo neutro, quando da escolha correta do solvente, que permitiria uma diminuição da solubilidade de óleo no solvente sem comprometer a extração dos ácidos graxos livres. A escolha da relação solvente/óleo bruto alimentado, número de estágios, remoção de diglicerídeos são algumas investigações necessárias para a análise, viabilidade e conclusão de que a extração líquido-líquido pode ser conduzida com sucesso.

CAPÍTULO 1

REVISÃO BIBLIOGRÁFICA

1.1. Desacidificação de óleos vegetais

Óleos vegetais brutos contêm impurezas como ácidos graxos livres, fosfatídios, glicerídeos parciais, pigmentos, ceras, metais, micotoxinas, pesticidas que são prejudiciais para a qualidade e estabilidade oxidativa.

A maioria dos óleos comestíveis é desacidificada por refino alcalino, por se tratar de um processo bastante conhecido, versátil e que pode ser aplicado a qualquer matéria-prima. Entretanto, pode causar grandes perdas de óleo neutro. Leibovitz & Ruckenstein (1983) apresentaram perdas de óleo neutro na faixa de (15 a 25) % para a neutralização de óleo de milho bruto contendo de (8 a 14) % de ácidos graxos livres. Na indústria brasileira, estas perdas são ainda maiores, para óleo de milho bruto contendo acidez em torno de 4% e portanto menor que o reportado por Leibovitz & Rubenstein (1983), a perda de óleo neutro chega a 14 % na centrifugação, sendo que o óleo de milho bruto produzido no Brasil pode conter até 9 % de ácidos graxos livres.

O refino físico é uma alternativa ao processo de refino químico e é aplicado principalmente para óleos de alta acidez, resultando em menores perdas de óleo neutro, mas por outro lado com maior consumo de energia. Este processo é conduzido a temperaturas de (240 a 270) °C e pressões de (2 a 4) mmHg para se alcançar a mínima concentração de ácidos graxos livres. Entretanto este processo também tem suas desvantagens, já que não pode ser aplicado a qualquer matéria-prima e pode causar alterações indesejáveis na cor e redução da estabilidade oxidativa do óleo.

A remoção de diglicerídeos foi comparada por Pérez-Camino *et al.* (1993), no refino químico e físico de óleo de oliva com 6,4 % e 1,1 % de ácidos graxos livres. No refino químico ocorreu remoção de (18 a 29) % do conteúdo inicial de diglicerídeos, contra valores de (7 a 9) % no refino físico.

Uma outra alternativa possível seria a desacidificação de óleos vegetais por extração líquido-líquido. Este processo é efetuado à temperatura ambiente e pressão atmosférica, portanto sob condições muito menos drásticas que as necessárias no refino físico

A extração líquido-líquido pode ser utilizada na separação de compostos com pequena diferença em seus pontos de ebulição, de compostos termolábeis, de compostos com alto ponto de ebulição, de produtos que formem azeótropo, na recuperação de compostos de soluções diluídas, na recuperação de vitaminas, na separação de cafeína, penicilina, aromas e fragrâncias, na lavagem de lecitina, no fracionamento de óleos com solventes e na remoção de glicerol da borra de neutralização com salmoura, na deterpenação do óleo essencial de laranja e quando a separação por destilação requer grande consumo de energia (Treybal, 1981; Hamm, 1992; Trujillo-Quijano, 1994; Haypek *et al*, 2000).

Segundo Thomopoulos (1971), a desacidificação usando solvente é baseada na diferença de solubilidade dos ácidos graxos livres e triglicerídeos no solvente e na volatilidade relativa do solvente em relação aos ácidos graxos. A desacidificação de óleos vegetais pode ser realizada com diversos solventes seletivos como furfural, acetato de etila, propanol, isopropanol, butanol, etanol, metanol, etil-metil cetona. Entretanto os melhores resultados foram obtidos com etanol 96 °GL.

Uma desacidificação por extração líquido-líquido considerada eficaz seria aquela que conseguisse reduzir a quantidade de ácidos graxos livres abaixo de 0,3 %, que é a concentração máxima de ácidos graxos livres permitida pelo Codex Alimentarius (1993), ao mesmo tempo que reduzisse as perdas de óleo neutro.

Novas investigações devem ser efetuadas para se testar condições de operação de um processo de extração líquido-líquido e seus efeitos na remoção de ácidos graxos livres, extração de diglicerídeos, quantificação da perda de óleo neutro devido a solubilidade do óleo no solvente e a manutenção de componentes naturais desejáveis como tocoferol, orizanol e pigmentos como no caso do óleo de palma.

1.2. Diagrama de equilíbrio

Os diagramas de equilíbrio líquido-líquido são apresentados à temperatura constante.

Em um sistema de coordenadas retangulares, a abscissa e a ordenada apresentam as concentrações do solvente (componente 3) e do soluto (componente 2), respectivamente, a hipotenusa do triângulo retângulo, a concentração do componente 1. A Figura 1 apresenta um exemplo de diagrama de equilíbrio para um sistema ternário.

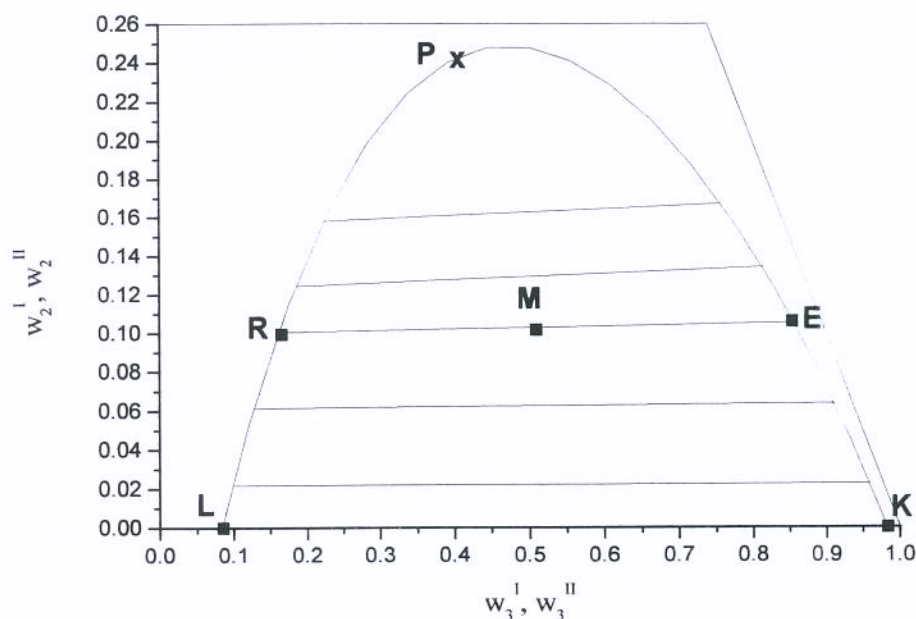


Figura 1 Diagrama de equilíbrio líquido-líquido de um sistema ternário.

(L – K, linha de base; R – E, linha de amarração; M, ponto de mistura; P – ponto crítico)

O componente 2 se dissolve completamente em 1 e 3, mas os componentes 1 e 3 dissolvem-se de forma limitada e são representados no diagrama de equilíbrio pela linha de base ou de solubilidade mútua. O ponto L representa a solubilidade do componente 3 em 1 e o ponto K a solubilidade do componente 1 em 3.

A curva LRPEK é a curva binodal e apresenta a mudança da solubilidade das fases I (curva LRP) e II (curva PEK) com a adição do soluto. Qualquer mistura acima desta curva será

uma solução homogênea de uma fase. Qualquer mistura dentro da curva, como por exemplo a mistura M, formará duas fases líquidas imiscíveis com as composições indicadas em R (rica no componente 1) e E (rica no componente 3). A linha RE é uma linha de amarração ou “tie-line”, que deverá passar necessariamente pelo ponto M, que representa a mistura como um todo. O ponto P, conhecido como ponto crítico ou “plait point”, representa a última linha de amarração e o ponto onde as curvas de solubilidade das fases rica no componente 1 e 3 se encontram.

A razão entre as composições das fases para o componente 2 define o coeficiente de distribuição:

$$k = \frac{w_i^{II}}{w_i^I} \quad (1)$$

No exemplo apresentado na Figura 1, a composição de 2 na fase II é maior que na fase I e portanto o coeficiente de distribuição será maior que 1.

1.3. Modelos Termodinâmicos

Para a simulação de processos químicos, como a extração líquido-líquido, são requeridas estimativas de propriedades de mistura. Como não é possível obter todos os dados para a mistura particular nas condições de temperatura, de pressão e de composição correspondentes à do estudo, é necessário manipular os dados experimentais disponíveis de tal forma a obter a melhor interpolação e extrapolação.

Para o cálculo da composição das fases em equilíbrio no processo de extração deve-se partir da condição de equilíbrio termodinâmico para cada componente i na mistura, onde as atividades do componente i são iguais:

$$a_i^I = a_i^{II} \quad (2)$$

onde

$$a_i = \gamma_i x_i \quad (3)$$

Muitas expressões semi-empíricas tem sido propostas na literatura para relacionar a energia livre de Gibbs em excesso principalmente à composição da mistura. Todas estas expressões contêm parâmetros ajustáveis a dados experimentais e permitem o cálculo do coeficiente de atividade. Os principais modelos sugeridos para descrição do equilíbrio de fases são os modelos NRTL e UNIQUAC.

Quando a diferença de massas molares entre os componentes dos sistemas estudados é grande, como no caso de sistemas graxos / álcoois de cadeia curta, é aconselhável empregar como unidade de concentração a fração mássica. Para os modelos UNIQUAC e UNIFAC, Oishi & Prausnitz (1978) já tinham utilizado este procedimento no cálculo da atividade do solvente em soluções poliméricas.

Neste caso a atividade seria descrita por:

$$a_i = \gamma_i^x x_i = \gamma_i^w w_i \quad (4)$$

onde

$$\gamma_i^x = \gamma_i^w M_i \sum_j^n w_j / M_j \quad (5)$$

No modelo NRTL, o coeficiente de atividade quando se emprega a concentração expressa em fração mássica assume a seguinte forma:

$$\ln \gamma_i = \frac{\sum_j^c \frac{\tau_{ji} G_{ji} w_j}{M_j}}{\sum_j^c \frac{G_{ji} w_j}{M_j}} + \sum_{j=l}^c \left[\frac{w_j G_{ji}}{M_j \sum_k^n \frac{G_{kj} w_k}{M_k}} \left(\tau_{ij} - \frac{\sum_k^c \frac{\tau_{kj} G_{kj} w_k}{M_k}}{\sum_k^c \frac{G_{kj} w_k}{M_k}} \right) \right] \quad (6)$$

onde

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (7)$$

$$\tau_{ij} = A_{ij} / T \quad (8)$$

$$\alpha_{ij} = \alpha_{ji} \quad (9)$$

Já o modelo UNIQUAC adquire a forma apresentada abaixo:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (10)$$

$$\ln \gamma_i^C = \ln \left(\frac{\phi_i'}{w_i / \zeta M_i} \right) + 1 - \frac{\zeta M_i \phi_i'}{w_i} + \frac{z}{2} M_i q_i' \ln \frac{\theta_i'}{\phi_i'} - \frac{z}{2} M_i q_i' \left(1 - \frac{\phi_i'}{\theta_i'} \right) \quad (11)$$

$$\text{onde } \zeta = \sum_j^C \frac{w_j}{M_j} \quad (12)$$

$$\theta_i' = \frac{q_i' w_i}{\sum_j^C q_j' w_j}; \phi_i' = \frac{r_i' w_i}{\sum_j^C r_j' w_j} \quad (13)$$

$$\text{e } r_i' = \frac{1}{M_i} \sum_k^G \nu_k^{(i)} R_k; q_i' = \frac{1}{M_i} \sum_k^G \nu_k^{(i)} Q_k \quad (14)$$

os parâmetros R_k e Q_k foram consultados em Magnussen *et al.* (1980)

$$\ln \gamma_i^R = M_i q_i' \left[1 - \ln \left(\sum_j^C \theta_j' \tau_{ji} \right) - \sum_j \left(\theta_i' \tau_{ij} / \sum_k^C \theta_k' \tau_{kj} \right) \right] \quad (15)$$

os parâmetros ajustáveis τ_{ij} e τ_{ji} são definidos como:

$$\tau_{ij} = \exp \left(- \frac{u_{ij} - u_{jj}}{RT} \right) = \exp \left(- \frac{A_{ij}}{T} \right) \quad (16)$$

$$\tau_{ji} = \exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right) = \exp\left(-\frac{A_{ji}}{T}\right) \quad (17)$$

Os modelos de contribuição de grupos UNIFAC (Fredenslund *et al.*, 1977) e ASOG (Kojima & Tochigi, 1979), quando se emprega a concentração expressa em fração mássica, assumem a seguinte forma:

Modelo UNIFAC

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (18)$$

Neste modelo, a parte combinatorial é usada diretamente do modelo

$$\ln \gamma_i^R = \sum_k^G v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (19)$$

onde $\Gamma_k^{(i)}$ é o coeficiente de atividade de grupo do grupo k na solução de referência contendo somente moléculas do mesmo tipo i

$$r_i' = \frac{I}{M_i} \sum_k^G v_k^{(i)} R_k; q_i' = \frac{I}{M_i} \sum_k^G v_k^{(i)} Q_k \quad (20)$$

$$\theta_i = \frac{q_i w_i}{\sum_j q_j w_j}; \phi_i = \frac{r_i w_i}{\sum_j r_j w_j} \quad (21)$$

$$\ln \Gamma_k = M_k Q_k \left[I - \ln \left(\sum_m \Theta_m' \Psi_{mk} \right) - \sum_m \left(\Theta_m' \Psi_{km} / \sum_n \Theta_n' \Psi_{nm} \right) \right] \quad (22)$$

$$\Theta_m' = \frac{Q_m W_m}{\sum_n Q_n W_n}; W_m = \frac{\sum_j v_m^{(j)} w_j}{\sum_j \sum_n v_n^{(j)} w_j} \quad (23)$$

$$\Psi_{mn} = \exp \left(- \frac{U_{mn} - U_{nn}}{RT} \right) = \exp \left(- a_{mn} / T \right) \quad (24)$$

Modelo ASOG

$$\ln \gamma_i = \ln \gamma_i^{FH} + \ln \gamma_i^G \quad (25)$$

$$\ln \gamma_i^{FH} = \ln \left(\frac{\zeta v_i^{FH}}{\sum_j \frac{w_j}{M_j} v_j^{FH}} \right) + I - \frac{\zeta v_i^{FH}}{\sum_j \frac{w_j}{M_j} v_j^{FH}} \quad (26)$$

$$\text{onde } \zeta = \sum_j^C \frac{w_j}{M_j} \quad (27)$$

$$\ln \gamma_i^G = \sum_k^G v_{ki} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (28)$$

$$\ln \Gamma_k = -\ln \sum_l^G W_l a_{k,l} + 1 - \sum_l^G \left(W_l a_{l,k} / \sum_m^G W_m a_{l,m} \right) \quad (29)$$

onde W é a fração mássica de grupo, calculada pela equação (23)

$$a_{k,l} = \exp \left(m_{k,l} + \frac{n_{k,l}}{T} \right) \quad (30)$$

Para o cálculo do equilíbrio de fases na simulação da desacidificação de óleos vegetais através da extração líquido-líquido, os modelos de contribuição de grupos, UNIFAC e ASOG apresentam-se mais adequados por permitir expandir os sistemas pseudo-ternários, óleo/ácido graxo/álcoois de cadeia curta, em multicomponentes com um número de grupos estruturais pequeno e conseqüentemente, um pequeno número de parâmetros de interação binária. Os parâmetros do UNIFAC de interação de grupo para equilíbrio líquido-líquido foram publicados por Magnussen *et al.* (1980) e os parâmetros do ASOG por Tochigi *et al.* (1990).

1.4. Simulação da Coluna de Extração

A representação esquemática deste processo é mostrada na Figura 2. Correntes de extrato (E_n) e refinado (R_n) escoam de estágio a estágio em contracorrente e propiciam a formação de duas correntes de produtos, refinado (R_N) e extrato (E_1).

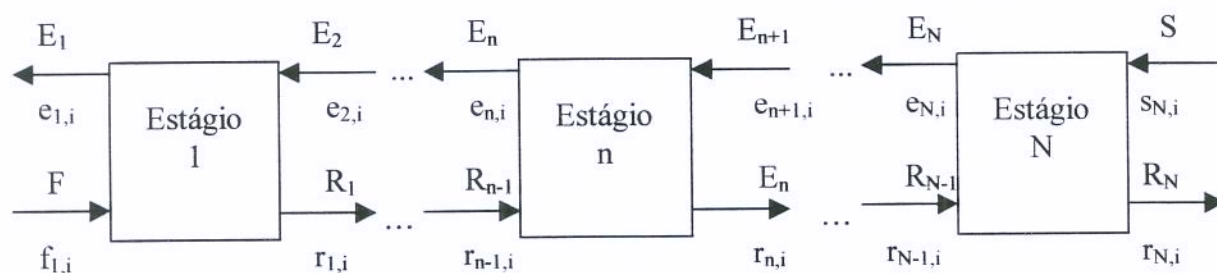


Figura 2 Representação esquemática da coluna de extração líquido-líquido

Neste desacidificação de óleos vegetais, a corrente de refinado final (R_N) é a corrente de óleo vegetal refinado e a corrente de extrato final (E_1) é a corrente de solvente contendo os ácidos graxos livres extraídos.

O algoritmo sugerido por Naphtali & Sandholm (1971), desenvolvido para simulação de colunas de destilação, mostra-se adequado para simulação de colunas de extração líquido-líquido, desde que as equações para balanço de massa e equilíbrio de fases sejam modificadas.

As equações de balanço de massa e equilíbrio de fases são agrupadas para cada componente e cada estágio. O grupo resultante das equações tem uma estrutura de bloco tridiagonal que permite rápida solução pelo método de Newton-Raphson.

Para cada estágio, pode-se estabelecer um grupo de relações independentes, “funções discrepância”, $F_{k(n,i)}$, que devem ser satisfeitas:

“Função Discrepância” 1: balanço de massa do componente i:

$$F_{1(n,i)} = r_{n,i} - r_{n-1,i} + e_n y_{n,i} - e_{n+1,i} \quad n = 2, 3, \dots, N-1 \quad (31)$$

$$i = 1, 2, \dots, C$$

$$F_{1(l,i)} = r_{l,i} - f_{l,i} + e_{l,i} - e_{2,i} \quad i = 1, 2, \dots, C \quad (32)$$

$$F_{1(N,i)} = r_{N,i} - r_{N-1,i} + e_{N,i} - s_{N,i} \quad i = 1, 2, \dots, C \quad (33)$$

“Função Discrepância” 2: condição de equilíbrio de fases:

$$F_{2(n,i)} = k_{n,i} E_n r_{n,i} / R_n - e_{n,i} \quad n = 2, 3, \dots, N-1 \quad (34)$$

$$i = 1, 2, \dots, C$$

$$\text{onde } k_{n,i} = \gamma_{n,i}^{w,I} / \gamma_{n,i}^{w,II} = w_{n,i}^{II} / w_{n,i}^I \quad (35)$$

$$F_{2(l,i)} = k_{l,i} E_l r_{l,i} / R_l - e_{l,i} \quad i = 1, 2, \dots, C \quad (36)$$

$$F_{2(N,i)} = k_{N,i} E_N r_{N,i} / R_N - e_{N,i} \quad i = 1, 2, \dots, C \quad (37)$$

As equações compõem um vetor de “funções discrepância”:

$$F(x) = \begin{Bmatrix} F_1 \\ F_2 \end{Bmatrix} = 0 \quad (38)$$

que contém 2NC elementos e que podem ser resolvidos para as variáveis desconhecidas:

$$x = \begin{Bmatrix} e \\ r \end{Bmatrix} \quad (39)$$

A equação (39) pode ser resolvida por iteração de Newton-Raphson, utilizando convergência simultânea de todas as variáveis independentes x .

Na iteração de Newton-Raphson, um novo grupo de valores x_r é gerado de uma estimativa prévia, x_{r-1} , da seguinte forma:

$$x_r = x_{r-1} - F_{r-1}(x_{r-1}) / (\partial F / \partial x)_{x_{r-1}} \quad (40)$$

Quando $|x_r - x_{r-1}|$ é suficientemente pequeno, o grupo correto de valores de x foi encontrado e a iteração cessa.

1.5. Planejamento Fatorial e Superfície de Resposta

Com o avanço computacional, a análise de um processo por simulação tem se tornado uma importante ferramenta para o estudo e otimização de processos sem grandes custos. Um dos problemas mais comuns quando se utiliza a simulação de processos é o grande número de variáveis envolvidas e a determinação da influência de uma ou mais variáveis sobre outra.

Uma técnica útil neste caso é a utilização de planejamento experimental e análise de superfície de resposta (Barros Neto *et al.*, 1995; Khuri & Cornell, 1987; Box & Hunter, 1978).

Rodrigues *et al.* (1993) usaram a análise de superfície de resposta na otimização de um processo de purificação de enzima e concluíram que esta metodologia ajudou a reduzir o número de simulações para determinar as condições ótimas do processo.

1.6. Nomenclatura

α - parâmetro do UNIFAC ou ASOG

A - parâmetro modelo NRTL e UNIQUAC

C - número de componentes

D - número de grupos de dados

D - número de grupos de dados

E - vazão mássica total de extrato

e - vazão mássica de um determinado componente no extrato

F - vazão mássica de alimentação no extrator

f – vazão mássica de um determinado componente na alimentação

G - número de grupos

G - parâmetro modelo NRTL

k – coeficiente de distribuição

m - parâmetro de interação de grupo

M - peso molecular

n - parâmetro de interação de grupo

N - número de estágios

Q - parâmetro de área de grupo

q - área molecular de van der Waals

R - parâmetro de volume de grupo ou

vazão total de refinado

r – vazão mássica de um determinado componente no refinado

r - volume molecular de van der Waals

S - vazão mássica total de solvente

s – vazão mássica de um determinado componente no solvente

t - temperatura ($^{\circ}\text{C}$)

T - temperatura (K)

U - energia de interação

u - energia potencial

w - fração mássica

W - fração mássica de grupo

Sobrescrita/ Subscrita

C - parte combinatorial

ex - experimental

FH - contribuição de tamanho

G - contribuição de grupo

I - fase refinado

II - fase extrato

i, j, k - componente

m, n, k, l - grupo

R - parte residual

Grega

α - parâmetro NRTL

ϕ - fração de volume

γ - coeficiente de atividade

σ - desvio padrão

ζ - equação (7)

τ - parâmetro NRTL ou UNIQUAC

θ - fração de área

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CAPÍTULO 2

OPTIMIZATION OF A SECONDARY REFLUX AND VAPORIZATION (SRV) DISTILLATION PROCESS USING SURFACE RESPONSE ANALYSIS

E. Batista, M. I. Rodrigues and A. J. Meirelles

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Optimization of a Secondary Reflux and Vaporization (SRV) distillation process using surface response analysis

E. Batista, M. I. Rodrigues and A. J. Meirelles^{*}

Department of Food Engineering - Faculty of Food Engineering - State University of Campinas

Abstract

SRV (Secondary Reflux Vaporization) distillation is based on heat exchange between the rectifying and stripping sections. This specific kind of distillation involves a large number of operating variables and details in design, and enormous computational efforts are traditionally necessary for its optimization. Factorial design and surface response analysis were used to optimize SRV extractive distillation in production of pure ethanol. Once such a distillation process is optimized, it involves substantially lower energy consumption than conventional ones.

Keywords: Extractive distillation, SRV distillation, Surface response analysis.

2.1. Introduction

With computational advances the process simulation has become an important tool for study and optimization of complex processes that normally involve a large number of variables. In such case, factorial design and surface response analysis are useful for determining the effect of operating variables without requiring a large number of simulations.

These techniques are a powerful tool for finding the optimal range of operating conditions for the operation of systems with large number of variables; such as distillation. They also make it possible to identify those variables which are the most significant in the optimization of the process.

Rodrigues et al. (1993) used surface response analysis to study the effect of details of operation and design on yield and productivity in the optimization of an enzyme purification process by

^{*} CP 6121, CEP 13083-970, Campinas, São Paulo, Brazil

continuous adsorption recycle extraction. Two levels and seven variables were studied. The methodology was found to reduce the number of simulations necessary to determine the conditions that maximize yield, while maintaining high productivity.

Meirelles et al. (1992) concluded that extractive distillation of ethanol/water/ethylene glycol may be energetically preferable to traditional azeotropic distillation with benzene, and showed the unusual behavior of the temperature profile in comparison with the normal distillation process, with a maximum in temperature occurring between the two feed plates due to the greater solvent concentration existing in this part of the column. This natural temperature difference suggests thermal integration such as the Secondary Reflux and Vaporization (SRV) developed by Mah et al. (1977).

In SRV distillation, the reflux and vaporization rates are deliberately manipulated to enhance the overall thermal efficiency. This manipulation is accomplished by heat exchange between the rectifying and stripping sections. In order to provide the necessary temperature difference for heat exchange between these sections, the former must be operated at a higher pressure than the latter. As a result of heat exchange between the two sections in this procedure, the liquid reflux rate steadily increases as one proceeds down the rectifying section, while the vapor flow rate steadily increases as one proceeds up the stripping section.

Batista and Meirelles (1997) studied the application of SRV thermal integration in extractive distillation and concluded that the internal fluid recirculation is a consequence of the heat exchange, which generally is a substitute for the effect of the reflux ratio on product purity. Integrated columns can thus be operated at lower reflux ratios without compromising the purity of the product which is an additional way of reducing energy consumption.

The present paper introduces surface response analysis as a tool for the increase of purity accompanied by a reduction in energy consumption for thermal SRV integration in extractive distillation.

2.2. Process Simulation

Conventional and integrated extractive distillation were simulated. In the former, the variables considered were: position of the stage of pure solvent feeding (n_s), the position of the stage of azeotropic mixture feeding (n_a), reflux ratio (r) and solvent to feeding ratio (S/F); for SRV

extractive distillation, not only were n_s , r and S/F considered, but two additional variables were introduced: pressure difference between paired stages (ΔP) and UA (U being the overall heat transfer coefficient and A being the heat transfer area). The position of the stage of azeotropic mixture feeding in SRV distillation was set at 13, because this provides the maximum number of paired stages for thermal integration. Without surface response analysis, about 700 simulations were necessary to select a good set of operating variables and design details and even then, no definite conclusions were made concerning the synergistic effect of all variables. Surface response analysis however permits a reduction in the number of simulations necessary, and only 43 process simulations were found necessary to define the optimal conditions to maximize product purity, while minimizing energy consumption. For purposes of comparison the conventional extractive distillation process was also optimized by surface response analysis. The algorithm used for simulation was that suggested by Naphtali and Sandholm (1971). Phase equilibrium was calculated by NRTL with temperature-dependent parameters. Liquid and vapor heat capacities, as well as the heat of vaporization, were determined according to Daubert and Danner (1985). Table 1 shows the specifications for the columns for both conventional and SRV extractive distillation.

Table 1 Specifications of extractive distillation columns

Number of stages	26
Murphree efficiency	1
Thermal state of azeotropic mixture	saturated liquid
Molar fraction of ethanol (1)/ water (2) mixture feeding	0.85 / 0.15
ΔP_p (kPa)	1.0132
Condenser stage	1
Reboiler stage	26
Feed stream (kmol/h)	1000
Overhead product stream (kmol/h)	850

2.3. Surface Response Analysis

This study was carried out by surface response analysis, based on the results from experimental factorial design and regression analysis (Box et al., 1978; Khuri and Cornell, 1987).

The experimental design, which requires the use of coded variables (Tables 2 and 3), was used as a tool to evaluate the influence of the main process variables on the product purity and energy consumption. Two levels were considered; 25 (2^4 + star) process simulations were necessary for conventional extractive distillation and 43 (2^5 + star) for thermal integrated extractive distillation.

Table 2 Coded variables for factors in conventional extractive distillation

	Level				
	-2	-1	0	+1	+2
n_s	2	4	6	8	10
n_a	12	14	16	18	20
S/F	0.4	0.6	0.8	1.0	1.2
r	0.1	0.3	0.5	0.7	0.9

Table 3 Coded variables for factors in SRV extractive distillation

	Level				
	-2.37	-1	0	+1	+2.37
n_s	2	3	4	5	6
S/F	0.463	0.600	0.700	0.800	0.937
r	0.026	0.300	0.500	0.700	0.974
ΔP	31.91	101.30	151.95	202.60	272.04
UA	9.6×10^4	1.2×10^7	2.1×10^7	3.0×10^7	4.2×10^7

In systems with many variables, there is a strong interest in assessing the effects of these variables on the overall behavior of the response. Such an assessment is possible through regression analysis. Thus, from the simulation results in the above mentioned range (25

simulations for conventional distillation and 43 for SRV distillation), a mathematical model for each type of response was obtained.

This permits the formulation of the following models, expressed in terms of coded variables (Tables 2 and 3):

For conventional extractive distillation:

- product purity

$$P = 0.995693 - 0.001275(n_s^*) + 0.001758(n_a^*) + 0.006458(S/F^*) - 0.002238(S/F^*)^2 + 0.003842(r^*) - 0.002688(r^*)^2 - 0.001813(S/F^*)(r^*) \quad (1)$$

- energy consumption

$$E = 74062.70 + 4676.75(S/F^*) + 7891.67(r^*) \quad (2)$$

For thermal integrated extractive distillation:

- product purity

$$P = 0.992502 - 0.001107(n_s^*) + 0.003803(S/F^*) + 0.006910(r^*) - 0.002282(r^*)^2 + 0.001469(\Delta P^*) - 0.000576(\Delta P^*)^2 - 0.003333(UA^*) - 0.001962(S/F^*)(r^*) - 0.001137(S/F^*)(UA^*) - 0.003444(r^*)(UA^*) \quad (3)$$

- energy consumption

$$E = 32554.86 - 145.71(n_s^*) - 1657.83(S/F^*) + 7012.99(r^*) + 1833.27(\Delta P^*) - 262.49(\Delta P^*)^2 - 427.93(UA^*) + 314.28(S/F^*)(\Delta P^*) - 164.13(\Delta P^*)(UA^*) \quad (4)$$

Table 4 provides an example of regression analysis for the energy consumption in SRV extractive distillation ($F = 2.15 \times 10^3$; $p \leq 0.01$). The same confidence level was obtained in all other cases as well.

Table 4 Results of regression analysis for energy consumption of SRV extractive distillation

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F test ^a
Regression	2.41×10^9	8	3.01×10^8	
Deviation	4.75×10^5	34	1.40×10^4	
Total variation	2.41×10^9	42	—	2.15×10^4
Correlation coefficient	0.9998	—	—	

^a $F_{0.99; 8, 34} = 3.098$

With these models, it is possible to generate surfaces that represent the influence of the specific variables on response. In the optimization of conventional extractive distillation, the surfaces generated showed that the ideal value for the position of the stage of pure solvent feeding (n_s) was 2, whereas that feeding the azeotropic mixture (n_a) was 20. The fact that these are extreme values for these two variables suggests that increasing the rectifying section showed improve performance of the column.

Figure 1 depicts the effect of the solvent to feeding ratio (S/F) as well as the reflux ratio (r) on the product purity. Product purity increases with an increase in S/F and r, with the effect of each being greater in the presence of a low value of the other.

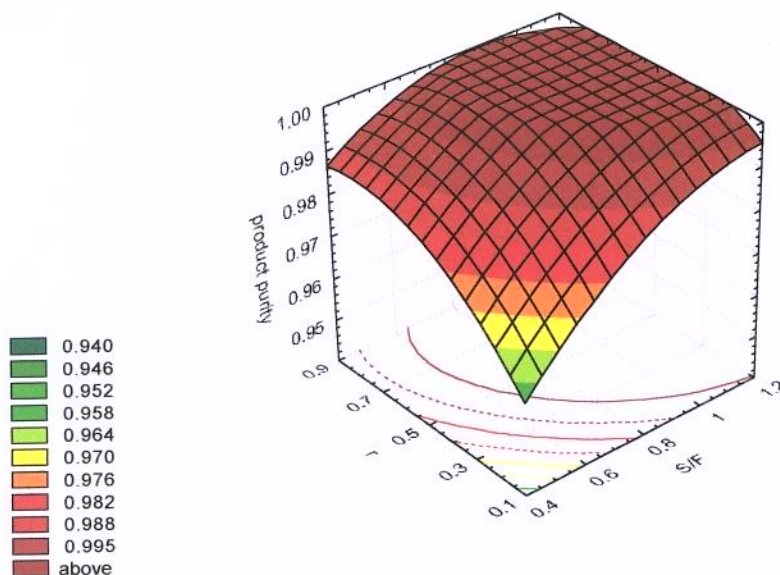


Figure 1 Effect of S/F and r on product purity for $n_s = 2$ and $n_a = 20$

The surface generated with S/F and r for energy consumption shows that this response increases with an increase in S/F and r , although the effect of r is more significant than that of S/F. It is thus preferable to increase S/F and decrease r to obtain minimal energy consumption. When these surfaces are superimposed, the optimal values found are 0.9 for S/F and 0.226 for r . The results of rigorous simulation with these optimized operating variables was compared to the values obtained from Models (1) and (2). Table 5 and 6 presents the optimal conditions and corresponding results and deviations.

Table 5 Optimal conditions for conventional extractive distillation

n_s	2	S/F	0.9
n_a	20	r	0.226

Table 6 Comparision of simulation and regression for conventional distillation under optimal conditions

	P (molar fraction)	E (kJ/kmol of ethanol)
Rigorous simulation	0.9956	67537
Regression analysis	0.9954	65589
Deviation (%)	0.02	2.88

In the optimization of SRV distillation, the surfaces generated revealed that the optimal position of the stage of pure solvent feeding (n_s) was 2.

The effect of reflux ratio (r) and pressure difference of paired stages (ΔP) on product purity are shown in Figure 2. Surface response analysis revealed that the effect of r is much more significant than that of ΔP . A similar behavior is also observed with the surface generated for energy consumption. When these two surfaces are superimposed, the optimal value for r is 0.5, and for ΔP it is 151.9 kPa, values which guarantee product purity greather than 0.995 (molar fraction of ethanol) with minimal energy consumption.

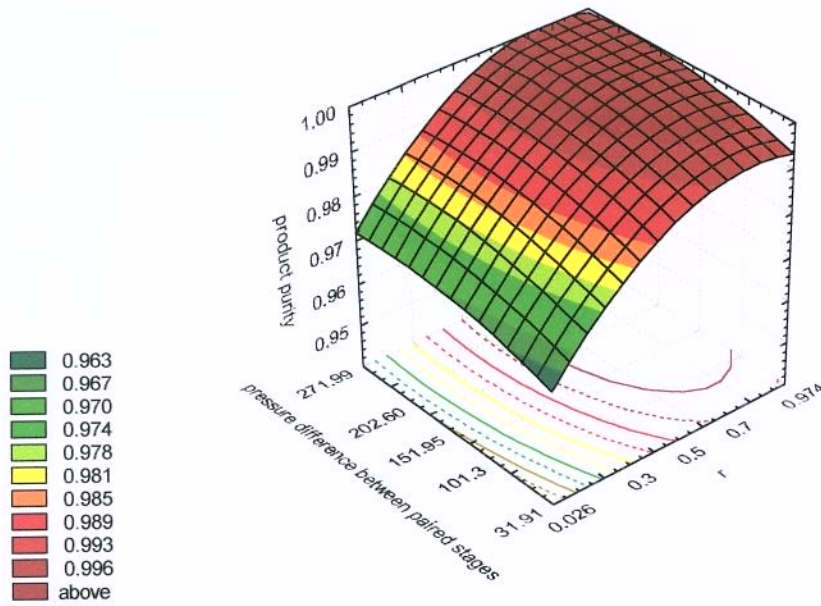


Figure 2 Effect of r and ΔP on product purity for $n_s = 2$, $S/F = 0.7$ and $UA = 2.1 \times 10^7$ kJ/h

The surface for the variables S/F and UA with r equal to 0.5 and ΔP equal to 151.9 kPa was then generated (Figure 3). The product purity increases when S/F and UA increase, whereas energy consumption decreases (Figure 4). This maximum product purity with minimal energy consumption is obtained in the extreme region of these two variables (S/F equal to 0.937 and UA equal to 4.2×10^7 kJ/h °C).

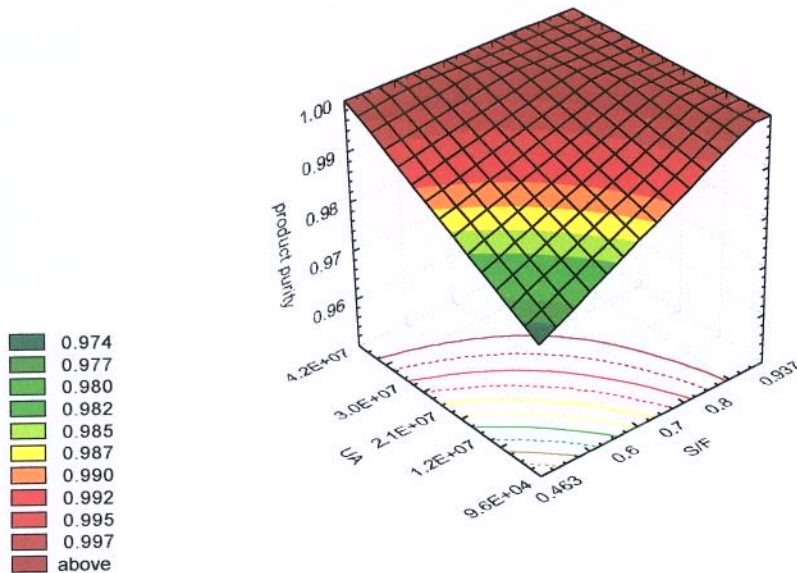


Figure 3 Effect of S/F and UA on product purity for $n_s = 2$, $r = 0.5$ and $\Delta P = 151.95$ kPa

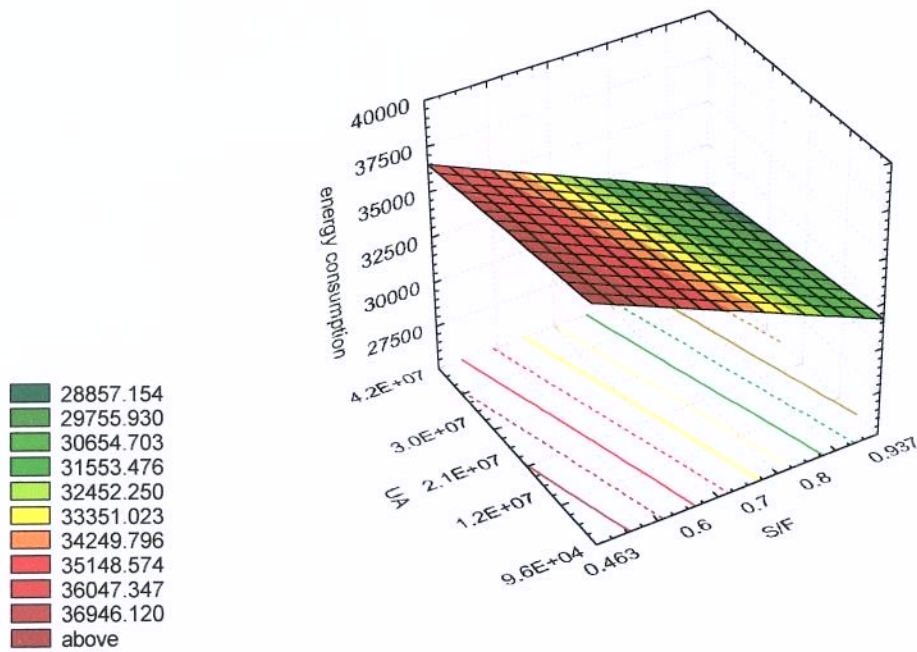


Figure 4 Effect of S/F and UA on energy consumption for $n_s = 2$, $r = 0.5$ and $\Delta P = 151.95$ kPa

Rigorous simulation was conducted with these optimized operating variables and the optimal conditions and corresponding results and deviations are presented in Tables 7 and 8.

Table 7 Optimal conditions for SRV distillation

n_s	2	ΔP	1.5 kPa
S/F	0.937	UA	4.2×10^7 kJ/h °C
r	0.5		

Table 8 Comparison of simulation and regression for SRV distillation under optimal conditions

	P (molar fraction)	E (kJ/kmol de ethanol)
Rigorous simulation	0.9976	28704
Regression analysis	1.0000	27957
Deviation (%)	0.24	2.60

2.4. Conclusions

Surface response methodology is a powerful tool for the optimization of complex processes such as SRV extractive distillation. The use of this procedure makes it possible to identify the effects of interaction of all the variables. For example, increasing the S/F and UA leads to a reduction in energy consumption and an increasing in product purity. This technique can thus help in reducing energy consumption of extractive distillation. When these results are compared with those presented in earlier publications (Batista e Meirelles, 1997; Meirelles et al, 1992), an energy saving of 21% can be obtained, the optimal conditions for SRV distillation results in a saving of 57.5% in energy consumption in relation to conventional extractive distillation

2.5. Notation

A	= heat transfer area	[m ²]
E	= energy consumption, including compression work in the case of SRV distillation	[kJ/kmol of ethanol]
n _s	= position of the stage of pure solvent feeding	
n _a	= position of the stage of azeotropic mixture feeding	
P	= product purity (ethanol molar fraction)	
r	= reflux ratio	
S/F	= solvent to feeding ratio	
U	= overall heat transfer coefficient	[kJ/h m ² °C]
ΔP _p	= pressure drop per plate	[kPa]
ΔP	= pressure difference between paired stages	[kPa]
<i>Superscript</i>		
*	= coded variable (Table 2 and 3)	

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CAPÍTULO 3

LIQUID-LIQUID EQUILIBRIUM FOR SYSTEMS OF CANOLA OIL, OLEIC ACID AND SHORT-CHAIN ALCOHOLS.

**Eduardo Batista; Sandra Monnerat; Kênia. Kato;
Luiz Stragevitch; Antonio J. A. Meirelles**

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Liquid-liquid equilibrium for systems of canola oil, oleic acid and short-chain alcohols.

Eduardo Batista; Sandra Monnerat; Kênia. Kato; Luiz Stragevitch; Antonio J. A. Meirelles

Keywords:

Liquid-liquid equilibrium, vegetable oil, NRTL, UNIQUAC

Summary

Vegetable oils can be deacidified by liquid-liquid extraction. The difference in polarity between the triglycerides, principal component of the oil, and the solvent guarantees the formation of two phases and permits the removal of free fatty acids. A knowledge of the equilibrium between the phases of such systems is important, however, if adequate equipment for the implementation of the process is to be designed. The present paper establishes experimental data for systems of canola oil, oleic acid and alcohols, subsequently adjusting the NRTL and UNIQUAC models to them for the calculation of activity coefficients. The results show the good descriptive quality of the models.

3.1. Introduction

Crude vegetable oils contain impurities, especially free fatty acids, yet the presence of these compounds can adversely affect oil quality and stability to oxidation. Most edible oils are produced by alkaline refining (Antoniassi *et al.*, 1998), since this is a highly versatile process applicable for all raw materials; however, it can result in great losses of the neutral oil.

For highly acidic oils, physical refining is also a possibility, as it results in less loss of neutral oil than the traditional process, but more energy is consumed. The process also has certain limitations, since its application is limited to specific raw materials; moreover, the finished product is subject to undesirable alterations in color and a reduction of stability to oxidation (Antoniassi *et al.*, 1998).

Another possible alternative to reduce energy consumption without loss of natural components is deacidification through liquid-liquid extraction, as this process is carried out at room temperature and atmospheric pressure. According to Thomopoulos (1971), this process is based on the difference in solubility of free fatty acids and neutral triglycerides in the solvent, as well as on the difference in boiling points of the solvent and the fatty acids during subsequent separation.

Deacidification of vegetable oils can be conducted using various selective solvents such as acetone, furfural, ethyl acetate, propanol, isopropanol, butanol, ethanol, methanol, and ethyl-methyl-cetone, although ethanol has been suggested to be the best solvent for the process (Thomopoulos, 1971). Experimental data relating to the equilibrium of such systems are scarce in the literature, despite the necessity for the study and design of equipment which make industrial-scale liquid-liquid extraction feasible for the refining of oils.

The present paper determines liquid-liquid equilibria data for systems of canola oil, oleic acid, and short-chain alcohols at different temperatures; focusing was on the effect of the structure of the solvent on the formation of the heterogeneous area and on the selectivity, as well as the distribution of oleic acid in the phases. The parameters of the NRTL and UNIQUAC models were then adjusted to the experimental data for the description of the liquid-liquid equilibrium phases.

3.2. Materials

Refined canola oil of the Purilev brand was utilized as a source of triglicerides, and commercial oleic acid of the Riedel-deHaën brand as the source of fatty acids. An initial study determined the chemical composition of these reagents.

The canola oil was analyzed by gas chromatography of the fatty acid methyl esters to determine the fatty acid composition. The official method 1-62 of the AOCS (1988) was adopted, and a Sigma 3B (Perkin-Elmer) gas chromatograph with flame ionization detector and integrator was used under the following experimental conditions: stainless steel column with 1/8" external diameter and 4 m length, packed with 10% Silar 10C (10% Cianopropilsiloxane in Chromosorb W), nitrogen as the carrier gas at a rate of 25 ml/min., an injection temperature of 225 °C, a column temperature of 175 °C, and a detection temperature of 225 °C. Samples were prepared in the form of fatty acid methyl esters according to the methodology developed by Hartman and Lago (1973).

The fatty acid composition of the canola oil is presented in Table 1.

From this fatty acid composition it was possible to determine the probable triglyceride composition of the oil (Table 2) by using the computational method developed by Antoniosi Filho *et al.* (1995). For this transition, two aspects should be considered. In first place, the principal triglyceride represents the component of greatest concentration in the isomer set with x carbons and y double bonds. For this reason, some fatty acids which appear in Table 1 (M, Po, A, B, E) do not appear

explicitly in Table 2; for example, the triglyceride PPOs is part of the 50:1 group, with a principal triglyceride of PPO. Moreover, groups with a total concentration of triglycerides less than 0.5% were ignored.

The average molecular weight calculated for the canola oil was $876.6339 \text{ g.mol}^{-1}$; this oil also has a residual acidity of 0.06%, expressed as oleic acid.

The fatty acid methyl esters of the Reidel-deHaën oleic acid were also analyzed by gas chromatography, using the methodology described above. The fatty acid composition is presented in Table 3. The average molecular weight of the oleic acid was $278.2067 \text{ g.mol}^{-1}$. The solvents used were methanol, ethanol, isopropanol, and n-propanol, all from Merck, with a purity greater than 99.5%.

Table 1 Fatty acid composition of canola oil

Symbol	Fatty Acid		M (g.mol^{-1})	% molar	% mass
M	Miristic	C14:0 ^(*)	228.38	0.0575	0.0469
P	Palmitic	C16:0	256.43	7.3757	6.7565
Po	Palmitoleic	C16:1	254.41	0.1910	0.1736
S	Stearic	C18:0	284.48	2.0964	2.1305
O	Oleic	C18:1	282.47	48.0179	48.4533
Li	Linoleic	C18:2	280.45	31.9683	32.0275
A	Arachidic	C20:0	312.54	0.4809	0.5369
Le	Linolenic	C18:3	278.44	9.2860	9.2365
B	Behenic	C22:0	340.59	0.2960	0.3602
E	Erucic	C22:1	338.58	0.2303	0.2785

^(*) C_x:y - x = number of carbons, y = double bonds M = molecular weight

Table 2. Probable triglyceride composition of canola oil

Group	Principal triglyceride	M (g.mol ⁻¹)	% molar	% mass
50:1 ^(*)	PPO	833.37	0.7558	0.7185
50:2	PPLi	831.35	0.5896	0.5591
52:2	POO	859.40	5.7515	5.6384
52:3	POLi	857.39	7.4897	7.3253
52:4	PLiLi	855.37	4.7095	4.5953
52:5	PLiLe	853.36	1.5166	1.4763
54:2	SOO	887.46	1.6612	1.6817
54:3	OOO	885.44	13.5808	13.7172
54:4	OOLi	883.43	24.2201	24.4078
54:5	OLiLi	881.41	22.3229	22.4445
54:6	OLiLe	879.40	12.3093	12.3481
54:7	LiLiLe	877.38	0.8564	0.8571
54:8	LiLeLe	875.36	4.2368	4.2306
Total			100.0000	100.0000

(*) X:Y - X number of carbons (except carbons of glycerol), Y double bonds

Table 3. Fatty acid composition of Riedel-deHaën oleic acid

Fatty Acid	% molar	% mass
M	1.8793	1.5427
P	4.8073	4.4311
Po	6.8541	6.2679
S	1.5490	1.5839
O	80.1066	81.3350
Li	4.3664	4.4017
Le	0.4373	0.4377

3.3. Experimental procedure

For the determination of liquid-liquid equilibrium data, equilibrium cells such as those suggested by Silva *et al.* (1997) were used. The cell temperature was regulated by thermostatic bath (Cole Parmer, model 12101-15, accurate to ± 0.01 °C), and the components were weighed on an A200 S Sartorius analytic balance, accurate to 0.0001 g. The mixture was stirred briskly with a magnetic stirrer (FISATOM, model 752A) for at least 15 minutes and left to rest for 4 hours. After this treatment, the two phases became clear and transparent, and the interface was well defined.

The quantity of fatty acids was determined using potentiometric titration (modified AOCS method Ca 5a-40, 1977) with an automatic burette (Dosimat 715 model from Metrohm), the solvent was determined by evaporation in an EDG vacuum oven (Model EIV-1) The water concentration was

determined by Karl Fisher titration. Having determined the concentration of fatty acids and the solvent, the concentration of triglycerides was obtained by the difference. All measurements were performed in triplicate and the standard deviations were $\pm 0.081\%$ for the canola oil, $\pm 0.066\%$ for oleic acid, $\pm 0.027\%$ for alcohols and $\pm 0.038\%$ for water.

3.4. Results

Tables 4-8 present the overall experimental composition of the mixtures and the corresponding tie-lines for the systems of interest. All concentrations are expressed as percentage of mass.

Table 4. Ternary liquid-liquid equilibrium data for the system of canola oil (1) + commercial oleic acid (2) + methanol (3)

t (°C)	Overall Composition			Alcohol Phase			Oil Phase		
	100w ₃	100w ₂	100w ₁	100w ₃	100w ₂	100w ₁	100w ₃	100w ₂	100w ₁
20	52.41	—	47.59	99.49	—	0.51	5.03	—	94.97
	51.20	4.84	43.96	94.55	4.57	0.88	7.24	5.08	87.68
	51.03	9.42	39.55	90.08	8.64	1.28	9.34	10.39	80.27
	47.65	19.14	33.21	76.44	18.82	4.74	16.58	19.60	63.82
	48.28	23.57	28.15	70.83	23.00	6.17	19.91	24.84	55.24
30	52.58	—	47.42	99.38	—	0.62	5.98	—	94.02
	52.72	3.16	44.12	96.56	2.78	0.66	6.70	3.51	89.80
	51.97	5.88	42.15	93.63	5.33	1.04	8.31	6.35	85.34
	47.95	9.28	42.77	89.31	8.82	1.87	10.85	9.56	79.59
	47.30	13.03	39.67	85.33	12.26	2.41	13.10	13.74	73.16

Table 5. Ternary liquid-liquid equilibrium data for the system of canola oil (1) + commercial oleic acid (2) + ethanol (4)

t (°C).	Overall Composition			Alcohol Phase			Oil Phase		
	100w ₄	100w ₂	100w ₁	100w ₄	100w ₂	100w ₁	100w ₄	100w ₂	100w ₁
20	52.73	—	47.27	95.28	—	4.72	12.65	—	87.35
	53.06	2.90	44.04	90.13	3.37	6.50	15.32	2.34	82.28
	52.8	5.87	41.33	84.23	6.56	9.21	18.93	4.88	76.19
	50.84	7.80	41.36	79.43	8.78	11.79	21.98	6.84	71.19
	50.84	9.61	39.55	74.05	10.55	15.40	25.38	8.47	66.15
	50.16	11.05	38.78	67.14	11.90	20.96	31.11	10.11	58.78
30	54.20	—	45.80	93.90	—	6.10	15.56	—	84.44
	52.15	1.25	46.60	91.51	1.40	7.09	16.93	1.17	81.90
	50.08	2.48	47.44	89.13	2.77	8.10	18.30	2.31	79.39
	50.87	3.30	45.83	87.2	3.70	9.10	19.55	2.92	77.53
	51.65	4.13	44.22	85.26	4.64	10.10	20.80	3.54	75.66
	50.74	5.05	44.21	83.05	5.70	11.25	21.89	4.38	73.73
	49.82	5.97	44.21	80.84	6.76	12.40	22.98	5.21	71.81
	48.1	7.97	43.93	74.48	8.97	16.55	27.24	7.35	65.41
	48.98	9.19	41.83	67.55	9.95	22.50	34.34	8.66	57.00

Table 6. Ternary liquid-liquid equilibrium data for the system of canola oil (1) + commercial oleic acid (2) + isopropanol (5)

t (°C)	Overall Composition			Alcohol Phase			Oil Phase		
	100w ₅	100w ₂	100w ₁	100w ₅	100w ₂	100w ₁	100w ₅	100w ₂	100w ₁
10	57.65	—	42.35	90.84	—	9.16	21.89	—	78.11
	53.81	1.68	44.51	86.59	1.85	11.56	24.92	1.49	73.59
	56.22	3.25	40.53	82.35	3.61	14.04	27.90	2.89	69.20
	58.08	4.95	36.97	76.33	5.37	18.30	32.44	4.63	62.93
20	70.04	—	29.96	84.95	—	15.05	30.76	—	69.24

Table 7. Ternary liquid-liquid equilibrium data for the system of canola oil (1) + commercial oleic acid (2) + n-propanol (6)

t (°C)	Overall Composition			Alcohol Phase			Oil Phase		
	100w ₆	100w ₂	100w ₁	100w ₆	100w ₂	100w ₁	100w ₆	100w ₂	100w ₁
10	58.73		41.27	67.74		32.26	40.77		59.23

Table 8. Quaternary liquid-liquid equilibrium data for the system of canola oil (1) + commercial oleic acid (2) + ethanol (4) + water (7)

t (°C)	Overall Composition				Alcohol Phase				Oil Phase			
	100 w ₄	100 w ₂	100 w ₁	100 w ₇	100 w ₄	100 w ₂	100 w ₁	100 w ₇	100 w ₄	100 w ₂	100 w ₁	100 w ₇
30	49.65	—	47.01	3.34	92.13	—	1.38	6.49	8.40	—	91.31	0.29
	48.17	2.25	46.34	3.24	89.43	2.23	1.85	6.49	9.47	2.16	88.00	0.37
	47.63	6.08	43.08	3.21	84.81	6.37	2.65	6.17	12.20	6.13	81.14	0.53
	47.63	9.83	39.33	3.21	79.65	10.52	4.01	5.82	15.44	10.03	73.85	0.68
	47.36	12.19	37.26	3.19	76.02	13.42	5.07	5.49	17.82	12.45	68.88	0.85
	46.56	15.20	35.10	3.14	70.59	16.70	7.52	5.19	21.28	15.82	61.80	1.10

3.5. Modeling

The experimental equilibrium data were used to adjust the parameters of the NRTL and UNIQUAC models for the calculation of activity coefficients. Due to the large difference in molecular weights between the components in the systems studied, the mass fraction was used as the unit of concentration, a procedure already utilized by Oishi and Prausnitz (1978) for the calculation of the activity of a solvent in polymeric solutions with the UNIQUAC and UNIFAC methods.

The adjustments were made by treating the system as a pseudo-ternary one composed of a single triglyceride having the average molecular weight, representing the canola oil, of a representative fatty acid with the molecular weight of the commercial oleic acid, and of the solvent. The values of r_i' and q_i' for the UNIQUAC model were calculated via equation 1, which considers the composition of the oil and the commercial oleic acid; the values are furnished in Table 9. The parameters R_i and Q_i were taken from Magnussen *et al.* (1981):

$$r_i' = \frac{I}{M_i} \sum_j x_j \sum_k^G v_k^{(i)} R_k; \quad q_i' = \frac{I}{M_i} \sum_j x_j \sum_k^G v_k^{(i)} Q_k \quad (1)$$

where x_j is the molar fraction of the triglycerides of the canola oil or fatty acids of the commercial oleic acid and $\overline{M}_i$ is the average molecular weight of the canola oil or the commercial fatty acid

Following the procedure developed by Stragevitch and d'Avila (1997), adjustments of the parameters were made by minimization of the maximum likelihood objective function:

$$S = \sum_m^D \sum_n^N \left\{ \left(\frac{T_{nm}^{calc} - T_{nm}^{ex}}{\sigma_{T_{nm}}} \right)^2 + \sum_i^{C-1} \left[\left(\frac{w_{inm}^{I,calc} - w_{inm}^{I,ex}}{\sigma_{w_{inm}^I}} \right)^2 + \left(\frac{w_{inm}^{II,calc} - w_{inm}^{II,ex}}{\sigma_{w_{inm}^{II}}} \right)^2 \right] \right\} \quad (2)$$

where D is the total number of groups of data, N and C are the total number of tie-lines and total number of components in the group of data m , respectively. T is the temperature, w is the mass fraction, the subscripts i , n and m are component, tie-line and group number, respectively and the superscript I and II are the phases; ex and calc are experimental and calculated. $\sigma_{T_{nm}}$, $\sigma_{w_{inm}^I}$ and $\sigma_{w_{inm}^{II}}$ are the standard deviations observed for temperature and composition for both liquid phases. Tables 10 and 11 present the adjusted parameters for the two models.

The experimental data were compared to the calculated values by liquid-liquid flash using the adjusted parameters. The percent of deviation of the experimental mass fractions from the calculated ones can be found in Table 12. The average percent of deviation was calculated as follows:

$$\Delta w = 100 \sqrt{\frac{\sum_{i=1}^C \left[\left(w_i^{I,ex} - w_i^{I,calc} \right)^2 + \left(w_i^{II,ex} - w_i^{II,calc} \right)^2 \right]}{2NC}} \quad (3)$$

Table 9. Parameters r_i' and q_i' for canola oil, Riedel-deHaën oleic acid, and short-chain alcohols

Compound	r_i'	q_i'
Canola oil (1)	0.044012	0.035659
Commercial oleic acid (2)	0.044120	0.037476
Methanol (3)	0.059332	0.063916
Ethanol (4)	0.055905	0.056177
Isopropanol (5)	0.054065	0.052007
Water (7)	0.051068	0.077713

Table 10. NRTL parameters for the systems of canola oil (1) + oleic acid (2) + methanol (3); of canola oil (1) + oleic acid (2) + ethanol (4); of canola oil (1) + oleic acid (2) + ethanol (4) + water (7); of canola oil (1) + oleic acid (2) + isopropanol (5).

t (°C)	pair ij	A_{ij} (K)	A_{ji} (K)	α
20	12	-228.130	-85.432	0.20001
	13	-427.020	2549.600	0.20004
	23	-1176.800	2237.400	0.20001
	14	-94.972	1538.900	0.41875
	24	-1252.200	1666.700	0.20036
30	12	-226.62	-84.303	0.20757
	13	-534.21	2776.6	0.20000
	23	-1293.0	2413.0	0.20005
	14	-95.552	1514.3	0.45906
	24	-1349.5	1726.5	0.20015
	17	1926.0	1586.1	0.20001
	27	-335.59	3000.0	0.46811
	47	870.17	-836.66	0.21646
10	12	-229.41	-86.784	0.20000
	15	-151.94	1302.2	0.47000
	25	-900.36	1063.9	0.25016

Table 11. UNIQUAC parameters for the systems of canola oil (1) + oleic acid (2) + methanol (3); of canola oil (1) + oleic acid (2) + ethanol (4); of canola oil (1) + oleic acid (2) + ethanol (4) + water (7); of canola oil (1) + oleic acid (2) + isopropanol (5).

t (°C)	pair ij	A_{ij} (K)	A_{ji} (K)
20	12	276.880	-224.890
	13	390.730	-62.549
	23	132.910	-62.700
	14	241.060	-49.959
	24	-27.228	-18.710
30	12	308.64	-233.63
	13	360.61	-50.713
	23	298.89	-148.91
	14	229.22	-46.158
	24	-35.259	-7.6708
	17	351.43	-151.23
	27	336.60	-267.29
10	47	-132.64	-382.54
	12	245.34	-216.24
	15	166.55	-36.742
	25	-47.947	-28.221

The high deviation of the NRTL model for canola oil/ commercial oleic acid/ ethanol/ water showed that was not possible to obtain a group of parameters that describes, with accuracy, the liquid-liquid equilibrium of the ternary system (canola oil/ commercial oleic acid/ ethanol) and of the quaternary system (canola oil/ commercial oleic acid/ ethanol/water). The addition of water causes a high impact in the liquid-liquid equilibrium, mainly decreasing the mutual solubility oil-ethanol and the distribution coefficient of the commercial oleic acid.

The experimental data for the systems of canola oil, oleic acid, and anhydrous isopropanol at 20 °C and of canola oil, oleic acid and anhydrous n-propanol at 10 °C were not used, since they formed only a minimal heterogeneous area.

Figures 1-5 show the experimental and calculated tie-lines and the calculated binodal curve.

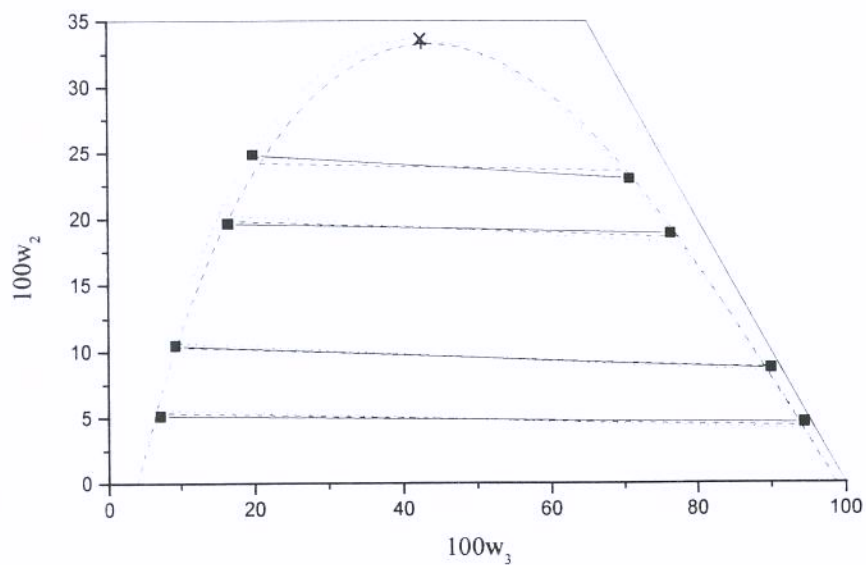


Figure 1. System of canola oil (1) + oleic acid (2) + methanol (3) at 20 °C (—■— experimental, - - - NRTL, . . . UNIQUAC, + plait point NRTL, x plait point UNIQUAC)

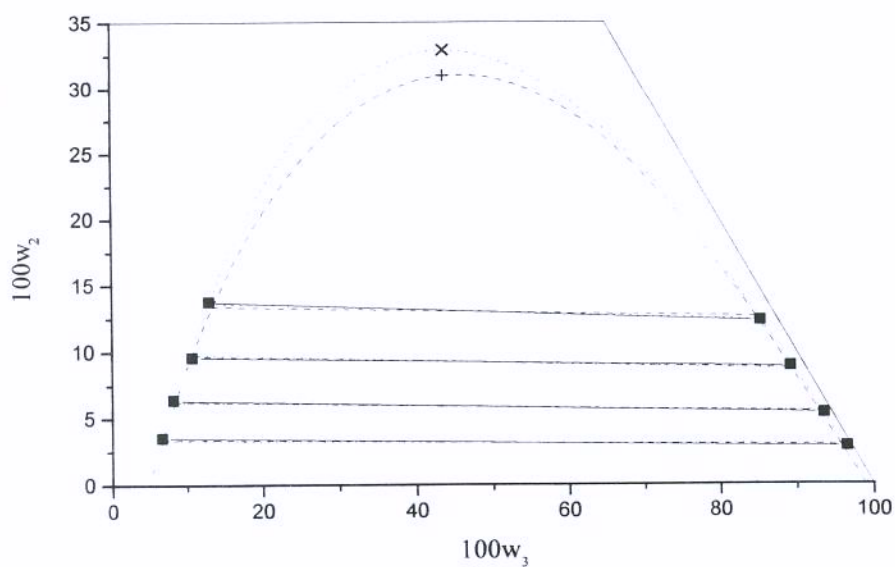


Figure 2. System of canola oil (1) + oleic acid (2) + methanol (3) at 30 °C (—■— experimental, - - - NRTL, . . . UNIQUAC, + plait point NRTL, x plait point UNIQUAC)

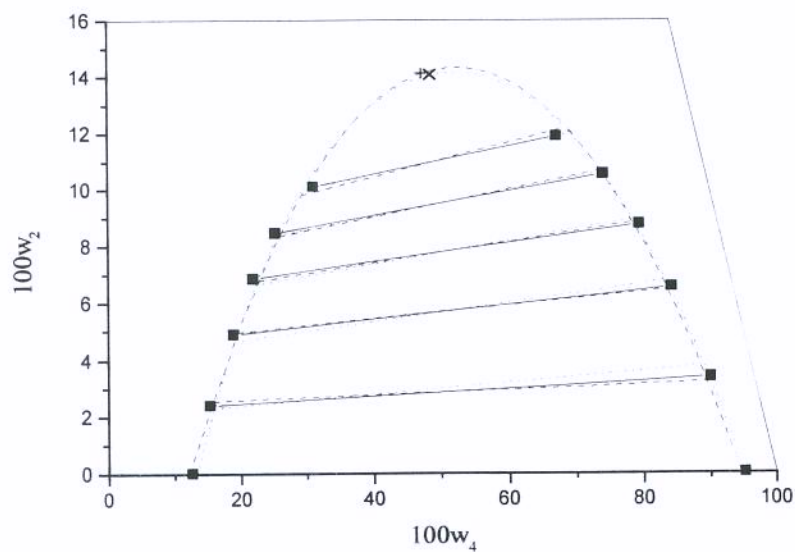


Figure 3. System of canola oil (1) + oleic acid (2) + ethanol (4) at 20 °C (—■— experimental, --- NRTL, ... UNIQUAC, + plait point NRTL, x plait point UNIQUAC)

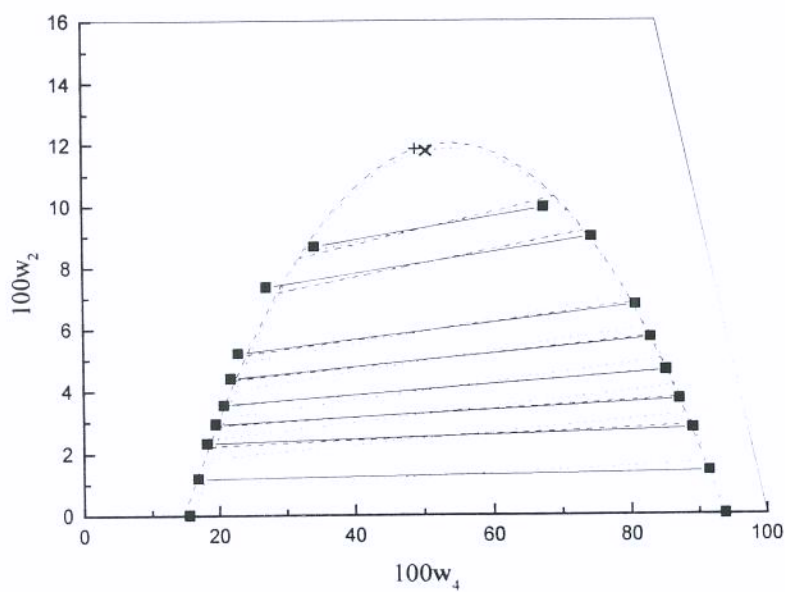


Figure 4. System of canola oil + oleic acid (2) + ethanol (4) at 30 °C (—■— experimental, --- NRTL, ... UNIQUAC, + plait point NRTL, x plait point UNIQUAC)

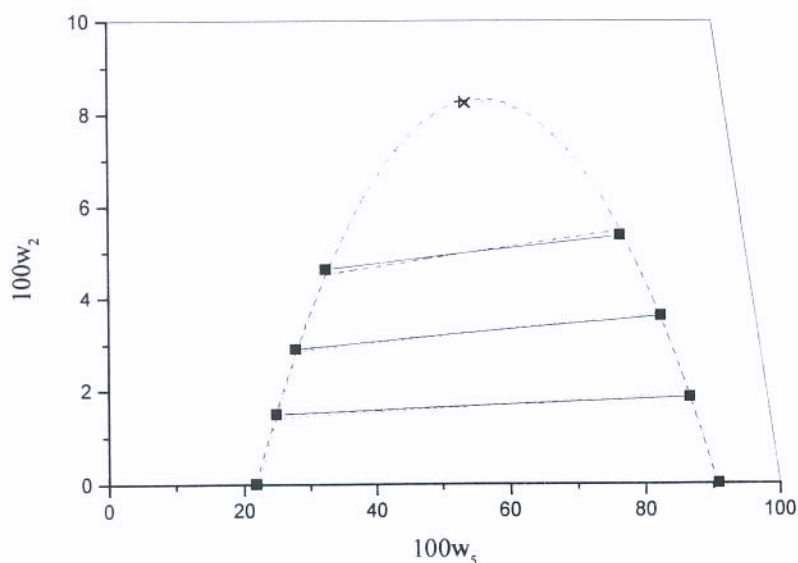


Figure 5. System of canola oil (1) + oleic acid (2) + isopropanol (5) at 10 °C

(—■— experimental, - - - NRTL, . . . UNIQUAC, + plait point NRTL, x plait point UNIQUAC)

Table 12. Average deviations in phase composition

System	$\Delta w(\%)$	
	NRTL	UNIQUAC
canola oil/ oleic acid/ methanol 20°C	0.53	0.55
canola oil/ oleic acid/ methanol 30°C	0.38	0.25
canola oil/ oleic acid/ ethanol 20°C	0.83	0.77
canola oil/ oleic acid/ ethanol 30°C	0.83	0.83
canola oil/ oleic acid/ isopropanol 10°C	0.12	0.16
canola oil/ oleic acid/ / ethanol/ water 30°C	1.09	0.28

For the systems studied, the information about mutual solubility of the oil and solvent is contained in the base tie-line of each diagram. It can be seen that for a given temperature the mutual solubility increases with an increase in the length of the carbon chain.

Figure 6 presents the distribution at 30 °C for the systems with methanol and ethanol as solvents. The coefficient of distribution (eq. 4) with ethanol is somewhat larger than one, while that for methanol is somewhat smaller. These results suggest that methanol has a somewhat lesser capacity for extraction of fatty acids, which can be explained by the lower polarity of the ethanol chain in relation to that of methanol. For the same reason, ethanol also dissolves more canola oil, thus presenting less

selectivity than methanol.

$$k_i = \frac{w_i^{II}}{w_i^I} \quad (4)$$

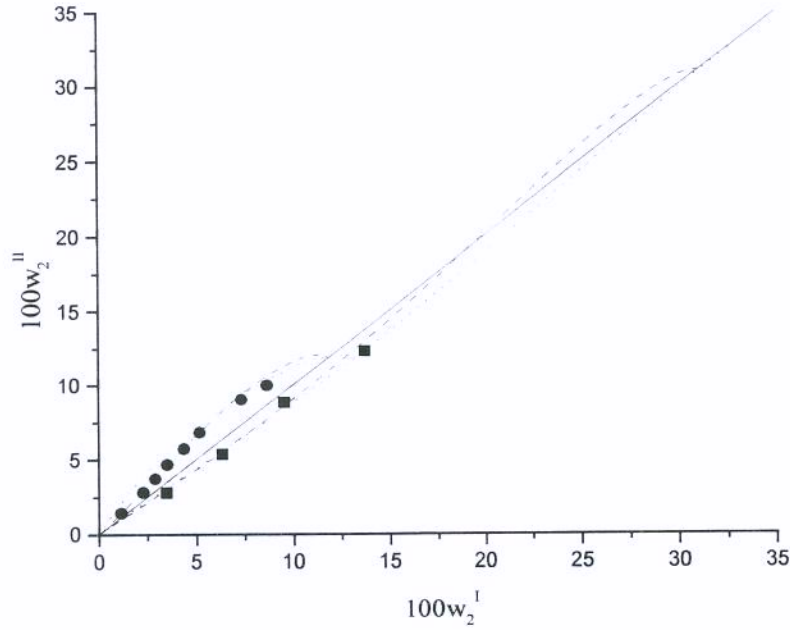


Figure 6. Distribution at 30 °C for systems of canola oil (1) + oleic acid (2) + methanol (3) and of canola oil (1) + oleic acid (2) + ethanol (4) (■ methanol, ● ethanol, - - - NRTL, . . . UNIQUAC)

The mutual solubility of oil and solvent for all systems increases with an increase in temperature. A comparison of Figures 1 with 2, and of 3 with 4 shows that the decrease in temperature from 30 to 20 °C caused a small increase in the two-phase region. In no case, however, did a significant change in the distribution coefficient occur. The increase in the heterogeneous region with only slight alterations in the distribution coefficient increases the selectivity of solvents upon a reduction of temperature.

3.6. Conclusion

For any given temperature, the increase in the length of the carbon chain of the solvent led to a

reduction in selectivity and an increase in the coefficient of distribution. For those solvents tested, methanol was the most selective solvent, but its distribution coefficient was less than one. Ethanol and isopropanol both have distribution coefficients greater than one, but ethanol is more selective. The size of the heterogeneous area increases with a decrease in temperature, especially for the system with ethanol.

The adjusted NRTL and UNIQUAC models expressed as mass fractions proved adequate and furnished practically identical liquid-liquid equilibria, even when commercial reagents with a very large number of components were used. It should be noted that, especially in the case of the UNIQUAC model, the good adjustments obtained in the present experiment are in contrast to those reported earlier in the literature (Zhang and Hill, 1991), as these authors were unable to obtain good adjustments for systems including a commercial reagent. It is probable that the great chemical similarity between the triglycerides of the canola oil and of the fatty acids in the commercial oleic acid may have contributed to the success of the use of the UNIQUAC model.

3.7. Acknowledgment

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CAPÍTULO 4

PREDICTION OF LIQUID-LIQUID EQUILIBRIUM FOR SYSTEMS OF VEGETABLE OILS, FATTY ACIDS, AND ETHANOL

**Eduardo Batista; Sandra Monnerat; Luiz Stragevitch; Carla G. Pina;
Cintia B. Gonçalves; Antonio J. A. Meirelles**

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Prediction of liquid-liquid equilibrium for systems of vegetable oils, fatty acids, and ethanol

Eduardo Batista; Sandra Monnerat; Luiz Stragevitch; Carla G. Pina; Cintia B. Gonçalves; Antonio J. A. Meirelles

Keywords:

Liquid-liquid equilibrium, vegetable oils, UNIFAC, ASOG

Summary

Group interaction parameters for the UNIFAC and ASOG models were specially adjusted for predicting liquid-liquid equilibrium (LLE) for systems of vegetable oils, fatty acids, and ethanol at temperatures ranging from 20 to 45 °C. Experimental liquid-liquid equilibrium data for systems of triolein, oleic acid, ethanol and of triolein, stearic acid, and ethanol were measured and utilized in the adjustment. The average percent deviation between experimental and calculated compositions was 0.79% and 0.52% for the UNIFAC and ASOG models, respectively. The prediction of liquid-liquid equilibrium for systems of vegetable oils, fatty acids, and ethanol were quite successful, with an average deviation of 1.31% and 1.32% for the UNIFAC and ASOG models, respectively.

4.1. Introduction

Liquid-liquid equilibrium data for systems of vegetable oils, fatty acids, and ethanol are scarce in the literature, yet such information is essential for the study of the deacidification of vegetable oils by liquid-liquid extraction. One feasible alternative which can extend the available results to other vegetable oils is the utilization of group contribution methods, UNIFAC (Fredenslund *et al.*, 1977) and ASOG (Kojima and Tochigi, 1979).

The previously-published group interaction parameters for the prediction of liquid-liquid equilibrium (Magnussen *et al.*, 1981) by the UNIFAC model are not satisfactory for the systems containing vegetable oils (Figure 1); for example, the average percentage of deviation for experimental data of systems containing canola oil, commercial oleic acid, and ethanol at temperatures of 20 to 30 °C is 11.2% in the mass fraction (Table 10), and the ASOG model cannot be used in such predictions due to the unavailability of certain necessary group interaction parameters.

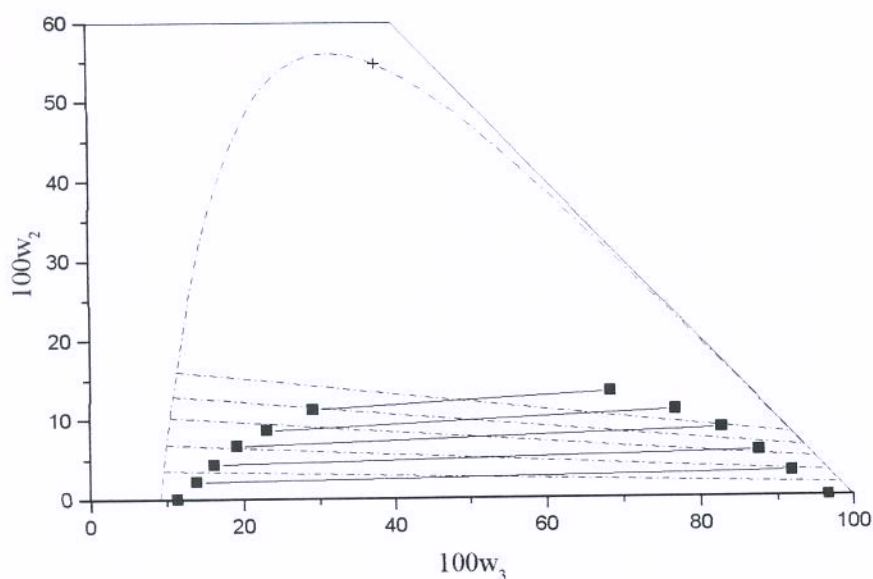


Figure 1. System of triolein (1) + oleic acid (2) + ethanol (3) at 20 °C (—■— experimental, --- Original UNIFAC, + plait point)

It is thus necessary to adjust new parameters for these group contribution methods when fatty systems are involved, as is the case here. The loss of convenience represented by the utilization of a single set of parameters for any class of compounds is, however, compensated by the improvements in the results predicted, as well as by the possibility of predicting liquid-liquid equilibria for systems involving a large number of vegetable oils, triglycerides and fatty acids.

The project reported in this paper was designed to develop a prediction method for liquid-liquid equilibrium of systems of vegetable oils, fatty acids, and ethanol. It is divided into three parts: the measurement of liquid-liquid equilibria of ternary systems of triolein, oleic acid, and ethanol and of triolein, stearic acid, and ethanol; the readjustment of certain group interaction parameters of the UNIFAC and ASOG models to these data; and the prediction of the liquid-liquid equilibria of systems containing vegetable oils, fatty acids, and ethanol.

4.2. Materials

Triolein and oleic acid used in the experiments are from Sigma, both with a minimal purity of 99% and oleic acid. The stearic acid, also from Sigma, has a purity greater than 90%, while the anhydrous ethanol was acquired from Merck, with a minimal purity of 99.8%.

Refined corn oil and commercial oleic acid from Riedel-deHaën were analyzed using the procedures previously proposed for canola oil (Batista *et al.*, 1999). The fatty acid composition of the corn oil is presented in Table 1.

Table 1. Fatty acid composition of corn oil

Symbol	Fatty Acid		M (g.mol ⁻¹)	% molar	% mass
M	Miristic	C14:0 ^(*)	228.38	0.0200	0.0164
P	Palmitic	C16:0	256.43	12.8500	11.8457
Po	Palmitoleic	C16:1	254.41	0.1300	0.1189
S	Stearic	C18:0	284.48	2.1500	2.1988
O	Oleic	C18:1	282.47	34.3200	34.8506
Li	Linoleic	C18:2	280.45	49.4400	49.8454
A	Arachidic	C20:0	312.54	0.8200	0.8208
Le	Linolenic	C18:3	278.44	0.2700	0.3034

^(*) C_x:y - x = number of carbons, y = double bonds M = molecular weight

Based on this fatty acid composition, it was possible to determine the probably triglyceride composition of the corn oil (Table 2) using the computational method developed by Antoniosi Filho *et al.* (1995). The following aspects should be considered: first, the main triglyceride is the component of greatest concentration in the set of isomers with x carbons and y double bonds. Thus, certain fatty acids which appear in Table 1 (M, Po, and A) do not appear explicitly in Table 2; for example, the triglyceride PPoS is part of the group 50:1, with a main triglyceride of PPO. Moreover, groups with a total triglyceride concentration less than 0.5% are ignored. The average molecular weight of the corn oil was 872.6131 g.mol⁻¹.

The probable composition of fatty acids of commercial oleic acid is presented in Table 3. The molecular weight obtained for the oleic acid was equal to 278.5868 g.mol⁻¹.

Table 2. Probable composition of triglyceride of corn oil.

Group	Main Triglyceride	M (g.mol ⁻¹)	% molar	% mass
50:1 ^(*)	PPO	833.37	1.7300	1.6540
50:2	PPLi	831.35	2.5300	2.4141
52:1	PSO	861.45	0.5800	0.5717
52:2	POO	859.40	5.4600	5.3741
52:3	POLi	857.39	13.3700	13.1387
52:4	PLiLi	855.37	9.9400	9.7409
54:2	SOO	887.46	0.9500	0.9637
54:3	OOO	885.44	6.3400	6.4336
54:4	OOLi	883.43	19.4100	19.6457
54:5	OLiLi	881.41	25.9400	26.2009
54:6	LiLiLi	879.43	13.1400	13.2407
54:7	LiLiLe	877.38	0.6200	0.6219
Total			100.0000	100.0000

^(*) X:Y - X number of carbons (except carbons of glycerol) and Y double bonds

Table 3. Fatty acid composition of Riedel-deHaën oleic acid

Fatty Acid	% molar	% mass
M	1.5889	1.3025
P	4.3945	4.0450
Po	6.3728	5.8197
S	0.5951	0.6077
O	81.9848	83.1276
Li	5.0178	5.0514
Le	0.0461	0.0461

4.3. Experimental Procedure

Equilibrium cells equivalent to those of Silva *et al.* (1997) for the determination of liquid-liquid equilibrium data were used. The cell temperature was controlled by thermostatic bath (Cole Parmer, Model 12101-15, accurate to ± 0.01 °C) and the component quantity was determined by weighing on a Sartorius analytical balance (Model A200 S, accurate to 0.0001 g). The mixture was stirred vigorously with a magnetic stirrer (FISATOM, Model 752A) for at least 15 minutes and left to rest for 4 hours. This led to the formation of two clear and transparent phases, with a well-defined interface.

The quantity of fatty acids was determined using potentiometric titration (Modified AOCS

Method Ca 5a-40, 1977) with an automatic burette (METROHM, Model Dosimat 715); the solvent was determined by evaporation in an EDG vacuum oven (Model EIV-1). Having determined the concentration of fatty acids and the solvent, the concentration of triglycerides was obtained by the difference. Measurements were made in triplicate, with standard deviations of 0.035% for the triolein, 0.056% for corn oil, 0.038% for fatty acids, and 0.012% for ethanol.

Table 4 shows the overall experimental composition of the mixtures and the corresponding tie-lines for systems of triolein, oleic acid and anhydrous ethanol, and Table 5 shows the overall experimental composition of the mixtures and the corresponding tie-lines for the systems of triolein, stearic acid and anhydrous ethanol. The fatty acids, stearic and oleic, were chosen to determine the effect of the presence of double bonds on the distribution coefficient.

Table 4. Liquid-liquid equilibrium data for the ternary system of triolein (1) + oleic acid (2) + anhydrous ethanol (3).

t (°C)	Overall Composition			Alcohol Phase			Oil Phase		
	100w ₃	100w ₂	100w ₁	100w ₃	100w ₂	100w ₁	100w ₃	100w ₂	100w ₁
20	53.42	—	46.58	96.75	—	3.25	11.41	—	88.59
	54.51	2.80	42.69	91.96	3.15	4.89	13.97	2.15	83.88
	54.28	5.24	40.48	87.70	5.82	6.48	16.28	4.35	79.37
	52.03	7.68	40.29	82.86	8.72	8.42	19.24	6.69	74.07
	49.73	10.13	40.14	76.81	11.03	12.16	23.16	8.64	68.20
	49.31	12.68	38.01	68.39	13.34	18.27	29.25	11.22	59.53
30	55.80	—	44.20	95.72	—	4.28	13.97	—	86.03
	54.98	2.83	42.19	90.40	3.19	6.41	17.10	2.26	80.64
	53.73	2.83	43.44	90.02	3.30	6.68	16.86	2.37	80.77
	54.99	5.28	39.73	85.42	5.75	8.83	20.09	4.47	75.44
	52.88	5.80	41.32	83.76	6.68	9.56	20.53	5.10	74.37
	52.10	7.67	40.23	79.50	8.46	12.04	24.04	6.81	69.15
	50.08	8.20	41.72	78.17	9.04	12.79	26.09	7.27	66.64
	49.80	10.21	39.99	71.52	10.71	17.77	30.27	8.95	60.78

w_i = mass fraction component i

Table 5. Liquid-liquid equilibrium data for the ternary system of triolein (1) + stearic acid (4) + anhydrous ethanol (3).

t (°C)	Overall Composition			Alcohol Phase			Oil Phase		
	100w ₃	100w ₄	100w ₁	100w ₃	100w ₄	100w ₁	100w ₃	100w ₄	100w ₁
30	54.11	2.48	43.41	90.95	2.40	6.65	16.89	1.99	81.12
	48.53	6.12	45.35	83.96	6.34	9.69	22.79	5.52	71.69
45	50.44	9.14	40.42	76.88	8.72	14.40	34.40	8.62	56.98

The experimental data for the system of corn oil, commercial oleic acid and anhydrous ethanol at 25 °C are presented in Table 6. All concentrations are expressed as percentage of mass.

Table 6. Liquid-liquid equilibrium data for ternary the system of corn oil (5) + commercial oleic acid (6) + anhydrous ethanol (3).

t (°C)	Overall Composition			Alcohol Phase			Oil Phase		
	100w ₃	100w ₆	100w ₅	100w ₃	100w ₆	100w ₅	100w ₃	100w ₆	100w ₅
25	52.08	—	47.92	94.20	—	5.80	14.27	—	85.73
	51.20	2.40	46.40	89.85	2.62	7.53	16.78	1.88	81.34
	50.04	4.90	45.06	84.89	5.46	9.65	18.44	4.28	77.28
	50.31	7.91	41.78	76.27	8.75	14.98	25.56	6.94	67.50
	49.43	10.03	40.54	67.63	10.82	21.55	32.68	9.19	58.13

4.4. Modeling

Following the procedure developed by Stragevitch and d'Avila (1997), adjustments of group interaction parameters of the UNIFAC and ASOG models were made by minimization of the maximum likelihood objective function.

The groups most characteristic of fatty systems in alcoholic solutions were selected. For the UNIFAC model, the following groups were selected: CH₂COO, CH=CH, COOH and OH and only the interaction parameters with these groups were readjusted. The parameters involving interaction with other groups present in the system were taken from Magnussen *et al.* (1981). Table 7 presents the new group interaction parameters for the UNIFAC model.

Table 7. New UNIFAC group interaction parameters

m	n	a_{mn}	a_{nm}
CH=CH	CH ₂ COO	-149.180	-2692.200
CH=CH	COOH	-851.340	194.320
CH=CH	OH	1172.400	-2457.900
CH ₂ COO	COOH	17.081	-167.6700
CH ₂ COO	OH	511.190	247.520
COOH	OH	-424.310	70.196

For the ASOG model, the following groups were selected: COO, C=C, COOH and OH. The other parameters were taken from Tochigi *et al.* (1990). Table 8 presents the new group interaction parameters.

Table 8. New ASOG group interaction parameters

k	l	$m_{k,l}$	$m_{l,k}$	$n_{k,l}$	$n_{l,k}$
C=C	COOH	0.23690	13.15200	435.010	-3000.000
C=C	COO	-0.84113	6.12620	710.960	-1584.800
C=C	OH	1.19260	-4.42290	-146.170	-1881.600
COOH	COO	-2.33200	1.68420	868.940	109.390
COOH	OH	-4.64600	-1.188190	2643.400	459.170
COO	OH	2.10340	0.06637	-859.160	-654.970

The experimental data were compared to those calculated by liquid-liquid flash using the adjusted parameters.

Figures 2 and 3 present the experimental and calculated tie-lines and the calculated heterogeneous area for the system of triolein, oleic acid and ethanol. Table 9 shows the average percent deviation in phase composition for this system.

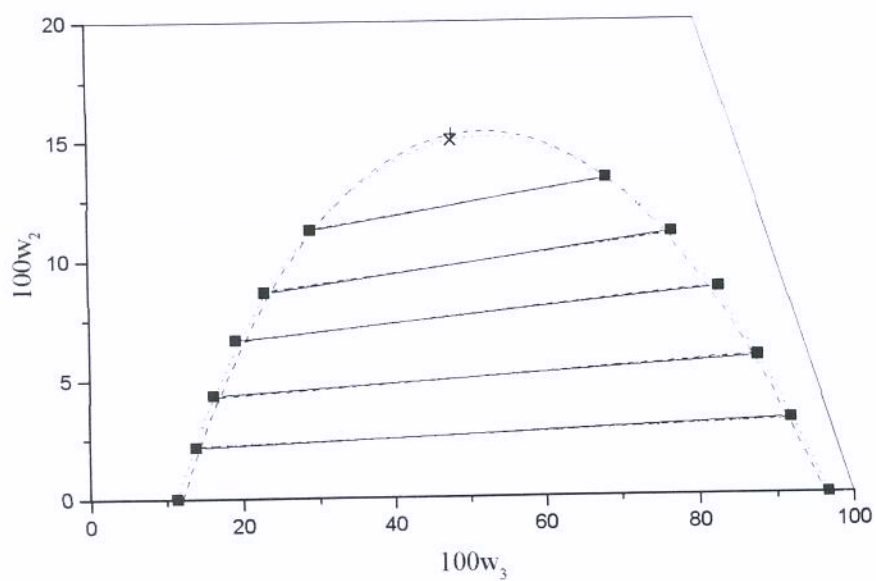


Figure 2. System of triolein (1) + oleic acid (2) + ethanol (3) at 20 °C (—■— experimental, --- UNIFAC, ··· ASOG, + plait point UNIFAC, x plait point ASOG)

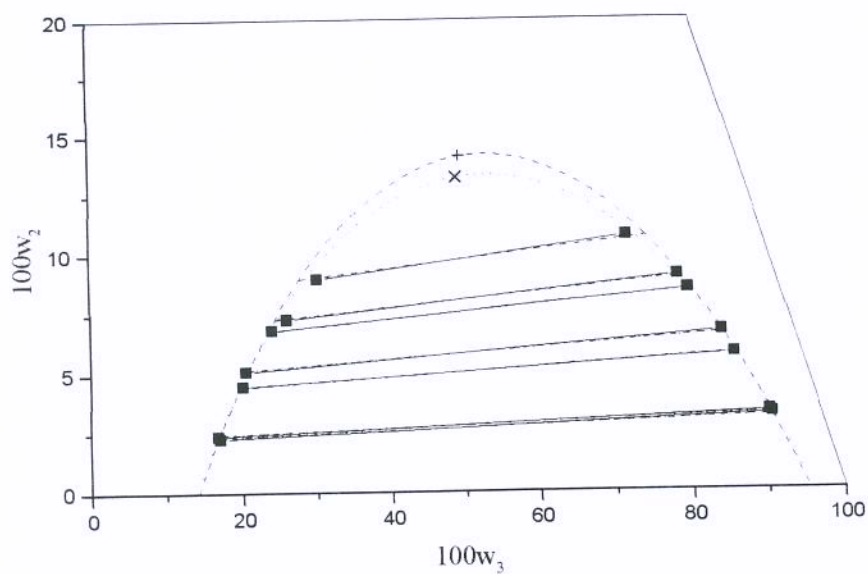


Figure 3. System of triolein (1) + oleic acid (2) + ethanol (3) at 30 °C (—■— experimental, --- UNIFAC, ··· ASOG, + plait point UNIFAC, x plait point ASOG)

Table 9 Average percent deviation in phase composition

System	Original UNIFAC	$\Delta w(\%)$	
		UNIFAC	ASOG
Triolein/ Oleic Acid/ Ethanol 20 °C	9.00	0.70	0.35
Triolein/ Oleic Acid/ Ethanol 30 °C	9.26	0.87	0.55
Triolein/ Stearic Acid/ Ethanol 30 °C	7.38	0.68	0.52
Triolein/ Stearic Acid/ Ethanol 45 °C	15.95	1.10	1.00
Global	9.52	0.79	0.52

Figure 4 presents the distribution of oleic acid and stearic acid at 30 °C. At this temperature, pure stearic acid is in a solid state, and the tie-line with the overall composition of the mixture containing 6.12% (w/w) of stearic acid is close to the limit of solubility (Bailey, 1950). Thus, the tie-line with the overall composition of the mixture containing 9.14% (w/w) of stearic acid (Table 5) was measured at 45 °C to avoid the formation of crystals of this acid.

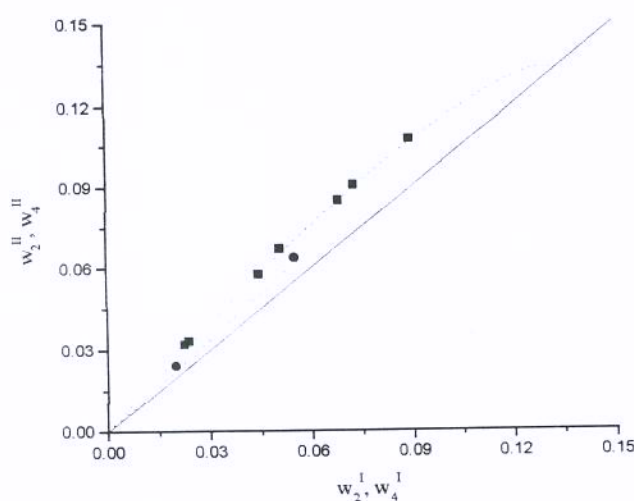


Figure 4. Distribution of the fatty acids in the ternary systems at 30 °C (■ oleic acid (2),
• stearic acid (4), --- ASOG)

It can be seen in Figure 4 that the solubility of fatty acids in ethanol increases with a increase in insaturation. In general, solubility decreases with an increase in molecular weight and increases with the number of double bonds (Bailey, 1950).

4.5. Prediction of liquid-liquid equilibrium for multicomponent systems

The adjusted parameters of the UNIFAC and ASOG models were tested in the prediction of liquid-liquid equilibria in systems of vegetable oils, fatty acids, and ethanol available in the literature. Experimental data for the following systems were used to validate the model: canola oil, commercial oleic acid, and ethanol (Batista *et al.*, 1999), corn oil, commercial oleic acid, and ethanol (from the present paper), and Spanish olive oil, oleic acid, and ethanol (Rius and Martinez Moreno, 1947).

For the olive oil system, the probable triglyceride composition proposed by Constante (1988) was used. The average molecular weight calculated for olive oil was $877.2282 \text{ g.mol}^{-1}$.

Liquid-liquid flash for the calculation of phase compositions was executed based on the overall experimental composition of the mixtures. The composition of oils and commercial oleic acid were used to expand the ternary overall composition of the mixture to the multicomponent. After the multicomponent flash, the mass fractions of triglycerides for each of the phases were grouped and compared to the experimental composition of the phases in vegetable oils. The same procedure was utilized for the fatty acids. The mass fractions of the different fatty acids were grouped and compared to the composition observed. Table 10 presents the average deviation for the systems studied.

Table 10. Average percent deviations for the systems studied

System	$\Delta w(\%)$		
	Original UNIFAC	UNIFAC	ASOG
Canola Oil/ Commercial Oleic Acid/ Ethanol 20 °C	11.38	1.87	1.34
Canola Oil/ Commercial Oleic Acid/ Ethanol 30 °C	11.00	0.79	1.54
Corn Oil/ Commercial Oleic Acid/ Ethanol 25 °C	11.99	0.69	0.68
Olive Oil/ Commercial Oleic Acid/ Ethanol 25 °C	5.56	1.58	1.31
Global	10.16	1.31	1.32

Figures 5 to 8 show the experimental tie-lines predicted for the systems of vegetable oil, fatty acids, and ethanol.

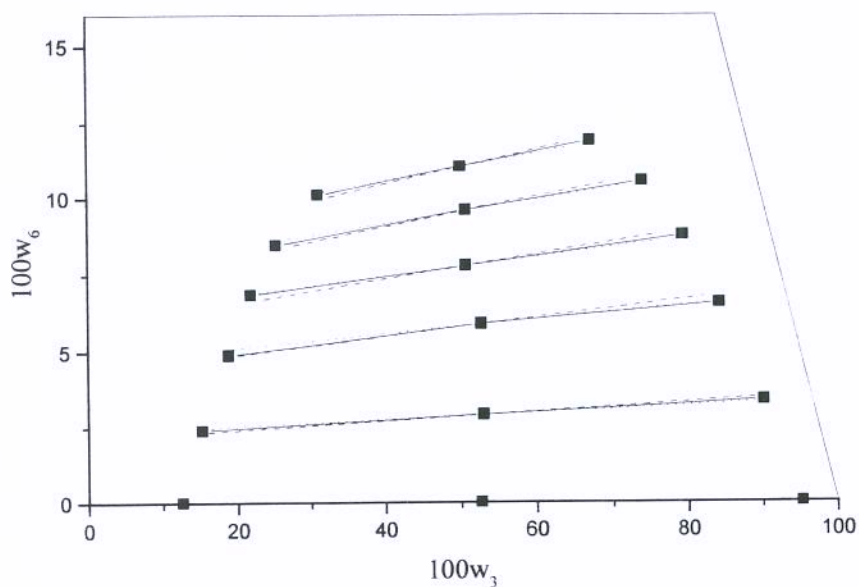


Figure 5. Prediction of liquid-liquid equilibrium for the system of canola oil (7) + commercial oleic acid (6) + ethanol (3) at 20 °C (—■— experimental, - - - UNIFAC, . . . ASOG)

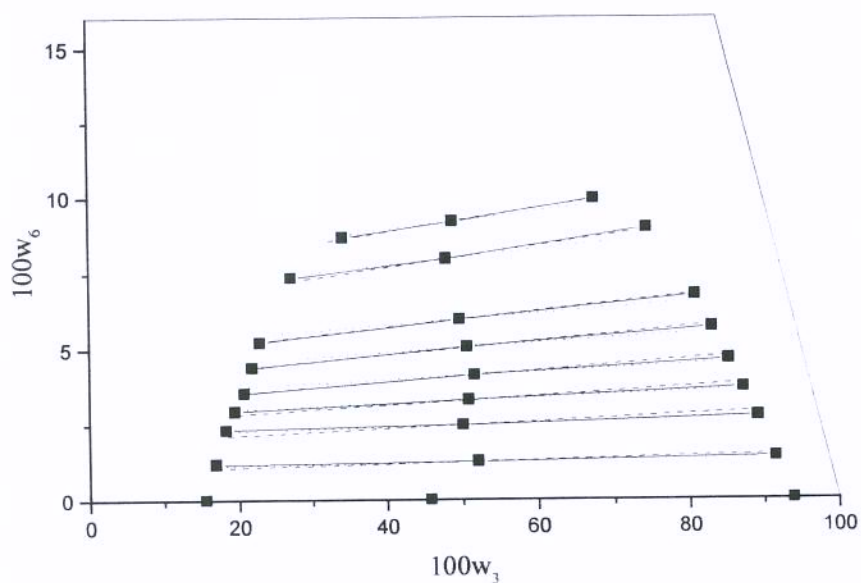


Figure 6. Prediction of liquid-liquid equilibrium for the system of canola oil (7) + commercial oleic acid (6) + ethanol (3) at 30 °C (—■— experimental, - - - UNIFAC, . . . ASOG)

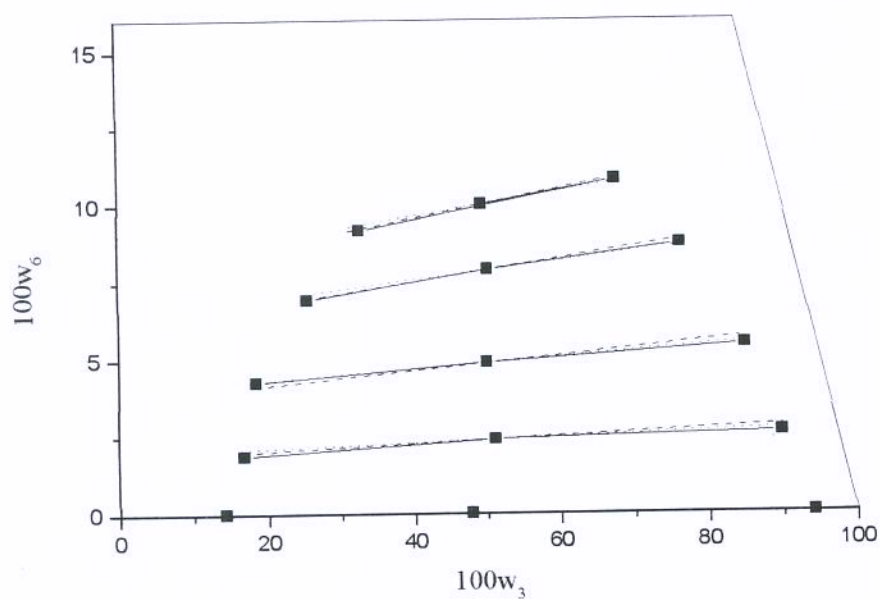


Figure 7. Prediction of liquid-liquid equilibrium for the system of corn oil (5) + commercial oleic acid (6) + ethanol (3) at 25 °C (—■— experimental, - - - UNIFAC, . . . ASOG)

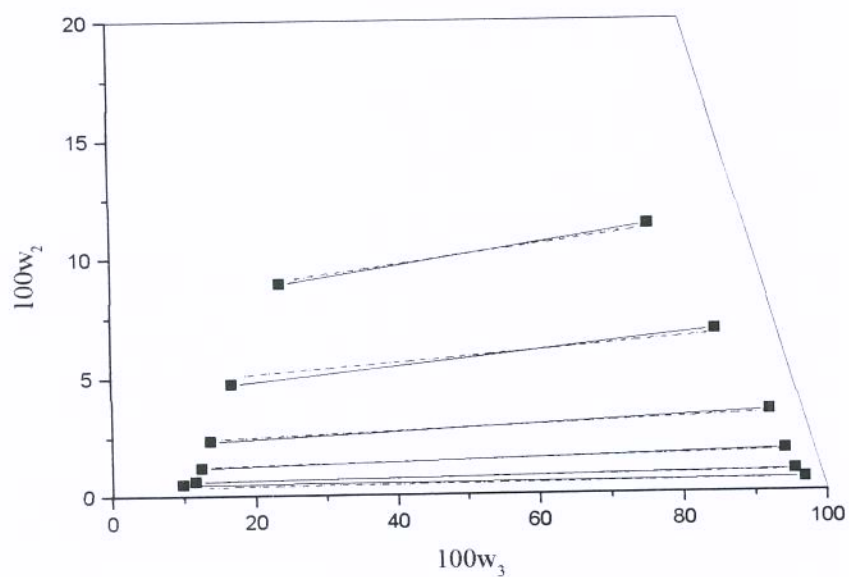


Figure 8. Prediction of liquid-liquid equilibrium for the system of olive oil (8) + oleic acid (2) + ethanol (3) at 25 °C (—■— experimental, - - - UNIFAC, . . . ASOG)

In addition to these multicomponent systems, the prediction was extended to systems with other solvents, such as those of canola oil, commercial oleic acid and methanol and of canola oil, commercial oleic acid, ethanol and water (Batista *et al.*, 1999). The mean percent deviations are presented in Table 11.

Table 11 Average percent deviations for systems with other solvents

System	$\Delta w(\%)$		
	Original UNIFAC	UNIFAC	ASOG
Canola Oil/ Commercial Oleic Acid/ Methanol 20 °C	8.05	3.07	4.66
Canola Oil/ Commercial Oleic Acid/ Methanol 30 °C	3.89	1.86	4.42
Canola Oil/ Commercial Oleic Acid/ Ethanol / Water 30 °C	5.71	2.33	2.98

The prediction for the system of ethanol and water as a solvent overestimated the concentration of canola oil and fatty acids in the oil phase, while simultaneously overestimating the amount of ethanol and water in the alcoholic phase, resulting in somewhat greater values for the average percent deviation.

4.6. Conclusion

The parameters for the UNIFAC and ASOG group contribution models presented here make predictions of liquid-liquid equilibrium possible for systems of vegetable oils, fatty acids, and ethanol between the temperatures of 20 °C and 45 °C. The improvements in the results predicted, as well as by the possibility of predicting liquid-liquid equilibrium for systems involving a large number of vegetable oils, triglycerides and fatty acids will support study of the deacidification of vegetable oils with better accuracy.

4.7. Acknowledgment

This work was supported financially by research grants from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP - Proc. 1997/10630-7) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

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Apêndice A.

Se considerarmos a provável composição em triglicerídeos do azeite de oliva a partir de sua composição em ácidos graxos

Table A1 Fatty acid composition of olive oil

Symbol	Fatty Acid		M (g.mol ⁻¹)	% molar	% mass
M	Miristic	C14:0 ^(*)	228.38	0.0564	0.0462
P	Palmitic	C16:0	256.43	13.8104	12.7079
Po	Palmitoleic	C16:1	254.41	1.9235	1.7560
S	Stearic	C18:0	284.48	2.4897	2.5415
O	Oleic	C18:1	282.47	75.6797	76.7099
Li	Linoleic	C18:2	280.45	4.5919	4.6211
Le	Linolenic	C18:3	278.44	0.6938	0.6932
A	Arachidic	C20:0	312.54	0.3296	0.3697
B	Behenic	C22:0	340.59	0.0756	0.0924
Lg	Lignoceric	C24:0	368.65	0.3493	0.4621
				100.0000	100.0000

^(*) Cx:y - x = number of carbons, y = double bounds

M = molecular weight

Table A2 Probable triacylglyceride composition of olive oil

Group	Main Trygliceride	M (g.mol ⁻¹)	% molar	% mass
50:1 ^(*)	POP	833.37	4.4778	4.2681
50:2	PpoO	834.39	1.6054	1.5321
52:1	POS	861.45	1.6074	1.5838
52:2	POO	859.4	24.5994	24.1800
52:3	PoOO	860.43	6.3561	6.2553
52:4	POLe	858.41	0.9470	0.9297
54:2	SOO	887.46	4.4282	4.4948
54:3	OOO	885.44	44.8862	45.4578
54:4	OOLi	883.43	8.1695	8.2548
54:5	OOLe	884.45	1.7144	1.7343
56:2	OOA	918.56	0.5919	0.6219
60:2	OOLg	974.66	0.6166	0.6874
			100.0000	100.0000

^(*) X:Y - X number of carbons (except carbons of glycerol) and Y double bounds

Table A3. Average percent deviations for other systems studied

System	$\Delta w(\%)$	
	Original UNIFAC	UNIFAC
Olive Oil/ Commercial Oleic Acid/ Ethanol 25 °C (*)	5.65	1.50
Olive Oil/ Commercial Oleic Acid/ Ethanol (4.98 %) 25 °C	5.85	4.38
Corn Oil/ Commercial Oleic Acid/ Ethanol (5 %) 25 °C	6.72	3.24
Corn Oil/ Commercial Oleic Acid/ Ethanol (8 %) 25 °C	4.68	3.37
Corn Oil/ Commercial Oleic Acid/ Ethanol (12 %) 25 °C	6.35	4.81
Corn Oil/ Commercial Oleic Acid/ Ethanol (18 %) 25 °C	5.33	4.49

(*) Considerando a composição em triglicerídeos da Tabela A2

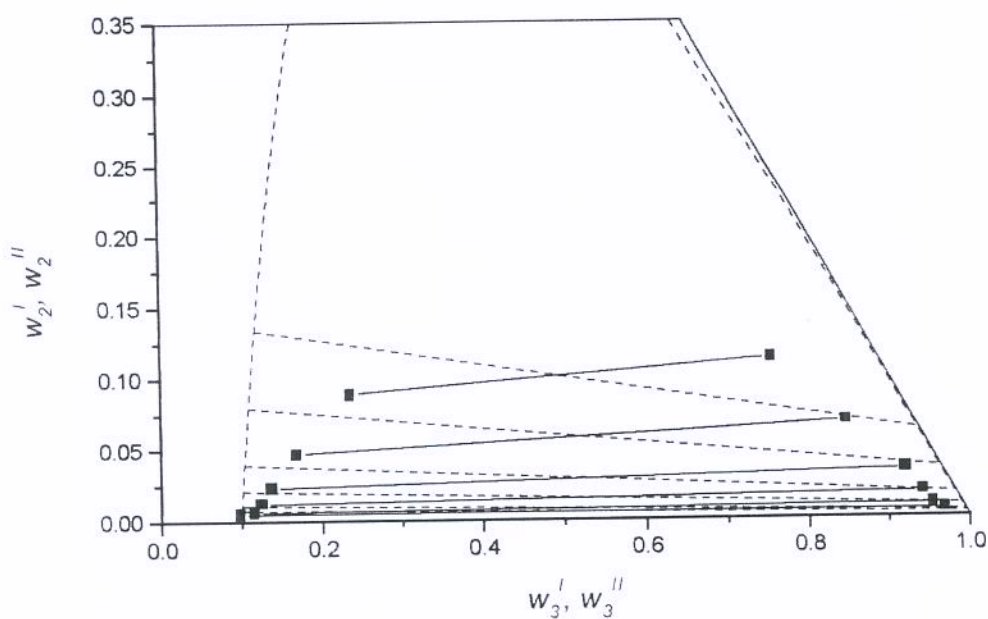


Figure A1 System of olive oil (1) + oleic acid (2) + ethanol (3) at 25 °C (-■- experimental, - - - Original UNIFAC)

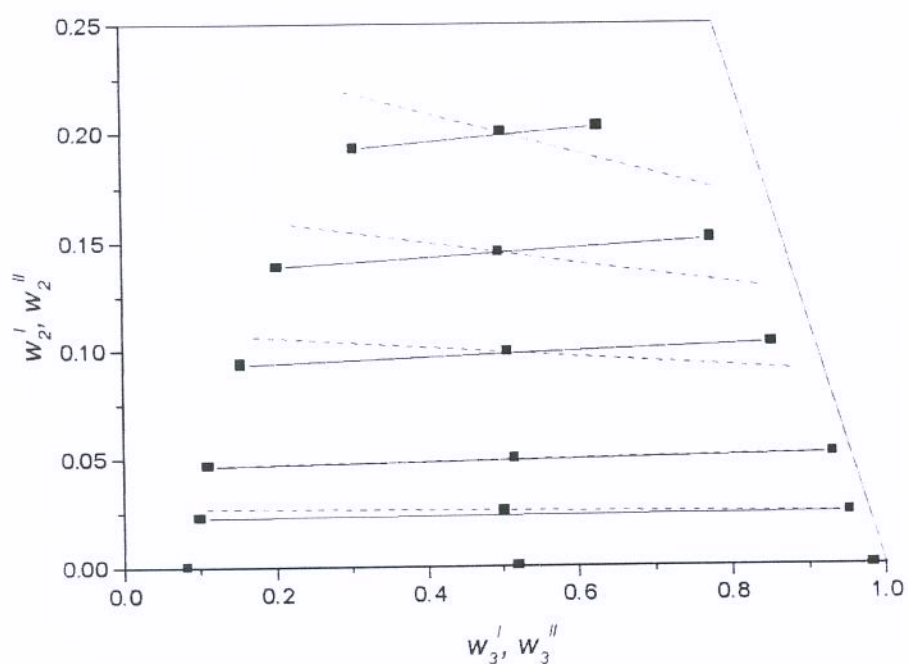


Figure A2 Prediction of liquid-liquid equilibrium for the system corn oil (1) + oleic acid (2) + aqueous ethanol (3) at 25 °C (-■- experimental, - - - UNIFAC)

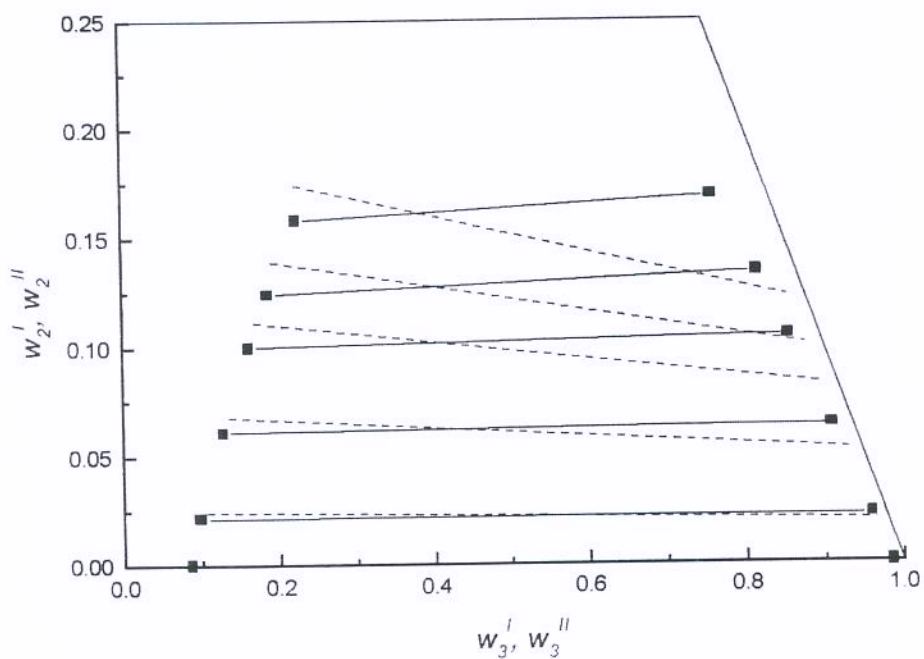


Figure A3 Prediction of liquid-liquid equilibrium for the system canola oil (1) + oleic acid (2) + aqueous ethanol (3) at 30 °C (-■- experimental, - - - UNIFAC)

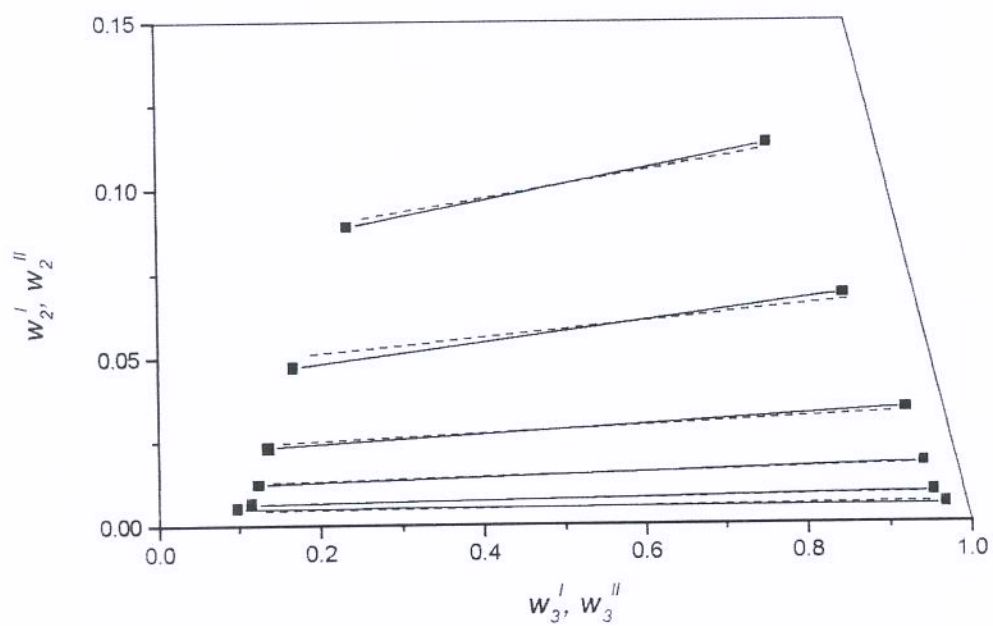


Figure A4 Prediction of liquid-liquid equilibrium for the system olive oil (1) + oleic acid (2) + ethanol (3) at 25 °C (-■- experimental, - - - UNIFAC)

CAPÍTULO 5

SIMULATION OF THE DEACIDIFICATION OF VEGETABLE OIL BY LIQUID-LIQUID EXTRACTION

E. Batista, M. R. Wolf Maciel and A. J. A. Meirelles

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Simulation of the Deacidification of Vegetable Oil by Liquid-Liquid Extraction

E. Batista⁽¹⁾, M. R. Wolf Maciel⁽²⁾ and A. J. A. Meirelles⁽¹⁾

⁽¹⁾ Physical Separation Laboratory, Faculty of Food Engineering , State University of Campinas (UNICAMP), CP 6121, CEP 13083-970, Campinas- SP, Brasil, e-mail:

tomze@ceres.fea.unicamp.br

⁽²⁾ Separation Process Development Laboratory, Faculty of Chemical Engineering, State University of Campinas (UNICAMP), CP 6066, CEP 13083-970, Campinas- SP, Brasil, e-mail:

wolf@feq.unicamp.br

Abstract

Crude vegetable oils present undesirable component, such as free fatty acids. They can be removed by alkali refining as well as physical refining. The liquid-liquid extraction is an alternative process because it reduces the energy consumption without losses of natural components and is carried out at room temperature and atmospheric pressure. This work aims at studying the simulation of the deacidification of vegetable oil by liquid-liquid extraction using surface response analysis. The results present an optimal region to obtain minimum free fatty acids in the refined oil with minimum loss of neutral oil

5.1. Introduction

The liquid-liquid extraction can be used in the separation of components with close boiling points, in the recovery of components of diluted solutions, in the separation of azeotropes, in the separation of termolable products, in the separation of components with high boiling point or when the separation by distillation requests a great consumption of energy. It can be accomplished at moderate temperature and atmospheric pressure (Treybal, 1981; Hamm, 1992)

In food and pharmaceutical industry, the liquid-liquid extraction can be used in the recovery of vitamins, in the separation of caffeine, penicillin, aroma and fragrance, in the wash of neutral oil with water to remove soaps, in the fractionating of lecithin and in the fractionating of oils with solvents.

In the case of vegetable oils, according to Thomopoulos (1971), the deacidification using solvent is based on the difference of solubility of free fatty acids and neutral triglyceride in the solvent and on the difference of the boiling point of the solvent and fatty acids. The deacidification of vegetable oils can be accomplished with several solvents: acetone, ethyl acetate, furfural, propanol, isopropanol, butanol, ethanol, methanol, ethyl methyl cetone.

Batista *et al.* (1999a) used various solvents, methanol, ethanol, n-propanol, isopropanol, aqueous ethanol in the deacidification of canola oil. They verified that ethanol and aqueous ethanol were the best solvents to the deacidification.

This work are focused on the simulation of the deacidification of vegetable oil employing the surface response analysis as a tool.

Batista and Meirelles (1998) used surface response analysis for optimize a distillation process and concluded that the factorial design is a powerful tool in the analysis of the effect of the studied variables. For this reason this technique was used to analyze the studied variables used in liquid-liquid extraction.

5.2. Phase Equilibrium

In a first, for simulation of liquid-liquid extraction processes, it is important to correlate activity coefficient models with liquid-liquid equilibrium experimental data to describe the phase equilibrium. A practical solution for this problem was already presented by Sorensen (1981). Stragevitch and D'Avila (1997) presented an algorithm based on the maximum likelihood. This algorithm can be considered a superior technique because it takes in consideration the uncertainties of the experimental data.

Activity coefficient models in their original form are expressed in mole fraction. Due to the difference in the molecular weights of the triglyceride (or triglyceride mixture) and the short chain solvent, it is more suitable use the mass fraction. Oishi and Prausnitz (1978) presented the modifications for UNIQUAC and UNIFAC models applied to polymer solutions, which presents a much more significant difference in the molecular weights. They concluded that those model showed good results for phase equilibrium.

Batista *et al.* (1999b) adjusted new parameters of the modified UNIFAC model, according to Oishi and Prausnitz (1978), to ternary system data. These ternary system were composed of a

pure triglyceride (triolein), a pure fatty acid (oleic acid) and anhydrous ethanol. The quality of these new parameter were tested in multicomponent systems (Batista et al., 1999a). The results showed an enormous improvement in prediction of fatty systems.

5.3. Characterization Of Canola Oil

Batista et al. (1999a) analyzed refined canola oil of the Purilev brand by gas chromatography of methyl esters. The fatty acid composition of the canola oil is presented in Table 1.

Table 1 Fatty acid composition of refined canola oil

Fatty Acid	Symbol	% mass
Myristic	M	0.0469
Palmitic	P	6.7565
Palmitoleic	Po	0.1736
Stearic	S	2.1305
Oleic	O	48.4533
Linoleic	Li	32.0275
Arachidic	A	0.5369
Linolenic	Le	9.2365
Behenic	B	0.3602
Erucic	E	0.2785
		100.0000

From this fatty acid composition it was possible to determine the probable triglyceride composition of the oil (Table 2) by using the computational method developed by Antoniosi Filho *et al.* (1995). The principal triglyceride represents the component of greatest concentration in the isomer set with x carbons and y double bonds

Table 2 Probable triglyceride composition of canola oil

Group		Principal triglyceride	MW (g/gmol)	% mass
1	50:1 ^(*)	PPO	833.37	0.7185
2	50:2	PPLi	831.35	0.5591
3	52:2	POO	859.40	5.6384
4	52:3	POLi	857.39	7.3253
5	52:4	PLiLi	855.37	4.5953
6	52:5	PLiLe	853.36	1.4763
7	54:2	SOO	887.46	1.6817
8	54:3	OOO	885.44	13.7172
9	54:4	OOLi	883.43	24.4078
10	54:5	OLiLi	881.41	22.4445
11	54:6	OLiLe	879.40	12.3481
12	54:7	LiLiLe	877.38	0.8571
13	54:8	LiLeLe	875.36	4.2306
Total				100.0000

^(*) X:Y - X number of carbons, Y double bonds

5.4. Process Simulation

The algorithm developed by Naphtali and Sandholm (1971) in the form proposed by Fredenslund et. al. (1977) was adapted to liquid-liquid extraction. Figure 1 shows a schematic representation of the extractor.

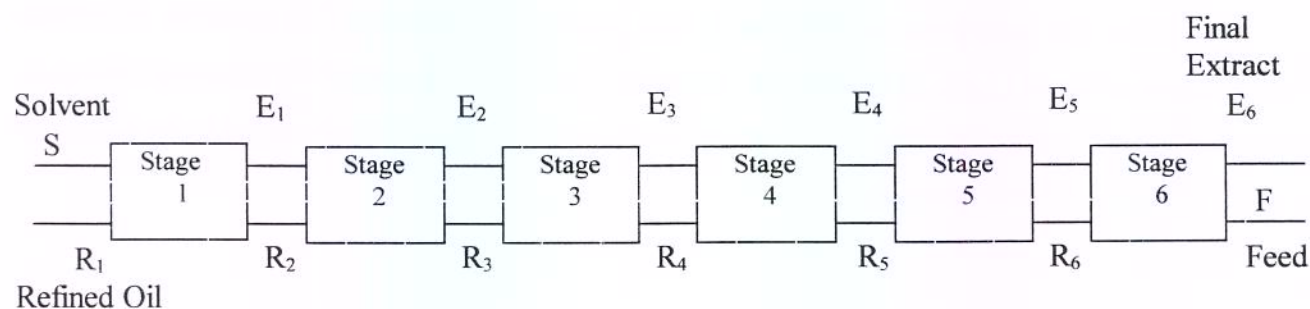


Figure 1 Schematic representation of extractor

The feed of the extractor was composed by triglycerides and free fatty acids in a proportion of 0.96 / 0.04 (mass fraction), respectively. All triglycerides of canola oil was used (Table 2) in feed. The free fatty acids were composed by the fatty acids in Table 1 with concentration superior to 0.5% (P, S, O, Li, A, Le). It was considered that the free fatty acids in crude canola oil present the same proportion of the fatty acids of the refined canola oil (Table 1). Anhydrous ethanol was used as solvent.

5.5. Surface Response Analysis

This study was carried out by surface response analysis based on the results from factorial design and regression analysis (Box et al., 1978; Khuri and Cornell, 1987). The experimental design, which requires the use of coded variables (Tables 3), was used as a tool to evaluate the influence of the main process variables on free fatty acids in refined oil (free of solvent) and loss of neutral oil in final extract. Two levels were considered; 9 (2^2 + star) process simulations were necessary for liquid-liquid extraction.

Table 3 Coded variables

	-	-1	0	+1	+1.4142
	1.41421				1
Ethanol flow	71.716	80	100	120	128.284
Temperature	22.929	25	30	35	37.071

From the simulation results in the above mentioned range, a mathematical model for each type of response was obtained.

This permits the formulation of the following models, expressed in terms of coded variables (Table 3):

free fatty acids in refined oil

$$FA = 0.1926 - 0.226666(EF^*) + 0.097722(EF^*)^2 + 0.015126(t^*) + 0.020421(t^*)^2 - 0.01192(EF^*)(t^*)$$

loss of neutral oil

$$O = 9.7008 + 1.368057(EF^*) - 0.089088(EF^*)^2 + 1.134259(t^*) + 0.029388(t^*)^2 + 0.189925$$

With these models, it is possible to generate surfaces that represent the influence of the specific variables on response.

Figure 2 depicts the effect of the ethanol flow, as well as the temperature on the free fatty acids in refined oil. The effect of ethanol flow on this response is much more significant than the temperature. The free fatty acids in refined oil decreases with the increase of ethanol flow. At high temperature the deacidification is prejudiced. It can be explained by the decrease of the selectivity of ethanol with the increase of temperature.

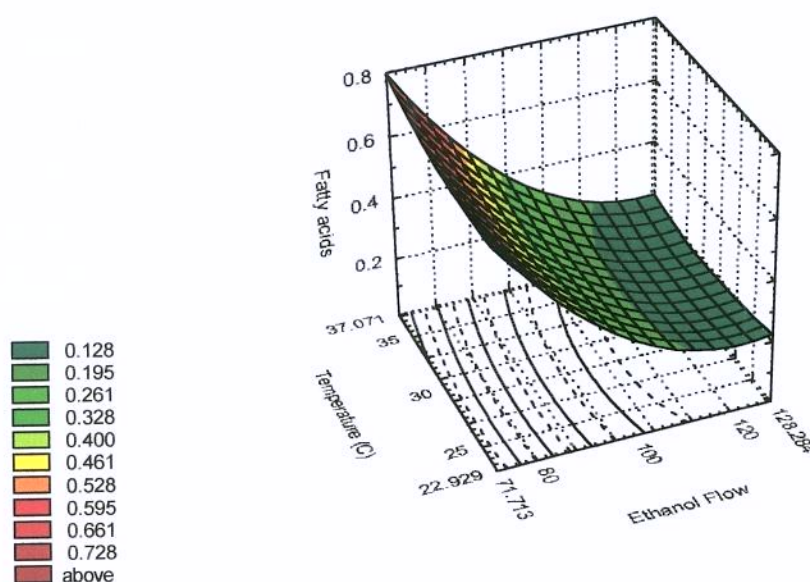


Figure 2 Effect of ethanol flow and temperature on fatty acid concentration in refined oil

Batista et al. (1999a) verified that the decrease in temperature from 30 to 20°C for canola oil - commercial oleic acid - ethanol caused a small increase in the two-phase region. However, did a significant change in the distribution coefficient occur. The increase in the heterogeneous region with only slight alterations in the distribution coefficient increases the selectivity of ethanol upon a reduction of temperature.

The effect of ethanol flow and temperature on loss of neutral oil are shown in Figure 3. The increase in ethanol flow and in temperature increase the loss of neutral oil. The effect of ethanol flow is a little more accentuated than the effect of temperature. The increase of temperature increase the solubility of oil in ethanol.

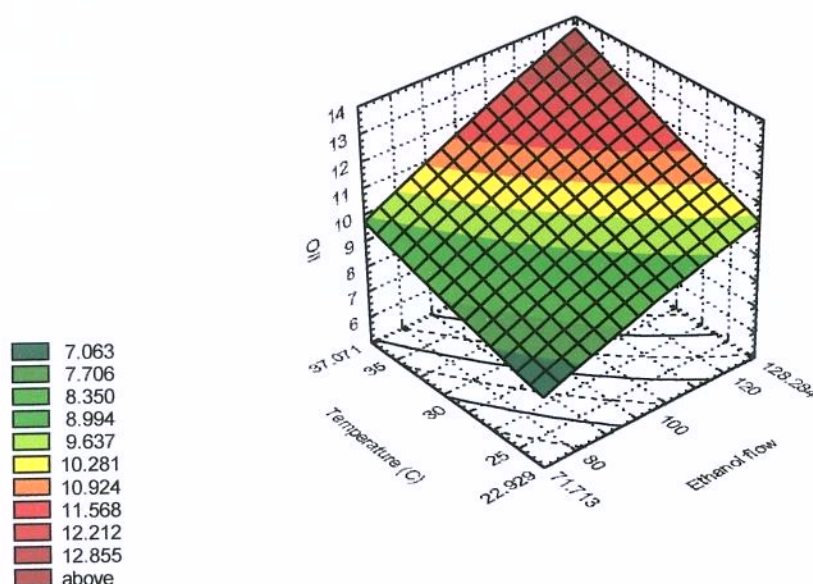


Figure 3 Effect of ethanol flow and temperature on loss of neutral oil

When these two surfaces are superimpose, the optimal range to operate the extractor can be found (Table 4). These values guarantee a concentration of free fatty acids in refined oil less than 0.3 % (Codex Alimentarius, 1993) as well as a minimum loss of neutral oil in final extract.

Table 4 Optimal Range

Ethanol flow	92 - 104
Temperature	22.929 - 26.5

To verify the results a rigorous simulation was conducted considering temperature and ethanol flow equal to 25 °C and 92. The concentration of free fatty acid was 0.29 % (m/m) and a loss of neutral oil equal to 8.1143%.

Figure 4 presents the composition (% m/m) in triglycerides of the refined canola oil and of the phases leaving the extractor. The composition of the refined oil and the oil phase are very close and different to the alcoholic phase. The concentration of the triglycerides (PLiLe, OLiLi, OLiLe, LiLiLe, LiLeLe) with 5 or more double bounds in the alcoholic phase is higher than in the oil phase. The increase in the number of double bounds increases the solubility in ethanol.

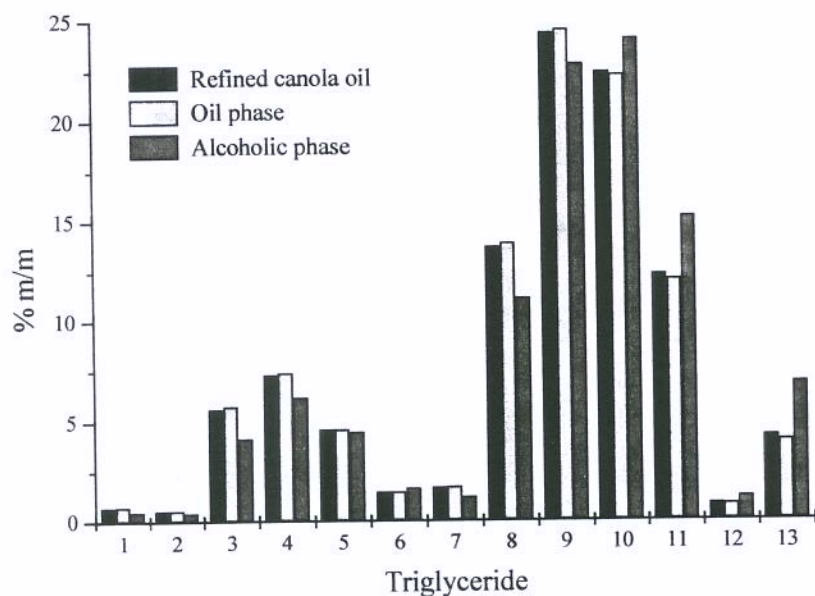


Figure 4 Distribution of triglycerides in refined canola oil, alcoholic and oil phases

5.6. Conclusion

The new parameters of the modified UNIFAC as well as the program developed make possible to simulate liquid-liquid extraction of a complex multicomponent system. All components of canola oil (13 triglycerides) and 6 fatty acids were considered in feed of the extractor without compromising the program convergence.

The surface response analysis help us to find the optimal range to operate the extractor with a minimum concentration of free fatty acids in the refined oil and a minimum loss of neutral oil.

The effect of ethanol flow is much more significant than the effect of temperature on the composition of free fatty acids in refined oil. In the case of loss of neutral oil, both of variables are important.

5.7. Notation

E	= alcoholic phase
EF	= ethanol flow
R	= oil phase
t	= temperature (° C)

Superscript

*	= coded variable (Table 3)
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CAPÍTULO 6

PREDICTION OF LIQUID-LIQUID EQUILIBRIUM FOR SYSTEMS OF CORN OIL, DIGLYCERIDES, FATTY ACIDS, AND ETHANOL.

Trabalho a ser submetido ao *Journal of the American Oil Chemist's Society*

Prediction of liquid-liquid equilibrium for systems of corn oil, diglycerides, fatty acids, and ethanol.

Keywords

Liquid-liquid equilibrium, corn oil, diglyceride, UNIFAC

Abstract

Deacidification of crude corn oil can be performed by liquid-liquid extraction. Information on liquid-liquid equilibrium for such fatty systems is essential to analyze the performance of this alternative process. UNIFAC model were utilized to predicted the liquid-liquid equilibrium for systems of corn oil, diglycerides, fatty acids, and ethanol. The average percent deviation between experimental and calculated compositions was 0.59 %. The diglyceride transfer and loss of triglycerides in the ethanol phase were also measured and predicted by UNIFAC model. The prediction results were quite successful.

6.1 Introduction

Corn oil has to be submitted to alkaline or physical refining for eliminating undesirable compounds such as free fatty acids and diglycerides. Most edible oils are produced by alkaline refining (Antoniassi *et al.*, 1998), but it can result in great losses of neutral oil. For high acidity oils, physical refining is a possibility and results in less loss of neutral oil than alkaline refining, but more energy is consumed and the refined oil might be subject to undesirable alterations in color and reduction of stability to oxidation (Antoniassi *et al.*, 1998).

Codex Alimentarius (1993) permits only 0.3 % of free fatty acids in the refined oil. Leibovitz and Ruckenstein (1983) reported losses of neutral oil in the range 15 to 25 % for neutralization of crude corn oil containing 8-14 % of free fatty acids. In Brazilian edible oil refining industries, the losses are comparatively higher, 14 % for crude corn oil with only 4 % of free fatty acids.

An alternative process for deacidification of crude edible oils is liquid-liquid extraction. It is based on the difference of solubility of free fatty acids and triglycerides in the solvent

and the difference of the boiling points of the solvent and free fatty acids (Thomopoulos, 1971).

In complex and multicomponent systems such as those containing edible oils, the utilization of group contribution models is a powerful tool for predicting liquid-liquid equilibrium. Batista *et al.* (1999) applied the UNIFAC model to fatty systems. After readjusting some group interaction parameters, the results were quite successful in the prediction of liquid-liquid equilibrium for different fatty systems..

There is a lack of information in the literature on the solubility of minor components in the solvents used to refine edible oils by liquid-liquid extraction. Antoniassi (1996) measured the distribution coefficient of diglyceride using anhydrous ethanol and aqueous ethanol as solvent and observed that the diglyceride transfer to the ethanol phase was very significant. The present paper utilizes the UNIFAC model to predict the liquid-liquid equilibrium data of systems of corn oil, diglyceride, fatty acids and ethanol. The diglyceride transfer and loss of neutral oil to alcohol phase were also calculated.

6.2 Experimental Data

The liquid-liquid equilibrium data of corn oil + diglycerides + fatty acids + solvent system were determined by Antoniassi (1996). The corn oil presented (1.04 – 4.30) % of free fatty acids (FFA) and (1.79 – 3.36) % of diglycerides. The solvent was anhydrous ethanol and aqueous ethanol (5.83 – 5.84 w%).

The quantity of fatty acids was determined using AOCS method Ca 5a-40. Ethanol of alcohol phase was removed by a rotary evaporator under nitrogen stream and the ethanol of oil phase by evaporation in an EDG vacuum oven. After evaporation of ethanol from alcohol phase, the extract was characterized by TLC FID chromatography. The quantity of di and triglyceride of oil phase were determined by mass balance.

6.3 Characterization of corn oil

The first step in the chemical characterization of an edible oil is to determine its fatty acid composition by gas chromatography of fatty acid methyl esters. The fatty acid composition of corn oil is presented in Table 1 (Antoniassi, 1996). From this fatty acid composition it is possible to estimate the triglyceride composition of the oil (Table 2) by using the algorithm

developed by Antoniosi Filho *et al.* (1995). The main triglyceride (Table 2) represents the component of greatest concentration in the isomer set with x carbons and y double bonds.

Table 1. Fatty acid composition of refined corn oil

n.	Symbol	Fatty Acid		M (g.mol ⁻¹)	% molar	% mass
1	M	Miristic	C14:0 ⁽¹⁾	228.38	0.0365	0.0300
2	P	Palmitic	C16:0	256.43	13.7943	12.7200
3	Po	Palmitoleic	C16:1	254.41	0.0874	0.0800
4	S	Stearic	C18:0	284.48	2.0333	2.0800
5	O	Oleic	C18:1	282.47	32.6848	33.2000
6	Li	Linoleic	C18:2	280.45	49.2415	49.6600
7	Le	Linolenic	C18:3	278.44	1.3782	1.3800
8	A	Arachidic	C20:0	312.54	0.6050	0.6800
9	B	Behenic	C22:0	340.49	0.1388	0.1700

⁽¹⁾ C_x:y - x = number of carbons, y = double bonds M = molecular weight

Table 2. Estimated triglyceride composition of corn oil

n.	Group	Main Triglyceride	M (g.mol ⁻¹)	% molar	% mass
1	50:1 ⁽¹⁾	POP	833.37	1.9072	1.8226
2	50:2	PLiP	831.35	2.9092	2.7735
3	52:1	POS	861.45	0.5616	0.5548
4	52:2	POO	859.40	5.3611	5.2836
5	52:3	POLi	857.39	13.6558	13.4267
6	52:4	PLiLi	855.37	10.7136	10.5090
7	52:5	PLiLe	853.37	0.6435	0.6298
8	54:2	SOO	887.46	0.9815	0.9988
9	54:3	OOO	885.44	5.5765	5.6623
10	54:4	OOLi	883.43	17.6755	17.9068
11	54:5	OLiLi	881.41	24.8117	25.0789
12	54:6	LiLiLi	879.43	13.5542	13.6694
13	54:7	LiLiLe	877.38	1.0442	1.0506
14	56:3	OLiA	913.52	0.6045	0.6333
Total				100.0000	100.0000

⁽¹⁾ X:Y - X number of carbons (except carbons of glycerol) and Y double bonds

The diglyceride composition can be estimated taking into account the probability of partial hydrolysis of each triglyceride (Table 2). For example, the partial hydrolysis of POS in the position 1 or 3 produces the diglycerides PO₋ and SO₋ and in position 2, the diglyceride P₋S, all diglycerides in equal molar proportion. The estimated diglyceride composition for corn oil is presented in Table 3.

Table 3. Estimated diglyceride composition of corn oil

n.	Group	Diglyceride	M (g.mol ⁻¹)	% molar	% mass
1	34:1	PO ₋ and P ₋ O	595.00	9.5850	9.3173
2	32:0	P ₋ P	568.96	1.6050	1.4919
3	34:2	PLi and P ₋ Li	592.98	13.8490	13.4164
4	34:3	PLe ₋	590.94	0.2150	0.2076
5	36:1	SO ₋ and S ₋ O	623.05	0.8410	0.8560
6	34:0	PS ₋ and P ₋ S	597.01	0.1870	0.1824
7	36:2	OO ₋ and O ₋ O	621.04	13.5820	13.7804
8	36:3	LiO ₋ and Li ₋ O	619.02	33.0790	33.4231
9	36:4	LiLi ₋ and Li ₋ Li	617.01	25.7440	25.9506
10	36:5	LeLi ₋ and Le ₋ Li	614.99	0.9110	0.9153
11	38:2	ALi ₋	649.06	0.2020	0.2142
12	38:1	O ₋ A	651.08	0.2020	0.2149
Total				100.0000	100.0000

D'Alonzo *et al.* (1982) analyzed refined and bleached fats and oils by high-temperature glass capillary column chromatography. Table 4 shows the glyceride composition by capillary gas chromatography for corn oil determined by D'Alonzo *et al.* (1982) and the values estimated in this work from the triglyceride composition given in Table 2. The proportionality of measured and estimated C34D and C36D compositions are very close.

Table 4 Corn oil composition

	Literature ^(a)	this work (%)
diglyceride		
C32D	—	1.60
C34D	0.7 (25 %)	23.84
C36D	2.1 (75 %)	74.16
C38D	—	0.40
triglyceride		
C46T	0.2 (0.21 %)	—
C48T	1.2 (1.25 %)	—
C50T	3.0 (3.13 %)	4.60
C52T	25.2 (26.30 %)	30.40
C54T	63.4 (66.19 %)	64.37
C56T	2.5 (2.61 %)	0.63
C58T	0.3 (0.31 %)	—

^(a) D'Alonzo *et al.* (1982); the values given in parenthesis were normalized to 100 %.

6.4 Prediction of liquid-liquid equilibrium for multicomponent system.

The UNIFAC model with parameters adjusted by Batista *et al.* (1999) and with original parameters were used in the prediction of liquid-liquid equilibria in systems of corn oil, diglycerides, free fatty acids, and ethanol.

Liquid-liquid flash calculations of phase compositions was executed based on the overall experimental composition of the mixture. The composition of corn oil (Table 2), fatty acids (Table 1) and diglycerides (Table 3) were used to expand the pseudo-quaternary mixture to the multicomponent one. After the multicomponent flash calculations

, the mass fractions of triglycerides for each of the phases were grouped and compared to the experimental composition of the phases. The same procedure were utilized for the diglycerides and fatty acids. It should be observed that the experimental results determined by Antoniassi (1996) were measured considering the system as a pseudo quaternary composed by corn oil, diglyceride, fatty acids and a solvent (anhydrous or aqueous ethanol).

The average percentage deviation of experimental mass fraction from the calculated ones can be found in Table 5. The average percent of deviation was calculated as follow:

$$\Delta w = 100 \sqrt{\frac{\sum_{i=1}^C \left[\left(w_i^{I,ex} - w_i^{I,calc} \right)^2 + \left(w_i^{II,ex} - w_i^{II,calc} \right)^2 \right]}{2NC}} \quad (1)$$

where N and C are the total number of tie-lines and total number of pseudo-components, w is the pseudo-component mass fraction, the superscript I and II are the phases; ex and calc are experimental and calculated.

Table 5 Average percent deviation in phase composition

System	Δw (%)	
	Original UNIFAC	New UNIFAC
Corn oil + diglyceride + fatty acids + ethanol	6.98	0.71
Corn oil + diglyceride + fatty acids + aqueous ethanol	1.54	0.46
	4.99	0.59

Figure 1 shows the experimental tie-lines and the predicted ones by original group interaction parameters (Magnussen *et al.*, 1981) and the new parameters (Batista *et al.*, 1999). The original group interaction parameters predict a higher heterogeneous area than experimental one and distribution coefficients of fatty acids less than one, although the experimental distribution coefficients are higher than one. The overall composition ($\blacktriangle$) with 3.22 % of fatty acids is a homogeneous mixture and the original group interaction parameters of UNIFAC predicted this mixture as a heterogeneous one. The new group interaction parameters predicted that is totally miscible, agreeing with the experimental information. The average percent deviations between experimental and predicted compositions were 9.12 % and 0.93 % in the mass fraction for original and new UNIFAC interaction parameter set, respectively.

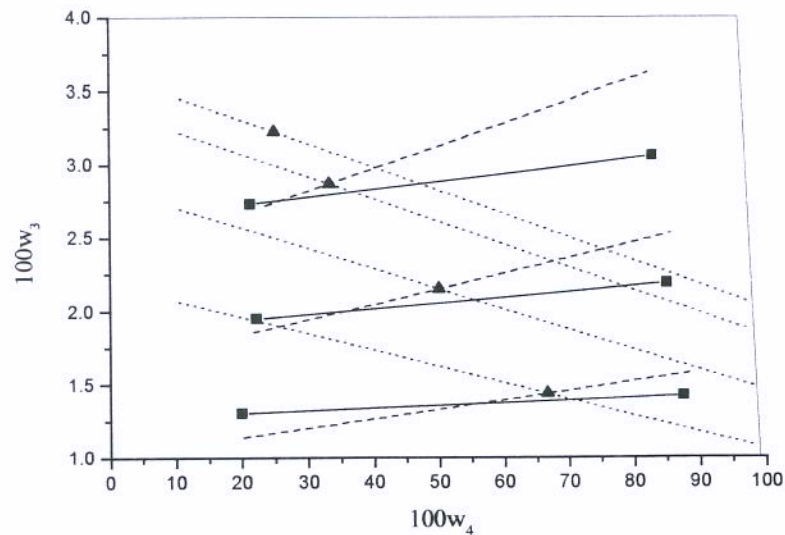


Figure 1 Prediction of the liquid-liquid equilibrium for the system of corn oil (1) + diglycerides (2) + fatty acids (3) + ethanol (4) at 40 °C

(—■— experimental, ▲ overall composition, ----- Original UNIFAC new UNIFAC)

Figure 2 and 3 show the experimental tie-lines predicted for the systems of corn oil, diglycerides, fatty acids, and anhydrous ethanol and aqueous ethanol at 30 °C, respectively.

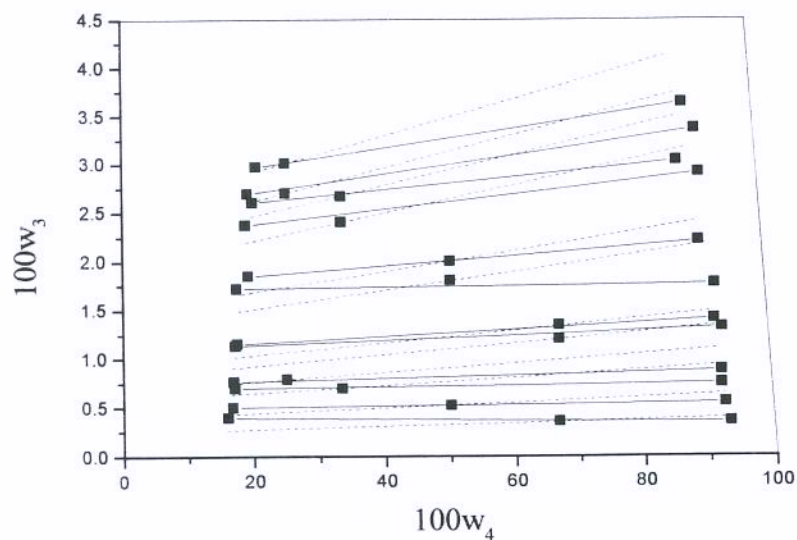


Figure 2 Corn oil (1) + diglyceride (2) + fatty acids (3) + ethanol (4) at 30 °C

(—■— experimental, ----- new UNIFAC)

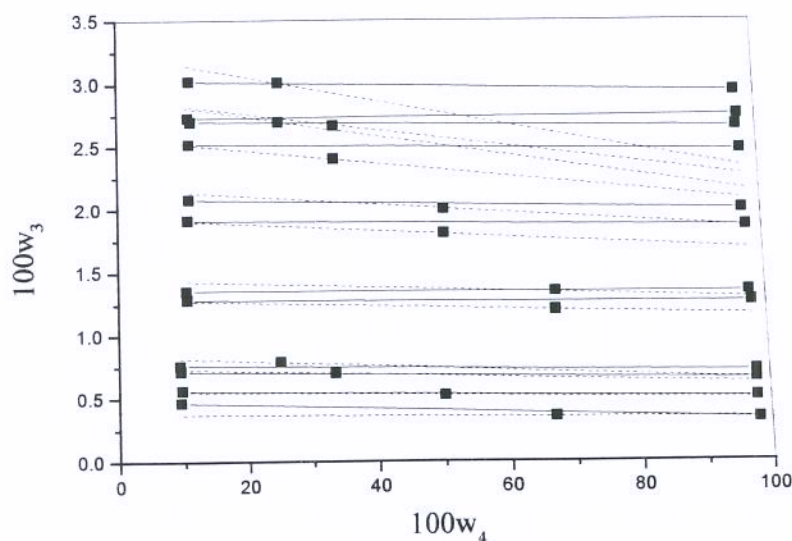


Figure 3 Corn oil (1) + diglyceride (2) + fatty acids (3) + aqueous ethanol (4) at 30 °C
(—■— experimental, ----- new UNIFAC)

Using the new UNIFAC parameters, the size of heterogeneous area is predicted successfully in both Figures 2 and 3. For the systems with anhydrous ethanol, the predicted distribution coefficients of fatty acids are higher than the experimental ones. For the systems with aqueous ethanol, the predicted distribution coefficients of fatty acids are lower than the experimental values, mainly for the tie-lines with fatty acid mass fraction higher than 0.02. The addition of water to the solvent decreases the mutual solubility, increasing the concentration range of the two-phase region.

6.5 Diglyceride transfer and loss of triglycerides

Antoniassi (1996) determined, experimentally, the percentage of diglyceride transfer (Tables 6 and 7) and the percentage of loss of triglycerides from crude oil to alcohol phase (Tables 7 and 8). The predicted percentage of diglyceride transfer and of loss of triglycerides were calculated by:

$$100 \frac{m^{AP} w_i^{AP}}{m^{OC} w_i^{OC}} \quad (2)$$

where m is mass, w is mass fraction, AP is alcohol phase, OC is overall composition, and i is diglyceride or triglyceride.

The diglyceride transfers to alcohol phase increased with the decrease of crude oil to solvent ratio. Diglyceride transfer using anhydrous ethanol as solvent is higher than the transfer with aqueous ethanol, provided the same crude oil to solvent ratio is used.

Table 6 Percentage of diglyceride transfers in systems using anhydrous ethanol as solvent

crude oil/solvent	3/1	2/1	1/1	0.5/1
Experimental	6.43	18.46	30.90	65.05
Predicted	7.28	19.17	41.52	63.32

Table 7 Percentage of diglyceride transfer in systems using as aqueous ethanol as solvent

crude oil/solvent	3/1	2/1	1/1	0.5/1
Experimental	5.32	14.21	28.04	51.94
Predicted	7.76	14.14	29.76	49.19

Figure 4 presents experimental and predicted percentage of diglyceride transfer in systems using aqueous ethanol.

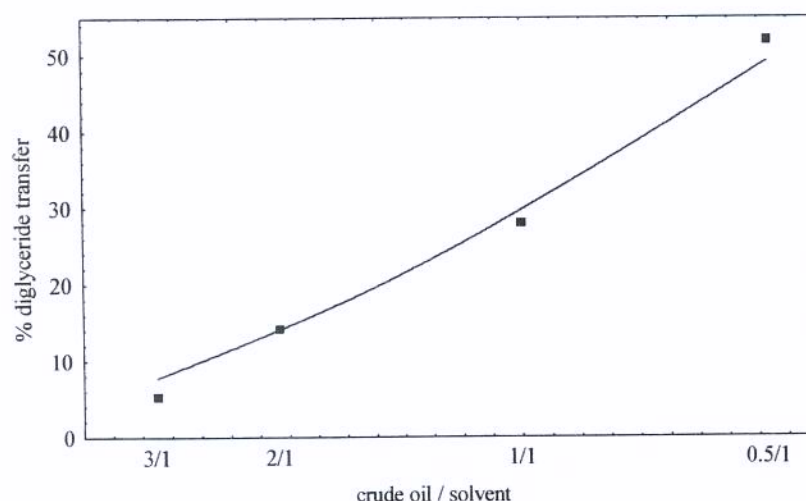


Figure 4 Percentage of diglyceride transfer using aqueous ethanol as solvent

(■ experimental, — new UNIFAC)

The distribution coefficients of fatty acids with anhydrous ethanol are somewhat larger than the corresponding values for aqueous ethanol (Figures 2 and 3). These results suggest that anhydrous ethanol has somewhat more capacity for extraction of fatty acids, but dissolves more corn oil (Table 8) than aqueous ethanol (Table 9). For this reason, aqueous ethanol presents more selectivity than anhydrous ethanol.

Table 8 Percentage of loss of triglycerides in systems using anhydrous ethanol as solvent

crude oil/solvent	3/1	2/1	1/1	0.5/1
Experimental	1.01	2.71	6.35	13.50
Predicted	0.93	2.51	9.75	13.21

Table 9 Percentage of loss of triglycerides in systems using as aqueous ethanol as solvent

crude oil/solvent	3/1	2/1	1/1	0.5/1
Experimental	0.40	0.70	1.66	3.36
Predicted	0.43	0.73	1.69	3.27

Figures 5 presents the experimental and predicted percentage of loss of triglycerides in systems using aqueous ethanol.

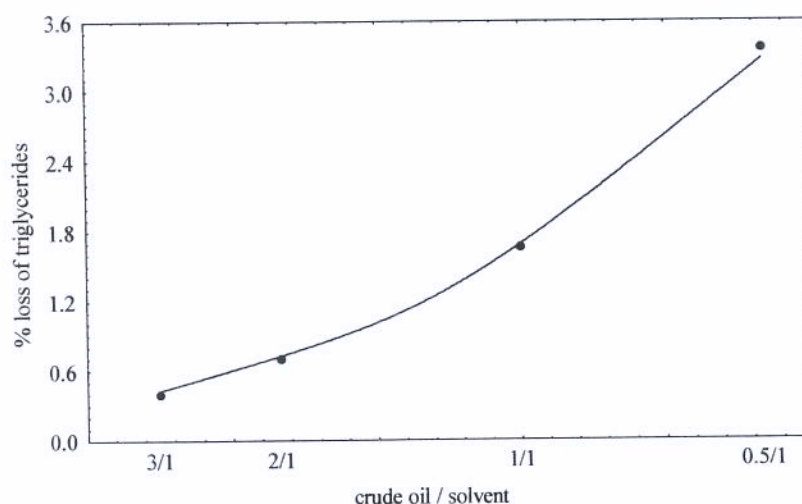


Figure 5 Percentage of loss of triglycerides using aqueous ethanol as solvent

(● experimental, — new UNIFAC)

6.6 Conclusion

The estimated diglyceride composition of corn oil was very close to experimental. The prediction of liquid-liquid equilibrium using the new parameters of UNIFAC was quite successful. The predicted percentage of diglyceride transfer and percentage of loss of triglycerides were very close to the experimental data. These results guarantee the use of the new UNIFAC parameters in the simulation of liquid-liquid extraction for deacidification of corn oil, with special attention to diglyceride extraction and loss of neutral oil.

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Apêndice B

Table B1 Liquid-liquid equilibrium data for system corn oil (1) + diglycerides (2) + fatty acids (3) + ethanol (4)

t (°C)	Overall Composition				Alcohol Phase			Oil Phase		
	100	100	100	100	100	100	100	100	100	100
	w ₄	w ₃	w ₂	w ₁	w ₄	w ₃	(w ₁ +w ₂)	w ₄	w ₃	(w ₁ +w ₂)
30 ^(a)	25.00	0.79	1.34	72.87	91.64	0.88	7.48	16.97	0.76	82.27
	33.33	0.70	1.19	64.78	91.60	0.75	7.65	17.10	0.70	82.20
	50.00	0.52	0.90	48.58	92.17	0.55	7.28	16.79	0.50	82.71
	66.67	0.35	0.60	32.38	92.97	0.35	6.68	16.05	0.39	83.56
30 ^(b)	25.00	3.01	2.52	69.47	85.82	3.64	10.54	20.59	2.97	76.44
	33.33	2.67	2.24	61.76	84.94	3.04	12.02	20.01	2.60	77.30
	50.00	2.00	1.68	46.32	88.26	2.21	9.53	19.28	1.85	78.87
	66.67	1.34	1.12	30.87	90.51	1.41	8.08	17.52	1.15	81.33
40 ^(c)	33.33	2.87	2.24	69.26	82.91	3.06	14.03	21.41	2.73	75.86
	50.00	2.15	1.68	61.56	84.98	2.19	12.83	22.35	1.95	75.70
	66.67	1.43	1.12	30.78	87.51	1.42	11.07	20.00	1.30	78.70

^(a) Bleached corn oil with 1.04 % of FFA and 1.79 % of diglycerides

^(b) Bleached corn oil with 4.01 % of FFA and 3.36 % of diglycerides

^(c) Bleached corn oil with 4.30 % of FFA and 3.36 % of diglycerides

Table B2 Liquid-liquid equilibrium data for system corn oil (1) + diglycerides (2) + fatty acids (3) + ethanol (4)

t (°C)	Overall Composition				Alcohol Phase				Oil Phase			
	100	100	100	100	100	100	100	100	100	100	100	100
	w ₄	w ₃	w ₂	w ₁	w ₄	w ₃	w ₂	w ₁	w ₄	w ₃	w ₂	w ₁
30	25.00	2.70	1.54	70.76	87.72	3.37	1.09	7.82	19.24	2.69	1.54	76.53
	33.33	2.40	1.37	62.90	88.35	2.91	1.13	7.61	18.94	2.37	1.33	77.36
	50.00	1.80	1.03	47.17	90.61	1.77	0.73	6.89	17.46	1.72	1.37	79.45
	66.67	1.20	0.69	31.44	91.76	1.32	0.66	6.26	17.26	1.13	0.57	81.04

Bleached corn oil with with 3.60 % of FFA and 2.06 % of diglycerides

Table B3 Liquid-liquid equilibrium data for system corn oil (1) + diglycerides (2) + fatty acids (3) + 5.83 wt % ethanol (4)

t (°C)	Overall Composition				Alcohol Phase			Oil Phase		
	100	100	100	100	100	100	100	100	100	100
	w ₄	w ₃	w ₂	w ₁	w ₄	w ₃	(w ₁ +w ₂)	w ₄	w ₃	(w ₁ +w ₂)
30	25.00	0.79	1.34	72.87	97.28	0.71	2.01	9.43	0.76	89.81
	33.33	0.70	1.19	64.78	97.32	0.65	2.03	9.52	0.71	89.77
	50.00	0.52	0.90	48.58	97.38	0.50	2.12	9.69	0.56	89.75
	66.67	0.35	0.60	32.38	97.75	0.33	1.92	9.54	0.46	90.00

Bleached corn oilwith 1.04 % of FFA and 1.79 % of diglycerides

Table B4 Quaternary liquid-liquid equilibrium data for system corn oil (1) + diglycerides (2) + fatty acids (3) + 5.84 wt % ethanol (4)

t (°C)	Overall Composition				Alcohol Phase			Oil Phase		
	100	100	100	100	100	100	100	100	100	100
	w ₄	w ₃	w ₂	w ₁	w ₄	w ₃	(w ₁ +w ₂)	w ₄	w ₃	(w ₁ +w ₂)
30 ^(a)	25.00	3.01	2.52	69.47	94.18	2.94	2.88	11.17	3.02	85.81
	33.33	2.67	2.24	61.76	94.38	2.66	2.96	11.40	2.70	85.90
	50.00	2.00	1.68	46.32	95.18	2.00	2.82	10.94	2.08	86.98
	66.67	1.34	1.12	30.87	96.19	1.34	2.47	10.54	1.35	88.11
40 ^(b)	25.00	3.22	2.52	69.26	93.60	3.02	3.38	13.25	3.17	83.58
	33.33	2.87	2.24	61.56	93.68	2.71	3.61	13.49	2.79	83.72
	50.00	2.15	1.68	46.17	94.39	2.06	3.55	13.52	2.14	84.34
	66.67	1.43	1.12	30.78	95.51	1.37	3.12	13.00	1.42	85.58

^(a) Bleached corn oil with 4.01 % of FFA and 3.36 % of diglycerides

^(b) Bleached corn oil with 4.30 % of FFA and 3.36 % of diglycerides

Table B5 Liquid-liquid equilibrium data for system corn oil (1) + diglycerides (2) + fatty acids (3) + 5.83 wt % ethanol (4)

t (°C)	Overall Composition				Alcohol Phase				Oil Phase			
	100	100	100	100	100	100	100	100	100	100	100	100
	w ₄	w ₃	w ₂	w ₁	w ₄	w ₃	w ₂	w ₁	w ₄	w ₃	w ₂	w ₁
30	25.00	2.70	1.54	70.76	94.63	2.75	0.79	1.83	10.98	2.73	1.66	84.63
	33.33	2.40	1.37	62.90	95.03	2.47	0.77	1.73	11.05	2.52	1.45	84.98
	50.00	1.80	1.03	47.17	95.77	1.86	0.64	1.73	10.73	1.91	1.20	86.16
	66.67	1.20	0.69	31.44	96.63	1.26	0.53	1.58	10.57	1.28	0.78	87.37

Bleached corn oil with 3.60 % of FFA and 2.06% of diglycerides

CAPÍTULO 7

LIQUID-LIQUID EXTRACTION FOR DEACIDIFICATION OF VEGETABLE OILS

Eduardo Batista, Rosemar Antoniassi, Maria Regina Wolf Maciel and Antonio J. A. Meirelles

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Liquid-Liquid Extraction For Deacidification Of Vegetable Oils

Eduardo Batista^{*}, Rosemar Antoniassi^{**}, Maria Regina Wolf Maciel^{***} and Antonio J. A. Meirelles^{*}

^{*}Faculty of Food Engineering, UNICAMP, CP 6121, CEP 13083-970, Campinas - SP, Brazil, e-mail: tomze@ceres.fea.unicamp.br

^{**} EMBRAPA, Av. Das Américas, 29501, CEP 23020-470, Rio de Janeiro - RJ, Brasil, e-mail: rosemar@ctaa.embrapa.br

^{***}Faculty of Chemical Engineering, State University of Campinas (UNICAMP), CP 6066, CEP 13083-970, Campinas - SP, Brazil, e-mail: wolf@feq.unicamp.br

Crude vegetable oils contains undesirable components, such as free fatty acids. They can be removed by alkali refining as well as physical refining. The liquid-liquid extraction is an alternative process that reduces the energy consumption for the oil refining without losses of natural components. This work aims at studying the simulation of corn oil deacidification by liquid-liquid extraction using aqueous ethanol as solvent. The obtained results indicate the best conditions for the deacidification by solvent extraction. The solvent to crude oil flow ratio, the number of stages and the water percent in ethanol could be selected to guarantee the minimum free fatty acids content in the refined oil with a minimum loss of neutral oil.

6.1. Introduction

In the food and pharmaceutical industries, liquid-liquid extraction can be used in the recovery of vitamins, in the separation of caffeine, penicillin, aroma and fragrance, in the separation of lecithin, in the deterpenation of orange essential oil and in the deacidification of vegetable oils [1,2]. In the conventional refining process of edible oils, the deacidification is conducted by neutralization of free fatty acids with alkali. This process is applied to any vegetable oil, but high concentration of

free fatty acids causes a high loss of neutral oil. Leibovitz and Ruckenstein [3] reported losses of neutral oil in the range 15 to 25 % for the neutralization of crude corn oil containing 8-14 % of free fatty acids. In Brazilian edible oil refining industry, the losses of neutral oil are proportionally higher, 14 % for crude corn oil with only 4 % of free fatty acids [4].

The deacidification of vegetable oils using solvent is based on the difference of the solubility of free fatty acids and neutral triglycerides in the solvent and on the difference of the boiling points of the solvent and fatty acids [5]. This process can be performed using several solvents: acetone, ethyl acetate, furfural, propanol, isopropanol, butanol, ethanol, methanol, ethyl methyl cetone, etc. Batista *et al.* [6] tested different solvents (methanol, ethanol, n-propanol, isopropanol, aqueous ethanol) for deacidification of canola oil. They verified that ethanol and aqueous ethanol were the best solvents for the deacidification process. The presence of water in ethanol increases the solvent selectivity, decreases the mutual solubility of the oil/ethanol mixture and reduces the loss of neutral oil in the final extract. This work is focused on the simulation of the deacidification process by solvent extraction and its optimization using surface response analysis. Batista *et al.* [7] used surface response analysis for optimizing a SRV distillation process and concluded that the factorial design is a powerful tool for analyzing the effects of the selected variables. For this reason this technique was employed in the present work to analyze the variables used in liquid-liquid extraction.

6.2. Characterization Of Vegetable Oils

The first step in the chemical characterization of a edible oil is to determine its fatty acid composition by gas chromatography of fatty acid methyl esters. The fatty acid composition of corn oil is presented in Table 1.

From this fatty acid composition it is possible to estimate the triglyceride composition of the oil (Table 2) by using the computational method developed by Antoniosi Filho *et al.* [8]. The main

triglyceride (Table 2) represents the component of greatest concentration in the isomer set with x carbons and y double bonds.

Table 1. Fatty acid composition of refined corn oil

n.	Symbol	Fatty Acid		M (g.mol ⁻¹)	% molar	% mass
1	M	Miristic	C14:0 ⁽¹⁾	228.38	0.0365	0.0300
2	P	Palmitic	C16:0	256.43	13.7943	12.7200
3	Po	Palmitoleic	C16:1	254.41	0.0874	0.0800
4	S	Stearic	C18:0	284.48	2.0333	2.0800
5	O	Oleic	C18:1	282.47	32.6848	33.2000
6	Li	Linoleic	C18:2	280.45	49.2415	49.6600
7	Le	Linolenic	C18:3	278.44	1.3782	1.3800
8	A	Arachidic	C20:0	312.54	0.6050	0.6800
9	B	Behenic	C22:0	340.49	0.1388	0.1700

⁽¹⁾ C_x:y - x = number of carbons, y = double bonds M = molecular weight

Table 2. Estimated triglyceride composition of corn oil

n.	Group	Main Triglyceride	M (g.mol ⁻¹)	% molar	% mass
1	50:1 ⁽¹⁾	POP	833.37	1.9072	1.8226
2	50:2	PLiP	831.35	2.9092	2.7735
3	52:1	POS	861.45	0.5616	0.5548
4	52:2	POO	859.40	5.3611	5.2836
5	52:3	POLi	857.39	13.6558	13.4267
6	52:4	PLiLi	855.37	10.7136	10.5090
7	52:5	PLiLe	853.37	0.6435	0.6298
8	54:2	SOO	887.46	0.9815	0.9988
9	54:3	OOO	885.44	5.5765	5.6623
10	54:4	OOLi	883.43	17.6755	17.9068
11	54:5	OLiLi	881.41	24.8117	25.0789
12	54:6	LiLiLi	879.43	13.5542	13.6694
13	54:7	LiLiLe	877.38	1.0442	1.0506
14	56:3	OLiA	913.52	0.6045	0.6333
Total				100.0000	100.0000

⁽¹⁾ X:Y - X number of carbons (except carbons of glycerol) and Y double bonds

The diglyceride composition can be estimated taking into account the probability of partial hydrolysis of each triglyceride (Table 2). For example, the partial hydrolysis of POS in the position 1 or 3 produces the diglycerides PO_ and SO_ and in position 2, the diglyceride P_S, all diglycerides in equal molar proportion. The estimated diglyceride composition for corn oil is presented in Table 3.

Table 3. Estimated diglyceride composition of corn oil¹

n.	Group	Diglyceride	M (g.mol ⁻¹)	% molar	% mass
1	34:1	PO_ and P_O	595.00	9.5850	9.3173
2	32:0	P_P	568.96	1.6050	1.4919
3	34:2	PLi and P_Li	592.98	13.8490	13.4164
4	34:3	PLe_	590.94	0.2150	0.2076
5	36:1	SO_ and S_O	623.05	0.8410	0.8560
6	34:0	PS_ and P_S	597.01	0.1870	0.1824
7	36:2	OO_ and O_O	621.04	13.5820	13.7804
8	36:3	LiO_ and Li_O	619.02	33.0790	33.4231
9	36:4	LiLi_ and Li_Li	617.01	25.7440	25.9506
10	36:5	LeLi_ and Le_Li	614.99	0.9110	0.9153
11	38:2	ALi_	649.06	0.2020	0.2142
12	38:1	O_A	651.08	0.2020	0.2149
Total				100.0000	100.0000

6.3. Process Simulation

The algorithm developed by Naphtali and Sandholm [9], in the form proposed by Fredenslund *et al.* [10], was adapted for simulating the liquid-liquid extraction. The phase equilibrium estimation in such a complex system, containing 14 triglycerides, 12 diglycerides, 9 fatty acids, a short chain alcohol and water, is a very difficult task. Phase equilibrium was predicted using the new

¹ Tabela corrigida.

parameters of UNIFAC adjusted by Batista *et al.* [11] for ternary systems composed by a pure triglyceride, a pure fatty acid and anhydrous ethanol.

The extractor feed stream was composed by triglycerides, diglycerides and free fatty acids in a proportion of 92 / 4 / 4, respectively. All triglycerides and diglycerides of corn oil (Table 2 and 3, respectively) were used in the feed stream. The free fatty acids were composed by the fatty acids presented in Table 1. It was considered that the free fatty acids present in crude corn oil have the same proportion of the fatty acid composition of refined corn oil (Table 1). Aqueous ethanol was used as solvent. A good deacidification by solvent extraction must provide a content of free fatty acids in refined oil lower than 0.3 mass% [12], without a great loss of neutral oil in final extract.

6.4. Surface Response Analysis

The optimization study was carried out by surface response analysis based on the results from factorial design and regression analysis [13]. The experimental design, which requires the use of coded variables (Table 4), was used as a tool to evaluate the influence of the main process variables on the free fatty acids content of refined oil (in a solvent free basis) and on the loss of neutral oil in final extract. Three levels were considered: 15 ($2^3 + \text{star}$) process simulations were necessary for optimizing the liquid-liquid extraction by surface response analysis.

Table 4. Coded variables

	-1.68179	-1	0	+1	+1.68179
Solvent to Crude Oil Ratio (S/O)	0.93182	0.90000	1.00000	1.10000	1.26818
Number of Stage (NS)	4	5	7	9	10
% Water in Solvent (W)	2.477	3.500	5.000	6.500	7.523

From the simulation results in the above mentioned range, a mathematical model for each type of response was obtained. This permits the formulation of the following models, expressed in terms of coded variables (Table 4):

free fatty acids in refined oil:

$$\begin{aligned} \% \text{ FFA} = & 0.511081 - 0.187174 (S/O^*) + 0.028290 (S/O^*)^2 - 0.140224 (NS^*) + \\ & + 0.034990 (NS^*)^2 + 0.290702 (W^*) + 0.046958 (W^*)^2 - 0.050325 (S/O^*) (W^*) \end{aligned} \quad (1)$$

loss of neutral oil:

$$\begin{aligned} L = & 2.51473 + 0.25968 (S/O^*) + 0.04090 (NS^*) - 1.18148 (W^*) + 0.24230 (W^*)^2 - \\ & - 0.08250 (S/O^*) (W^*) \end{aligned} \quad (2)$$

where superscript * defines coded variable.

With these models, it is possible to generate surfaces that represent the influence of the specific variables on each response. In the first analysis with the variables S/O and NS, the value for NS that guarantees a fatty acid concentration of 0.3 % and a lower loss of neutral oil was 10. The next step was to generate a surface with NS equal to 10 (Figure 1) for representing the effect of the solvent to crude oil flow ratio (S/O), as well as the water percent in that solvent (W), on the free fatty acid concentration in refined oil and on the loss of neutral oil. Both variables, S/O and W, have a significant effect on the responses. The free fatty acids in refined oil decreases with the increase of solvent/oil flow ratio. At high W-values, in this case ethanol with 7.523 % water, the deacidification is affected because the solvent has a lower capacity of extracting free fatty acids, nevertheless the solvent becomes more selective with the water increase, reducing expressively the loss of neutral oil. The effect of W is much more significant than that of S/O. The loss of neutral oil in the final extract decreases as the S/O ratio decreases and also decreases, but much more significantly, with the increase of the water content in solvent. In fact, the addition of water to ethanol has a very significant influence on the mutual solubility of oil and the mixed solvent, reducing its value. When the surfaces are superimposed, the maximum concentration of free fatty acids permitted by legislation (0,3 %), with a minimum loss of neutral oil, is obtained for a S/O-value equal to the maximum one (1.26818).

The surface for NS and W with S/O equal to 1.26818 was then generated (Figure 2). The free fatty acid concentration decreases with the increase in NS and with the decrease of W, but the

effect of W is higher than the effect of NS. When these figures are superimposed, the operating condition that permits a minimum loss of neutral oil and assures 0.3 % of free fatty acids in final product is $NS = 10$ and $W = 5.75$ %.

Using this procedure the optimal condition for solvent extraction can be found (Table 5). These values guarantee a concentration of free fatty acids in refined oil lower than 0.3 % [12] as well as a minimum loss of neutral oil in final extract. To check these optimal conditions a rigorous simulation was conducted using their values. The simulation results indicate that for these optimal conditions the concentration of free fatty acid in the refined oil is 0.27 %, the loss of neutral oil is equal to 2.40 % and 60.7 % of diglycerides was extracted. This loss of neutral oil is much lower than the loss presented in the literature, 8-14 % [3] and 14 % [4]. Batista *et al.* [14] found 8.11% of neutral oil loss in the deacidification of canola oil with 4 % of free fatty acids. In this case the authors employed anhydrous ethanol as solvent. This result proves that the maximum concentration of free fatty acids in neutral oil, 0.3%, can be obtained with a significant decrease in the loss of neutral oil in the final extract using aqueous ethanol as solvent.

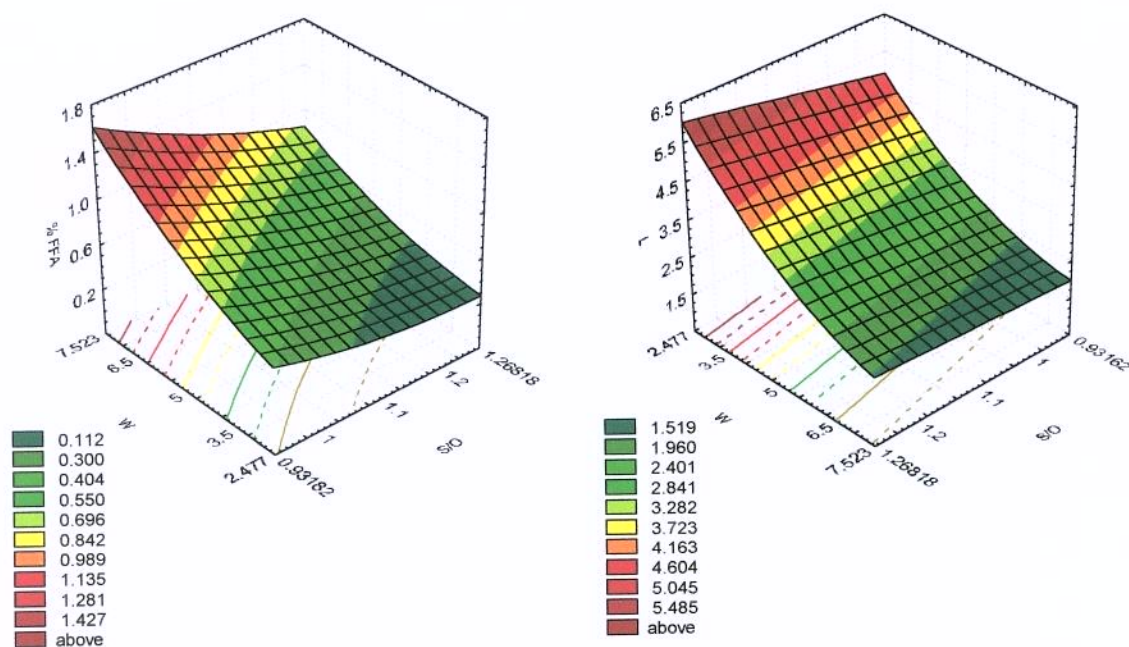


Figure 1 Effect of S/O and W on % FFA and on L (NS=10)

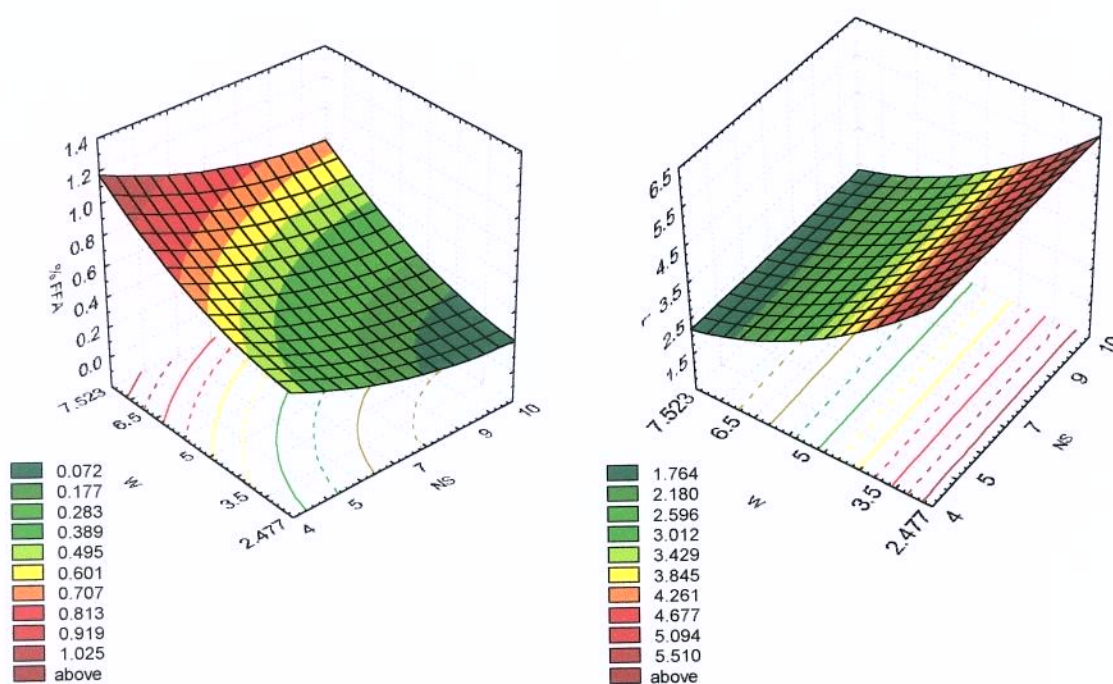


Figure 2 Effect of NS and W on % FFA and on L (S/O = 1.26818)

It should also be noted that experimental results [2] indicated that mechanical extractors can be used in oil deacidification of relatively high solvent to crude oil ratios without hydrodynamic problems, such as phase inversion.

Table 5. Optimal conditions for deacidification by solvent extraction

Solvent to Oil Ratio (S/O)	Number of Stages (NS)	Water Percent in Solvent (W)
1.26818	10	5.75 %

6.5. Conclusion

The new parameters of the modified UNIFAC as well as the program developed allows to simulate liquid-liquid extraction of a complex multicomponent system. All components of corn oil

(Tables 1, 2 and 3) were considered in the extractor feed stream without compromising the program convergence. The surface response analysis help us to find the optimal condition to operate the extractor with a concentration of free fatty acids in the refined oil lower than 0.3 % and a minimum loss of neutral oil. The presence of water in ethanol guarantees losses of neutral oil substantially lower.

6.6. Acknowledgements

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6.7. References

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