UNIVERSIDADE ESTADUAL DE CAMPINAS
Faculdade de Engenharia Química
Departamento de Processos Químicos

OBTENÇÃO DE MONOGLICERÍDEOS DE ALTA CONCENTRAÇÃO ATRAVÉS DO PROCESSO DE DESTILAÇÃO MOLECULAR

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Resumo Geral

Monoglicerídeos são emulsificantes amplamente utilizados em alimentos, fármacos e cosméticos. Industrialmente, são produzidos através da interesterificação de triglicerídeos com glicerol, a altas temperaturas (>200°C), na presença de catalisadores inorgânicos. Também conhecida como glicerólise, esta reação produz uma mistura com aproximadamente 50% de monoglicerídeos. Este nível de concentração é adequado a muitos tipos de aplicações, no entanto, para fabricação de alguns produtos como margarinas, sorvetes e recheios, devem ser utilizados monoglicerídeos de alta concentração (teor mínimo de 90%), os quais são normalmente produzidos através do processo de destilação molecular. Assim, neste trabalho, foi utilizado um destilador molecular centrífugo com área de evaporação igual a $0{,}0046 m^2$, para a obtenção de monoglicerídeos de alta concentração (até 96,3%). A metodologia de análise de superfície de resposta foi utilizada para a identificação das condições operacionais ótimas de enriquecimento de monoglicerídeos na corrente de destilado. Além disso, um planejamento experimental 2^3 foi empregado para estudarem-se os efeitos de alguns parâmetros reacionais sobre a concentração de monoglicerídeos na condição de equilíbrio químico da reação de glicerólise de óleo de soja refinado, catalisada por hidróxido de sódio. Então, utilizando-se as condições de destilação otimizadas através da metodologia de análise de superfície de resposta, os produtos reacionais foram destilados, aumentando-se assim a concentração de monoglicerídeos.

Abstract

Monoglycerides are emulsifiers widely used in food, pharmaceutical, and cosmetic fields. Current industrial processes for monoglycerides production consist on the interesterification of triglycerides with glycerol in the presence of inorganic catalysts at high temperatures (>200°C). This reaction is known as glycerolysis and produces a mixture of approx 50 % of monoglycerides. This level of concentration is suitable for many applications, although, some specific uses like margarine, icing and cream filling require distilled monoglycerides, which are purified monoglycerides (min. 90%) normally obtained by molecular distillation process. Therefore, in this work, a centrifugal molecular distillator of evaporation area of $0.0046m^2$ was used to obtain monoglycerides with up to 96.3% of purity. Response surface methodology was applied as a tool to identify operating conditions that can lead to higher monoglycerides purity in the distillate stream. Furthermore, a 2^3 factorial design was employed to evaluate the effects of reaction parameters on the monoglycerides concentration after the interesterification reaction of refined soybean oil with glycerol in the presence of sodium hydroxide as catalyst. The monoglycerides content in the reaction product was enhanced, using the optimized distillation conditions obtained by the response surface methodology.

Introdução Geral

Atualmente, há no Brasil uma grande demanda por monoglicerídeos de alta concentração, devido a suas excelentes propriedades emulsificantes. Apesar do grande número de indústrias consumidoras deste tipo de produto no país, não foi encontrado nenhum fabricante nacional. Desta forma, neste trabalho, foi utilizada toda a infra-estrutura e experiência do Laboratório de Desenvolvimento de Processos de Separação (LDPS), pioneiro na área de destilação molecular no Brasil, para se estudar o processo de concentração de monoglicerídeos a partir de misturas relativamente pobres nestes componentes, utilizando o processo de destilação molecular. Os resultados obtidos representam uma contribuição importante, do ponto de vista tecnológico, para as indústrias produtoras de emulsificantes que têm interesse na produção de monoglicerídeos de alta concentração.

Esta dissertação encontra-se organizada em ordem cronológica, ou seja, à medida que os experimentos eram feitos, os capítulos eram redigidos. Assim, inicialmente, foram realizados experimentos para a caracterização do sistema em estudo (destilador molecular centrífugo), em que a metodologia de análise de superfície de resposta foi utilizada como ferramenta para a obtenção de modelos empíricos capazes de descrever o comportamento do processo. A partir dos modelos obtidos, conseguiu-se mapear as regiões ótimas de operação do destilador molecular estudado, que se traduziram na obtenção de monoglicerídeos com altas concentrações na corrente de destilado, partindo-se de uma mistura de triglicerídeos, diglicerídeos e monoglicerídeos, produzida industrialmente através da reação de glicerólise de gorduras vegetais parcialmente hidrogenadas.

Através de experiência prévia, sabe-se que na destilação molecular, pequenas variações nas condições operacionais do processo acarretam em grandes alterações na eficiência de separação. Desta forma, este estudo inicial de caracterização do sistema foi conduzido variando-se a temperatura do evaporador e a vazão de alimentação, uma vez que estas são duas variáveis operacionais importantes na destilação molecular. As composições das correntes de saída do processo foram determinadas através da cromatografia de permeação em gel ou cromatografia de exclusão por tamanhos (cromatograma típico é mostrado no anexo). Obedecendo a organização deste trabalho, este primeiro estudo é apresentado no Capítulo II.

Como mencionado acima, para a obtenção dos modelos empíricos apresentados no Capítulo II, foi utilizada como matéria prima uma mistura de acilgliceróis produzida industrialmente a partir de óleos parcialmente hidrogenados. No entanto, no Capítulo III, foi realizado um estudo de otimização de algumas condições de reação para a síntese de monoglicerídeos, em batelada, através da glicerólise de óleo de soja refinado. Uma vez encontradas as condições de reação que alcançaram uma maior concentração de monoglicerídeos no equilíbrio químico, os produtos reacionais foram submetidos a destilações moleculares para a produção de monoglicerídeos com teores acima de 90%. Para se atingir tal nível de concentração, foram utilizadas as condições operacionais de destilação otimizadas no Capítulo II. Além da cromatografia de permeação em gel para a determinação da composição da classe de lipídeos, no capítulo III, foram realizadas análises da composição de ácidos graxos durante a reação de glicerólise através da cromatografia gás-líquido (cromatograma típico é mostrado no anexo).

No Capítulo IV, foi realizado um estudo com o intuito de se avaliar os efeitos de algumas condições operacionais de destilação sobre a eficiência do processo. Neste estudo, além da temperatura do evaporador e vazão de alimentação, já exploradas no Capítulo II, foram também estudadas simultaneamente a temperatura do condensador e a temperatura de alimentação. Assim, foi possível comprovar a maior significância das variáveis temperatura do evaporador e vazão de alimentação sobre o sistema estudado.

Para alcançar os objetivos desta etapa, os ensaios foram conduzidos seguindo um planejamento experimental fracionário. Desta forma, pôde-se obter as informações desejadas de uma forma bastante organizada, com um número reduzido de experimentos.

Ainda no capítulo IV, foram obtidos modelos empíricos para a predição da concentração de diglicerídeos nas correntes de saída do processo e, por fim, tanto estes modelos quanto os obtidos no capítulo II foram validados através de dados experimentais.

As principais dificuldades experimentais encontradas durante as destilações moleculares estavam relacionadas com a solidificação de material nas tubulações do equipamento, assim como no condensador. Tais problemas acarretavam no entupimento das linhas e dificuldade de escoamento da corrente de destilado. Para contornar estas dificuldades, todas as tubulações foram aquecidas por meio de fitas térmicas a uma temperatura mínima de 50ºC. Assim como nas tubulações, em algumas condições, fazia-se necessário o aquecimento do condensador por meio de um banho termostático acoplado ao mesmo.

Além disso, para evitar a contaminação dos produtos das destilações devido a resíduos de materiais provenientes de operações anteriores, após cada passo de destilação, o equipamento era cuidadosamente limpo.

Objetivos Gerais

Com base no que foi comentado na introdução geral, os objetivos deste trabalho podem ser enumerados da seguinte forma:

1. Aplicação de planejamento de experimentos para a otimização da concentração de monoglicerídeos, utilizando o processo de destilação molecular.
2. Definição de ferramentas analíticas adequadas aos objetivos deste trabalho.
3. Desenvolvimento de uma estratégia para obtenção de monoglicerídeos de alta pureza, baseando-se nos resultados obtidos nos Planejamentos Experimentais.
4. Validação experimental dos modelos matemáticos ajustados.
5. Síntese de monoglicerídeos através da reação de glicerólise do óleo de soja, utilizando hidróxido de sódio como catalisador.
6. Destilação molecular dos produtos obtidos na reação de glicerólise.

CAPÍTULO I

Revisão Bibliográfica Geral

1.1 Lipídeos

Não há uma definição exata de lipídeos, porém alguns autores apresentaram algumas diferentes definições que, de forma geral, mencionam a característica de lipídeos em apresentar solubilidade em solventes orgânicos como clorofórmio, benzeno, etc (O'Keefe, 1998). Porém estas definições baseadas em solubilidade apresentam problemas óbvios, já que alguns compostos considerados como lipídeos, como alguns ácidos graxos de cadeias curtas, são completamente miscíveis em água.

Apesar deste problema com a definição de lipídeos, estes podem ser divididos em algumas classes de compostos mais simples como ácidos graxos, acilgliceróis (mono-, di- e triglicerídeos) e lipídeos mais complexos tais como ceras, fosfoglicerídeos (fosfolipídeos), esfingolipídeos, lipoproteínas, esteróis e vitaminas liposolúveis.

Com relação ao nome da classe de ácidos graxos, embora a IUPAC (*International Union of Pure and Applied Chemistry*) recomende a substituição do termo "ácido graxo livre" por apenas "ácido graxo", na literatura o termo mais utilizado ainda é "ácido graxo livre". Assim, neste trabalho, muitas vezes ácidos graxos serão chamados de ácidos graxos livres.

Na natureza, estes ácidos graxos são mais comumente encontrados não na forma livre, mas na forma de triglicerídeos (triacilgliceróis), que são moléculas constituídas por uma molécula de glicerol ligada a três moléculas de ácidos graxos, Figura 1.

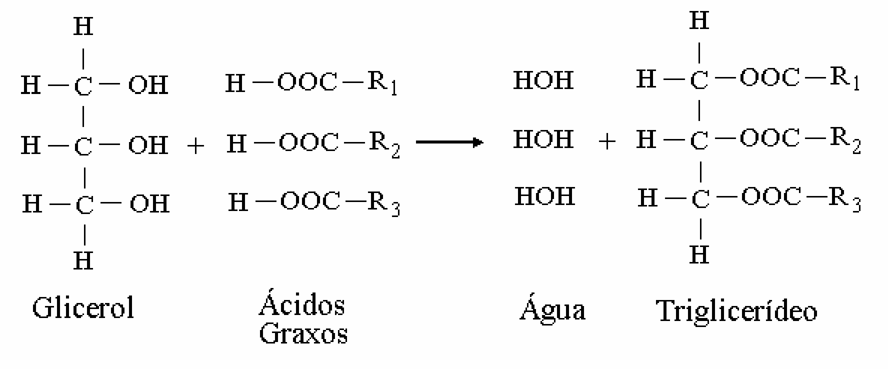

Figura 1: Formação de uma molécula de Triglicerídeo.

As cadeias dos ácidos graxos representados por R_1, R_2 e R_3 são geralmente alifáticas e com diferentes números (normalmente pares) de carbonos. Os ácidos graxos com 2 – 4 átamos de carbonos são considerados de cadeia curta; de 6 a 12 átomos de carbono, cadeia média e de 14 a 24 átomos de carbono de cadeia longa. Estes ácidos graxos podem não possuir duplas ligações (ácidos graxos saturados), ou podem possuir uma ou mais duplas ligações, geralmente na forma de isômeros *cis*. Ácidos graxos com uma dupla ligação são chamados de ácidos graxos monoinsaturados e ácidos graxos com mais de uma dupla ligação são chamados de ácidos graxos poliinsaturados, Figura 2.

Alguns símbolos são utilizados para identificar os diferentes tipos de ácidos graxos, como é o caso do símbolo C18:2 (9,12), representando o ácido linoléico, e C18:3 (6,9,12), representando o ácido γ-linolênico (GLA). O número justaposto ao símbolo C indica o número de átomos de carbono e o segundo número a quantidade de duplas ligações. As posições das duplas ligações na cadeia do ácido graxo são indicadas entre parênteses, pela indicação do átomo que contém a dupla ligação, contando-se a partir da hidroxila terminal da molécula.

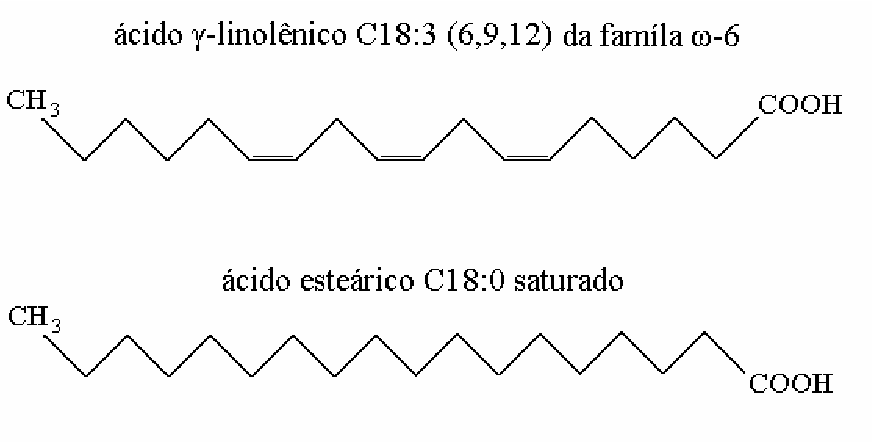

Figura 2: Representações simplificadas de ácidos graxos poliinsaturado e saturado.

No entanto, a IUPAC recomenda a utilização de nomes sistemáticos, os quais indicam, além das posições das duplas ligações, as configurações das ligações, ou seja, ligações na configuração *cis* são representadas pelo símbolo *c*-, enquanto que ligações na configuração *trans* são representadas pelo símbolo *t*-. Assim, nesta nomenclatura, o ácido γ-linolênico (GLA) é conhecido como ácido *c*-6, *c*-9, *c*-12-octadecatrienóico.

Em conseqüência da importância nutricional de alguns tipos de ácidos graxos poliinsaturados, existe também uma outra nomenclatura, na qual é presumido que as duplas ligações ocorrem na forma de ligações conjugadas (duplas ligações intercaladas com ligações simples) na configuração *cis*,*cis*-1,4 (Rossel, 1991). Nesta nomenclatura, os ácidos graxos são divididos em famílias ou séries, dependendo da localização da primeira ligação dupla, contando-se agora a partir do grupo metílico terminal da molécula. São chamados de ácidos graxos da família ω-6, aqueles que possuem a primeira dupla ligação no sexto carbono a partir do grupo metílico terminal da molécula, enquanto ácidos graxos da família ω-3 contêm esta primeira dupla ligação no terceiro carbono. Desta forma, através da Figura 2, observa-se que o ácido γ-linolênico é um ácido poliinsaturado pertencente à família ω-6, que pode ser representado pelo símbolo 18:3n-6. O símbolo n-6 indica que o ácido graxo pertence a família ω-6. A Tabela 1 apresenta diferentes tipos de ácidos graxos poliintaturados das famílias ω-3, ω-6 e ω-9.

Tabela 1: Diferentes tipos de ácidos graxos poliinsaturados.

Símbolos	Nomes descritivos	Nomes sistemáticos
16:3n-3		*c*-7, *c*-10, *c*-13-hexadecatrienóico
16:4n-3		*c*-4, *c*-7, *c*-10, *c*-13-hexadecatetraenóico
18:2n-6	ácido linoléico	*c*-6, *c*-9-octadecadenóico
18:3n-6	ácido γ-linolênico (GLA)	*c*-6, *c*-9, *c*-12-octadecatrienóico
18:3n-3	ácido α-linolênico (ALA)	*c*-9, *c*-12, *c*-15-octadecatrienóico
18:4n-3	ácido estearidônico	*c*-6, *c*-9, *c*-12, *c*-15-octadecatetraenóico
20:3n-9		*c*-5, *c*-8, *c*-11-eicosatrienóico
20:3n-6	ácido dihomo-γ-linolênico	*c*-8, *c*-11, *c*-14-eicosatrienóico
20:4n-3		*c*-8, *c*-11, *c*-14, *c*-17-eicotetraenóico
20:4n-6	ácido araquidônico	*c*-5, *c*-8, *c*-11, *c*-14-eicosatetraenóico
20:5n-3	ácido timnodônico (EPA)	*c*-5, *c*-8, *c*-11, *c*-14, *c*-17-eicosapentaenóico
22:4n-6	ácido adrênico	*c*-7, *c*-10, *c*-13, *c*-16-docosatetraenóico
22:4n-3		*c*-10, *c*-13, *c*-16, *c*-19-docosatetraenóico
22:5n-6	ácido docosapentaenóico	*c*-4, *c*-7, *c*-10, *c*-13, *c*-16-docosapentaenóico
22:5n-3	ácido clupanodônico (DPA)	*c*-7, *c*-10, *c*-13, *c*-16, *c*-19-docosapentaenóico
22:6n-3	ácido cervônico (DHA)	*c*-4, *c*-7, *c*-10, *c*-13, *c*-16 , *c*-19-docosahexaenóico

1.2 Monoglicerídeos

Monoglicerídeos são moléculas constituídas por uma molécula de glicerol ligada a uma molécula de ácido graxo, Figura 3. Por apresentarem um balanço hidrofílico-hidrofóbico em suas estruturas (sendo o glicerol hidrofílico e o ácido graxo hidrofóbico), possuem importantes aplicações industriais. Nas indústrias alimentícia, farmacêutica e de cosméticos, representam cerca de 70% de todos os emulsificantes sintéticos utilizados (Ferreira-Dias et al., 2001). Dentre as aplicações de monoglicerídeos, destaca-se seu uso direto na produção de produtos de panificação, bolos, massas e margarinas (Bailey, 1995; Backels, 1976). Além disso, monoglicerídeos também são utilizados como matéria-prima para a produção de diversos outros tipos de emulsificantes, em que grupos hidroxila do glicerol são substituídos por diferentes tipos de moléculas como ácido acético, lático, cítrico, tartárico, etc (Danisco, 2005).

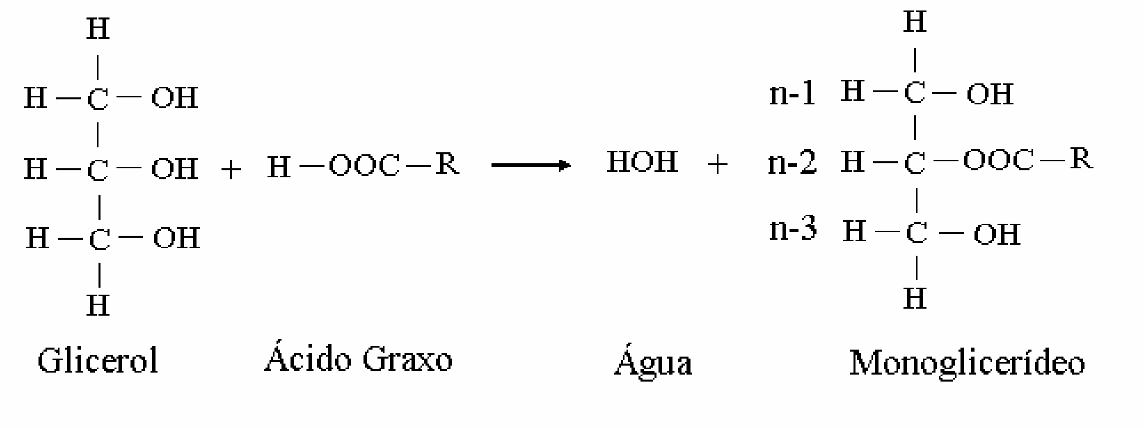

Figura 3: Representação de uma molécula de 2-Monoglicerídeo ou β-Monoglicerídeo.

A síntese de monoglicerídeos pode ser conduzida de diversas formas como, por exemplo: esterificação direta de glicerol com ácidos graxos, transesterificação de ésteres de ácido graxos com glicerol e glicerólise de triglicerídeos (Bancquart, et al., 2001).

Como na natureza, os lipídeos mais abundantes são os triglicerídeos, industrialmente, monoglicerídeos são produzidos normalmente através da reação de glicerólise (UIC-GmbH, 2005), que é um caso particular de alcoólise, consistindo na reação entre moléculas de glicerol (álcool) e moléculas de triglicerídeos, Figura 4.

Esta reação normalmente é conduzida a temperaturas acima de 200ºC, na presença de catalisadores homogêneos. Nestas condições, normalmente obtém-se, no equilíbrio químico, uma mistura que contém em torno de 50% de monoglicerídeos, 40% de diglicerídeos e 10% de triglicerídeos (Sonntag, 1982). Para a produção de 3 mols de monoglicerídeos, são necessários 2 mols de glicerol para cada mol de triglicerídeos.

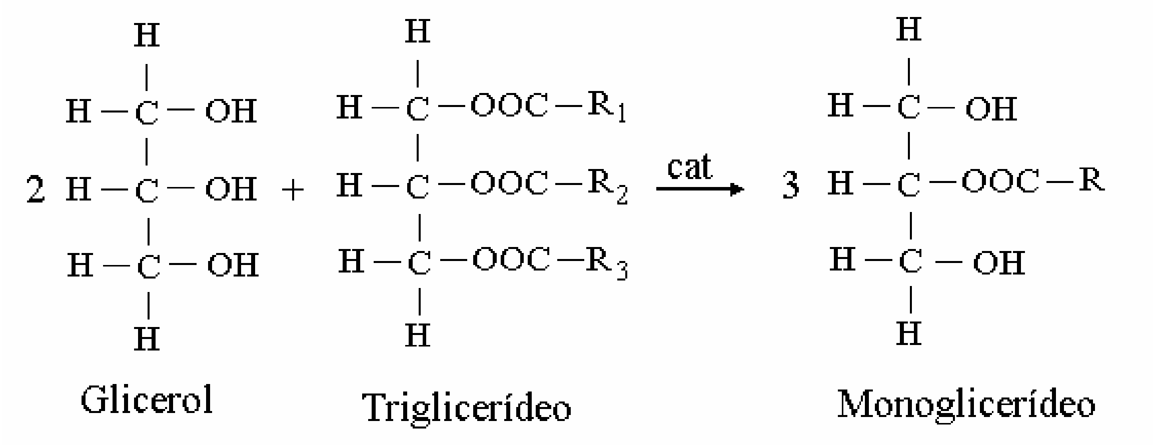

Figura 4: Representação simplificada da reação de glicerólise.

Este é um esquema simplificado da reação uma vez que considera apenas a formação de monoglicerídeos, no entanto, como mostrado na Figura 5, triglicerídeos reagem com glicerol produzindo isômeros de monoglicerídeos e diglicerídeos. Então diglicerídeos reagem novamente com moléculas de glicerol para a formação de novas moléculas de monoglicerídeos (Corma et al.,1998). Devido às altas temperaturas utilizadas na produção de monoglicerídeos, fabricantes normalmente utilizam óleos parcialmente ou completamente hidrogenados para minimizar reações de polimerização e conseqüente formação de produtos indesejáveis (Sukiyama et al., 2001), as quais conferem à mistura reacional cor escura e odor desagradável.

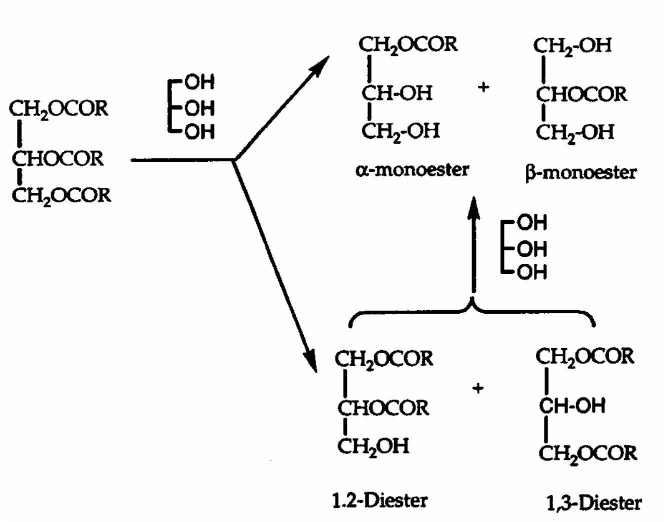

Figura 5: Etapas da reação de glicerólise.

Como mencionado anteriormente, misturas contendo aproximadamente 50% de monoglicerídeos são produzidas, industrialmente, através da reação de glicerólise. Tal nível de concentração é inadequado a certos tipos de aplicações como é o caso de algumas coberturas, recheios e sorvetes, em que o comportamento de derretimento destes alimentos na boca é um ponto crítico (Bailey, 1996). Isso porque, como monoglicerídeos são produzidos a partir de gorduras parcialmente ou completamente hidrogenadas, os triglicerídeos e diglicerídeos residuais apresentam um alto ponto de fusão, comprometendo a sensação de derretimento na boca (Martinello, 2005). Além disso, deve-se destacar a maior capacidade de monoglicerídeos em se complexarem com amido, quando comparados aos diglicerídeos.

Assim, nestes casos específicos de aplicação, emulsificantes conhecidos como monoglicerídeos destilados devem ser utilizados, os quais são monoglicerídeos de alta concentração, normalmente com teor acima de 90%, obtidos através do processo de destilação molecular ou destilação de percurso curto (Cvengros, 1995).

Recentemente, tem-se destacado na literatura o interesse pelo desenvolvimento de processos enzimáticos que possam substituir as tradicionais rotas químicas para a produção de monoglicerídeos. As principais vantagens destes processos catalisados por enzimas são as condições amenas de temperatura e de pH utilizadas, ou seja, baixas temperaturas e pH próximo do neutro (Ferreira-Dias, 2003). Tais condições diminuem o consumo energético e minimizam a ocorrência de reações indesejadas de polimerização. Além destas vantagens, pesquisadores podem explorar a seletividade das lipases em relação aos ácidos graxos e sua regioseletividade pela primeira posição das moléculas de glicerol (posição α) em relação à segunda (posição β). Dentro das reações enzimáticas que têm sido exploradas para a produção de monoglicerídeos estão a hidrólise ou alcoólise de triglicerídeos, glicerólise de triglicerídeos e esterificação ou transesterificação de glicerol com ácidos graxos livres ou ésteres (Bornscheuer, 1999).

Apesar dos processos enzimáticos apresentarem algumas vantagens em relação aos processos catalisados quimicamente, o custo de produção ainda elevado inviabiliza produções em grande escala. Também recentemente, a aplicação de catalisadores heterogêneos (zeólitas) tem sido estudada como uma alternativa aos processos tradicionais para a produção de monoglicerídeos (Pérez-Pariente et al., 2003).

1.3 Destilação Molecular

A destilação molecular consiste em um processo de destilação apropriado para a separação e purificação de substâncias termicamente sensíveis, assim como de líquidos com baixa pressão de vapor (Micov, 1997).

Basicamente, existem dois tipos de destiladores moleculares: destilador de filme descendente e destilador centrífugo (Batistella, 1996). Ambos os modelos têm como princípio de separação o alto vácuo e a formação de um filme líquido sobre a superfície do evaporador. Este filme é responsável por promover efetivas transferências de massa e calor. Tais características permitem a utilização de temperaturas amenas de operação para a realização das separações, quando comparadas às temperaturas utilizadas em processos convencionais de destilação. Além disso, a formação do filme líquido sobre a superfície do evaporador permite que haja apenas um curto tempo de exposição do líquido a ser destilado às temperaturas de operação, devido ao reduzido tempo de residência das moléculas no interior do destilador.

Destiladores moleculares de filme descendente utilizam a força da gravidade para promoverem a formação do filme líquido sobre a superfície do evaporador cilíndrico, geralmente com agitadores responsáveis pela distribuição uniforme do filme sobre toda a superfície do evaporador (Cvengros et al., 2001). Quando há a presença destes agitadores em destiladores de filme descendente, alguns autores preferem utilizar o termo "destiladores de filme agitado" (Martins, 2005).

Já os destiladores moleculares centrífugos utilizam a força centrífuga para promoverem a distribuição do filme líquido sobre o evaporador, que possui forma cônica. A Figura 6 apresenta um esquema simplificado de um destilador molecular centrífugo com suas correntes de saída, as quais são denominadas: corrente de destilado (formada pelas moléculas mais leves que são evaporadas e atingem a superfície do condensador) e corrente de resíduo (formada pelas moléculas mais pesadas que permanecem no evaporador).

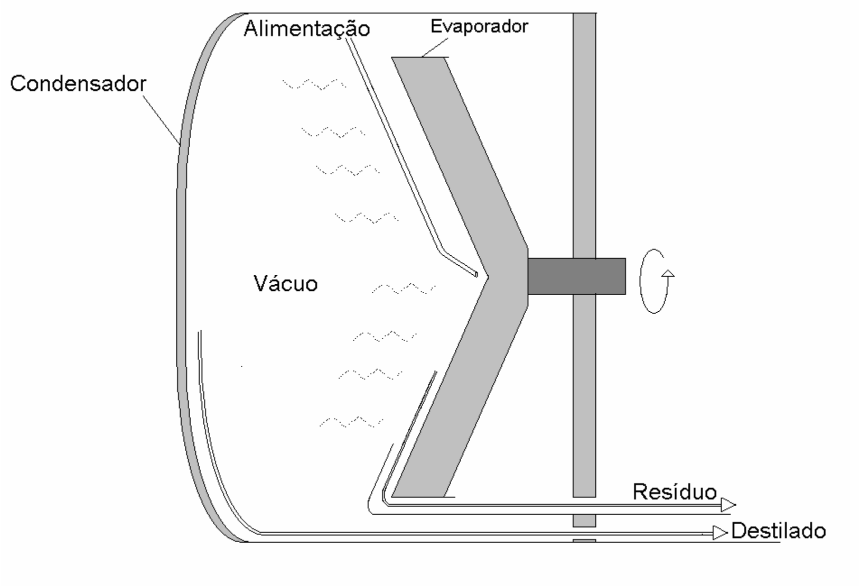

Figura 6: Ilustração simplificada de um destilador molecular centrífugo.

Na destilação molecular, as moléculas de vapor formadas encontram um caminho livre entre as superfícies do evaporador e condensador, ou seja, a distância entre estes dois componentes é menor do que o livre percurso médio das moléculas evaporadas. Nestas condições, teoricamente não há retorno de moléculas da fase vapor para a fase líquida devido à colisão entre moléculas (Batistella, 2000). No entanto, em plantas industriais, a distância entre as superfícies do condensador e do evaporador é maior do que o livre percurso médio das moléculas de vapor. Neste caso, o processo passa a ser chamado de destilação de percurso curto (Chen et al., 2005).

A eficiência do processo depende de variáveis de projeto, tais como geometria do evaporador (Kawala, 2002), tipo de condensador (Cvengros, 2000), presença de componentes entre o evaporador e o condensador (Lutisan, 1998) etc, assim como de condições de operação do processo, como pressão de operação, temperatura de alimentação da matéria prima, temperatura do condensador entre outras.

Com relação à aplicação da destilação molecular na área de lipídeos, além da concentração de monoglicerídeos, um vasto número de trabalhos tem sido publicado na área, como a recuperação de carotenóides a partir do óleo de palma (Batistella et al., 2002), recuperação de tocoferol a partir destilado da desodorização do óleo de soja (Moraes et al., 2004), purificação e desodorização de lipídeos estruturados (Xu et al., 2002) e preparação de concentrados de ácidos graxos poliinsaturados (Breivik, 1997).

1.4 Referência Bibliográfica

Bailey, A. E., Bailey's Industrial Oil & Fat Products, quinta ed., Editado por Y. H. Hui, John Wiley, New York, 1996. p. 569-601.

Bakels, B. J., Distilled Monoglycerides, Food Manufacture 2 (1976) 25.

Bancquart, S., Vanhove, C., Pouilloux, Y., Barrault, J., Glycerol Transesterification with Stearate over Solid Basic Catalysts I. Relationship Between Activity and Basicity, Applied Catalysis A 218 (2001) 1-11.

Batistella, C. B., Maciel, M. R. W., Modeling, Simulation and Analysis of Molecular Distillators: Centrifugal and Falling Film, Computers & Chemical Engineering 20 (1996) S19-S24.

Batistella, C. B., Maciel, M. R. W., Maciel Filho, R., Rigorous Modeling and Simulation of Molecular Distillators: Development of a simulator under conditions of non ideality of the vapor phase, Computers & Chemical Engineering 24 (2000) 1309-1315.

Batistella, C. B., Moraes, E. B., Maciel Filho, R., Maciel, M. R. W., Molecular Distillation Process for Recovering Biodiesel and Carotenoids from Palm Oil, Applied Biochemistry and Biotechnology 98 (2002) 1149-1159.

Bornscheuer, U. T., Kazlauskas R. J., Hydrolases in Organic Synthesis: Regio- and Stereoselective Biotransformations. Weinheim: Wiley-VCH, 1999. p. 164-167.

Breivik, H., Haraldsson, G. G., Kristinsson, B., Preparation of Highly Purified Concentrates of Eicosapentaenoic Acid and Docosahexaenoic Acid, Journal of the America Oil Chemists Society 74 (1997) 1425-1429.

Chen, F. , Cai, T., Zhao, G., Liao, X., Guo, L., Hu, X., Optimizing Conditions for the Purification of Crude Octacosanol Extract from Rice Bran Wax by Molecular Distillation Analyzed Using Response Surface Methodology, Journal of Food Engineering 70 (2005) 47-53.

Corma, A., Iborra, S., Miquel, S., Primo, J., Catalysts for the Production of Fine Chemicals: Production of Food Emulsifiers, Monoglycerides, by Glycerolysis of Fats with Solid Base Catalysts, Journal of catalysis 173 (1998) 315-321.

Cvengros, J., Three-Stage Wiped-Film Molecular Evaporator: Design and Application, Chemical Engineering Technology 18 (1995) 49-58.

Cvengros, J., Mikov, M., Lutisan, J., Modelling of Fractionation in a Molecular Evaporator with Divided Condenser, Chemical Engineering and Processing 39 (2000) 191-199.

Cvengros, J., Pollák, S., Mikov, M., Lutisan, J., Film Wiping in the Molecular Evaporator, Chemical Engineering Journal 81 (2001) 9-14.

Danisco Corporation. Disponível em <http://www.danisco.com>. Acesso em: 21 nov. 2005.

Ferreira-Dias, S., Correia, A. C., Baptista, F. O., da Fonseca, M. M. R., Contribution of Response Surface Design to the Development of Glycerolysis Systems Catalyzed by Commercial Immobilized Lipases, Journal of Molecular Catalysis B: Enzymatic 11 (2001) 699-711.

Ferreira-Dias, S., Correia, A. C., da Fonseca, M. M. R., Response Surface Modeling of Glycerolysis Catalyzed by *Candida rugosa* Lipase Immobilized in Different Polyurethane Foams for the Production of Partial Glycerides, Journal of Molecular Catalysis B: Enzymatic 21 (2003) 71–80.

IUPAC. Nomenclature of Organic Chemistry. London: Pergamon Press, 1979. p.182.

Kawala, Z., Dakiniewicz, P., Influence of Evaporation Space Geometry on Rate of Distillation in High-Vacuum Evaporator, Separation Science & Technology 37 (2002) 1877-1895.

Lutisan, J., Micov, M., Cvengros, J., The Influence of Entrainment Separator on the Process of Molecular Distillation, Separation Science & Technology 33 (1998) 83-96.

Martinello, M. A., Molina, F., Pramparo, M., Purification of Crude Monoglycerides by Two Stages Molecular Distillation. In: 2nd Mercosur Congress on Chemical Engineering, 4th Mercosur Congress on Process Systems Engineering, 2005, Costa Verde, RJ, Anais do do evento (versão eletrônica).

Martins, P. F., Implantação das Metodologias de Caracterização e Estudo da Remoção de Ácidos Graxos Livres dos Destilados Desodorizados de Óleos Vegetais por Meio da Destilação Molecular. 2005. Dissertação (Mestrado em Engenharia Química) – Faculdade de Engenharia Química, Universidade Estadual de Campinas, Campinas.

Micov, M., Lutisan, J., Cvengros, J., Balance Equations for Molecular Distillation, Separation Science & Technology 32 (1997) 3051-3066.

Moraes, E. B., Batistella, C. B., Alvarez, M. E. T., Maciel Filho, R., Maciel, M. R. W., Evaluation of Tocopherol Recovery through Simulation of Molecular Distillation Process, Applied Biochemistry and Biotechnology 113 (2004) 689-711.

O'Keefe, S., F., Nomenclature and Classification of Lipids. In: Akoh, C. C., Min, D. B. Food Lipids. New York: Marcel Dekker, 1998. p. 1-36.

Pérez-Pariente, J., Díaz, I., Mohino, F., Sastre, E., Selective Synthesis of Fatty Monoglycerides by Using Functionalised Mesoporous Catalysts, Applied Catalysis A: General 254 (2003) 173-188.

Rossel, J. P., Vegetable Oils and Fats. In: ______.Analysis of Oilseeds Fats and Fatty Foods. New York: Elsevier Science Publishers, 1998. p. 261-327.

Sonntag, N. O. V., Glycerolysis of Fats and Methyl-Esters – Status, Reviewed and Critique, Journal of the American Oil Chemists Society 59 (1982) A795-A802.

Sukiyama, T., Yoshimi, T., Tanaka, A., Ozaki, S., Nakanishi, K., Analysis of Monoglyceride Synthetic Reaction in a Solvent-Free Two-Phase System Catalyzed by a Monoacylglycerol Lipase from *Pseudomonas sp*. LP7315, Journal of Bioscience and Bioengineering 91 (2001) 88-90.

UIC-GmbH. Disponível em <http://www.uic-Gmbhgmbh.de/ger/pfd_global/druckschriften/08%20Monoglyceride-e.pdf>. Acesso em: 21 nov. de 2005.

Xu, X., Jacobsen, C., Nielsen, N. S., Heinrich, M. T., Zhou, D., Purification and Deodorization of Structured Lipids by Short Path Distillation, European Journal of Lipid Science and Technology 104 (2002) 745-755.

CAPÍTULO II

Response Surface Methodology Applied to Optimization of Distilled Monoglycerides Production

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Response Surface Methodology Applied to Optimization of Distilled Monoglycerides Production

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Abstract: This work demonstrates that response surface methodology (RSM) is a powerful tool for the optimization of the production of distilled monoglycerides (MG). Experiments with a centrifugal molecular distillator having an evaporation area of $0.0046m^2$ were carried out using RSM to identify operating conditions that can lead to higher MG purity. The independent variables studied were the evaporator temperature (TEV) and the volumetric feed flow rate (Q). The experimental range was from 100 to 300°C for TEV and between 5 and 15 mL/min for Q. High-performance size exclusion chromatography (HPSEC) was used to evaluate triglycerides (TG), diglycerides (DG), MG, free fatty acids (FFA) and glycerol (GL) compositions. Results were presented as MG concentration surfaces. Starting from a material with 10.8% of TG, 37.7% of DG, 43.6% of MG, and 7.2% of GL, the maximum MG purity in the distillate stream with just one distillation step was 82.6% at a TEV equal to 250 ºC and Q equal to 5 mL/min. At these conditions, the MG recovery was 61%. A strategy was developed to obtain distilled MG with 96.3% of purity.

KEY WORDS: Distilled monoglycerides; molecular distillation; monoglycerides enhancement; response surface methodology, short path distillation.

2.1 Introduction

Monoglycerides (MG) are widely used in food, pharmaceutical, and cosmetic industries as emulsifiers [1]. They impart stability and the required viscosity. MG also are building blocks for syntheses of lipids, liquid crystals, and drug carries [2].

Researchers have developed three lipase-catalyzed routes to MG—(i) hydrolysis of triglycerides (TG), (ii) alcoholysis of TG, and (iii) esterification or transesterification of glycerol (GL)[3]—considering the mild conditions requirements of the lipases, which are low temperatures and near neutral pH. In these routes, researchers explore the fatty acid selectivity of the lipases and their regioselectivity for the primary vs. secondary positions in the glycerol.

However, industrially, MG production is carried out through a glycerolysis reaction at temperatures above 200ºC, using inorganic catalysts, since this process is cheaper than a lipase-catalyzed reaction. In this industrial reaction, the MG content in the final product is 35–50%. This level of concentration is suitable for many applications, although for some specific uses such as cake or frosting, the mouth melt of the product is critical. The use of a commercially prepared MG emulsifier could negatively affect texture or mouthfeel of the product [4], so distilled MG, which are purified MG (minimum 90%), are required for this use. Normally, MG are obtained by using the molecular distillation process [5]. Also known as short-path distillation, molecular distillation is characterized by a short exposure of the distilled liquid to high operating temperature and vacuum [6,7]. This process has been widely applied to lipid-containing products, including the recovery of carotenoids from palm oil [8], recovery of tocopherol from crude deodorizer distillate of soybean oil [9], the purification and deodorization of structured lipids [10] and the preparation of purified concentrates of polyunsaturated fatty acids [11].

In this work, the molecular distillation process was applied for MG concentration, and response surface methodology (RSM) was used to obtain MG concentration surfaces in the residue and distillate streams, both of which are product streams from the distillator. The independent variables studied were the evaporator temperature (TEV) and the feed flow rate (Q). Furthermore, a strategy was developed to purify MG using only the molecular distillation process, without the GL stripping process.

2.2 Materials and Methods

2.2.1 Materials

The commercial MG (10.8% TG, 37.7% DG, 43.6% MG, 0.7% FFA, and 7.2% GL) that was fed into the molecular distillator was donated by Braswey S.A. (Pirapozinho, SP, Brazil). It is produced from partially hydrogenated vegetable oil.

2.2.2 Method of analysis

Gel permeation chromatography, also called high-performance size-exclusion chromatography (HPSEC), was used for the acylglycerols, FFA and GL analyses [12]. The chromatographic system consisted of an isocratic HPLC pump (model 515; Waters, Milford, MA), a differential refractometer detector (model 2410; Waters), and an oven for columns maintained at 40ºC by a temperature control module (Waters). The samples were injected using a manual injector (model 7725i; Rheodyne; Alltech, Deerfield, IL), with a 20-µL sample loop. Two HPSEC columns, Styragel HR 1 and HR 2 (Waters), with dimensions of 7.8 × 300 mm and particule size of 5 µm, were connected in series. These columns are packed with styrenedivinylbenzene co-polymer. The mobile phase used was HPLC-grade THF from Tedia Inc. (Fairfield, OH) at a flow rate of 1 mL/min. The typical pressure at this flow rate was 450 psi (3102 kPa). All the standards were obtained from

Supelco, Inc. (Bellefonte, PA). Data processing was done by the Millenium software 2010 Chromatography Manager Software from Waters.

2.2.3 Molecular distillator

The model used in this work was a centrifugal distillator system from Myers Vacuum Inc. (Kittanning, PA), with an evaporation surface area of $0.0046 m^2$. The feed temperature was 60ºC and the condenser temperature was 30ºC in the first factorial design and 60ºC in the second. The typical pressure of the system was 16 Pa, and the evaporator rotation velocity was 1350 rpm.

2.2.4 Surface Response Methodology

The aim of this work was to optimize conditions for the MG concentration and then to develop a strategy to obtain distilled MG. Therefore, RSM, a set of mathematical and statistical methods developed for modeling phenomena, was applied to find combinations of a number of experimental factors that will lead to optimum responses [13].

In RSM, simple coded models such as linear and quadratic expressions are fitted. In this work, independent and dependent variables were fitted to a second-degree polynomial equation (Eq. 1), where y is the estimated response (MG concentration in the distillate stream, MGD, or MG concentration in the residue stream, MGR), b_0 is a constant, b_{ij} are the coefficients for each term, and x_i are the independent factors in coded values (x_1 corresponds to the coded value for TEV and x_2 corresponds to the coded value for Q).

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{22} x_2^2 + b_{12} x_1 x_2 \qquad (1)$$

By analyzing Equation 1, which is a quadratic model with two variables, one can see that it contains 6 parameters, so the number of combinations of the independent variable levels must be higher than 6, since it is not possible to predict values when the number of equation parameters is higher than the number of independent variable levels. Thus, factorial designs consisting of 2^2 trials plus a star configuration (4 axial points) with 3 central points were carried out. The distance of the axial points from the central point is calculated from the equation $\alpha = (2^n)^{1/4}$, where α is the distance of the axial points from the central points and n is the number of independent variables [14]. This kind of factorial design, also known as central composite design, is suitable for the fit of Equation 1, because, for two independent variables, it contains 9 different combinations of the independent variable levels. The 3 central points are important since they represent a set of experimental conditions at which 3 replicates are carried out. The variation between them represents the deviation of all experiments [15]. Furthermore, they provide additional degrees of freedom (DF) for error estimation.

All data were treated with the aid of STATISTICA 7 from Statsoft Inc. (Tulsa, OK). The quality of the fitted models was evaluated by the analysis of variance (ANOVA), based on *F*-test [16] and on the percentage of explained variance, which provides a measurement of how much of the variability in the observed response values could be explained by the experimental factors and their interactions [17].

2.3 Results and Discussion

2.3.1 Factorial Designs

In the molecular distillation process, two product streams are generated: distillate (rich in the molecules that escape from the evaporator) and residue (rich in the heavier molecules). The process initially was carried out following a factorial design to characterize the system behavior and to verify whether the experimental value range should be adjusted to surround the optimum region, which means the maximum of MG concentration in the distillate stream (MGD). The independent variables studied were TEV and Q, since they are very important process variables in the molecular distillation process.

Experimental values were chosen according to previous experience. Values of feed flow rate lower than 4 mL/min may not be high enough to form a uniform thin film on the evaporator surface. A uniform thin film promotes efficient mass and energy transfers [18]. For feed flow rate, values higher than 15 mL/min, the system operated with low effectiveness because the residence time of the molecules on the evaporator is too low. Therefore, the feed flow rate varied from 5 to 15 mL/min. The TEV was varied from 100 to 250°C. At 100 ºC, the first significant GL drops on the condenser wall can be observed. The experimental conditions and the results for the first factorial design are shown in Table 1.

The fitted coded models for the MGD and MGR are shown in Equations 2 and 3 respectively, where all the coefficients of Equation 1 were considered.

$$MGD = 56.18 + 22.43xTEV - 7.90xTEV^2 - 11.06xQ - 6.81xQ^2 - 4.60xTEVxQ \qquad (2)$$

$$MGR = 42.62 - 1.82xTEV - 1.85xTEV^2 + 0.64xQ - 0.11xQ^2 + 0.82xTEVxQ \qquad (3)$$

By analyzing the ANOVA, shown in Table 2, one may conclude that the models fit the experimental data quite well, since the calculated *F* values (lack of fit/pure error) are lower than the critical *F* value ($F_{0.95;3;2}$ = 19.16) at 95 % of confidence (i.e., at this confidence level, there is no evidence of lack of fit for the models).

Table 1: Coded levels, real levels (in parentheses), and concentration of MG in the distillate and residue streams for the first (**A**) and second factorial design[a] (**B**).

	(**A**) First factorial design				(**B**) Second factorial design			
Run	TEV (ºC)	Q (mL/min)	MGD (%)	MGR (%)	TEV (ºC)	Q (mL/min)	MGD (%)	MGR (%)
1	-1 (122)	-1 (6.5)	19.6	42.2	-1 (215)	-1 (6.5)	78.1	37.5
2	+1 (228)	-1 (6.5)	79.6	38.0	+1 (285)	-1 (6.5)	70.9	25.7
3	-1 (122)	+1 (13.5)	9.1	42.5	-1 (215)	+1 (13.5)	56.3	41.8
4	+1 (228)	+1 (13.5)	50.8	41.5	+1 (285)	+1 (13.5)	77.7	36.1
5	-1.41 (100)	0 (10)	14.7	41.8	-1.41 (200)	0 (10)	56.9	41.5
6	1.41 (250)	0 (10)	69.2	35.3	1.41 (300)	0 (10)	65.2	29.3
7	0 (175)	-1.41 (5)	61.7	41.6	0 (250)	-1.41 (5)	74.8	26.8
8	0 (175)	1.41 (15)	26.9	42.5	0 (250)	1.41 (15)	68.8	41.0
9	0 (175)	0 (10)	55.1	41.9	0 (250)	0 (10)	75.2	37.4
10	0 (175)	0 (10)	60.9	42.9	0 (250)	0 (10)	77.5	36.6
11	0 (175)	0 (10)	51.8	43.0	0 (250)	0 (10)	73.1	36.6

[a]TEV, evaporator temperature; Q, volumetric feed flow rate; MGD, MG concentration in the distillate stream; MGR, MG concentration in the residue stream.

Furthermore, the results show that the model for the MGD accounted for a high percentage of explained variance (97.36 %) and the calculated *F* value (regression/residual) is more than seven times higher than the critical *F* value at 95 % of confidence ($F_{0.95,5,5}$ = 5.05), indicating that the regression is statistically significant.

As can be seen in Figure 1, obtained from Equation 2, the MG concentration depends more on TEV than on Q, however, both operating variables are important. An increase in TEV and a decrease in Q led to an increase in the MGD. Therefore, to maximize MGD, TEV must be kept at the highest tested levels and Q must be kept at the lowest levels. The maximum of MGD seems to be near TEV = 250ºC and Q = 5 mL/min.

Table 2: ANOVA for the fitted models [a].

Source of Variation	Model	Sum of Square	Degrees of Freedom	Mean Square	*F*-ratio
Regression	Equation 2	5549.264	5	1109.853	36.84 [b]
	Equation 3	52.620	5	10.524	11.37 [b]
	Equation 4	570.002	5	114.000	10.57 [b]
	Equation 5	323.592	5	64.718	66.93 [b]
Residual	Equation 2	150.615	5	30.123	–
	Equation 3	4.629	5	0.926	–
	Equation 4	53.919	5	10.783	–
	Equation 5	4.833	5	0.967	–
Lack of Fit	Equation 2	105.507	3	35.205	1.56 [c]
	Equation 3	3.925	3	1.308	3.71 [c]
	Equation 4	44.262	3	14.754	3.06 [c]
	Equation 5	4.373	3	1.458	6.34 [c]
Pure error	Equation 2	45.108	2	22.554	–
	Equation 3	0.704	2	0.352	–
	Equation 4	9.657	2	4.829	–
	Equation 5	0.460	2	0.230	–
Total	Equation 2	5699.879	10		
	Equation 3	57.248	10		
	Equation 4	623.921	10		
	Equation 5	328.425	10		

[a] Equation 2, percent of explained variance, 97.36; percent of explicable variance, 99.21. Equation 3, percent of explained variance, 91.92; percent of explicable variance, 98.77. Equation 4, percent of explained variance, 91.36; percent of explicable variance, 98.45. Equation 5, percent of explained variance, 98.53; percent of explicable variance, 99.86. [b] *F*-ratio (regression/residual). [c] *F*-ratio (lack of fit/pure error).

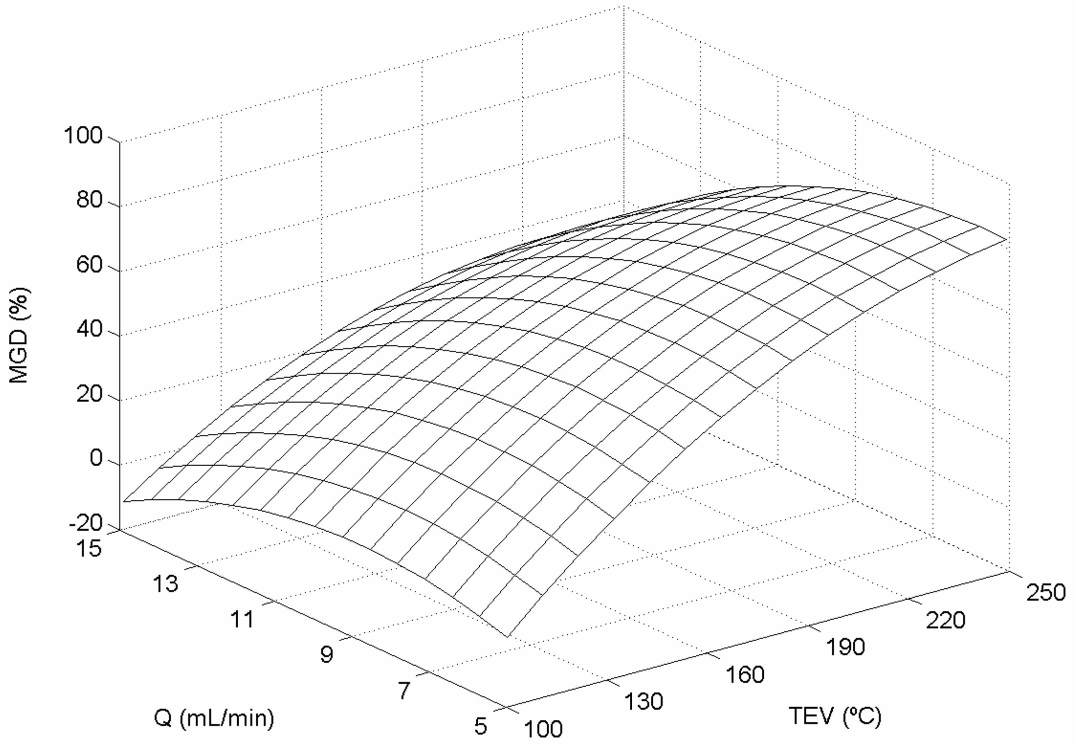

Figure 1: Response surface for the MG concentration in the distillate stream for the first factorial design. TEV, evaporator temperature; Q, volumetric feed flow rate; MGD, MG in the distillate stream.

From Equation 2, the dependent variable has negative values at high Q and low TEV, which has no physical meaning. This happens owing to the low MGD at this condition (high GL concentration in the distillate stream). However, this does not compromise the conclusions from the surface analysis.

The surface shown in Figure 2 was obtained from Equation 3. This figure shows a small increase in MG content in the residue when the temperature is increased from 100 to approximately 160ºC. In explanation, at these conditions, the evaporation rate of GL (molecule of lowest vapor pressure in the starting material) is higher than the evaporation rate for MG, so a considerable amount of GL leaves the distillator in the distillate stream, which does not occur with the MG molecules. Figure 2 confirms that TEV is more important than Q since, at a given TEV, the MGR varies just slightly.

At high temperatures and low feed flow rate, MGR decreases drastically (Fig. 2) since a significant amount of MG leaves the distillator in the distillate stream. This observation agrees with Figure 1.

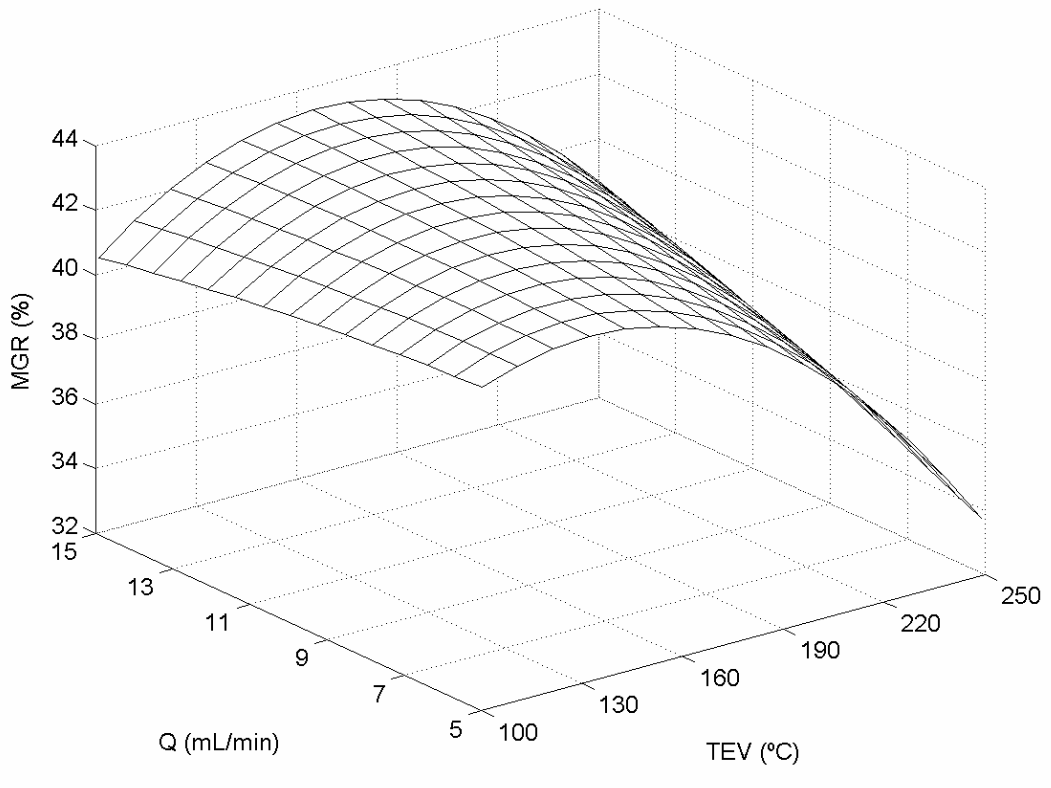

Figure 2: Response surface for the MG concentration in the residue stream for the first factorial design. For abbreviations see Figure 1.

Thus, based on the first factorial design, a second factorial design was carried out to confirm the tendency presented in Figure 1 and to find the optimum region for the MGD.

In the second factorial design, the level of Q was kept the same while the TEV experimental range was increased. The new TEV experimental range was from 200 to 300ºC, as shown in Table 1.

Table 3 contains experimental data on the ratio of D to F at different operating conditions, where F is the mass of the starting material fed into the distillator and D is the mass of the distillate stream obtained in the distillation. It can be noted that, as expected, TEV and Q are also important operating variables in the yield of the process. D/F increases with increasing TEV and decreases with increasing Q owing to the diminution of the residence time of the molecules on the evaporation surface.

The coded models for the MGD and MGR in the new factorial design are shown in Equations 4 and 5, respectively, where, again, all the coefficients of Equation 1 were considered.

$$MGD = 75.27 + 3.25 x TEV - 6.04 x TEV^2 - 2.94 x Q - 0.66 x Q^2 + 7.13 x TEV x Q \qquad (4)$$

$$MGR = 36.88 - 4.37 x TEV - 0.59 x TEV^2 + 4.35 x Q - 1.32 x Q^2 + 1.51 x TEV x Q \qquad (5)$$

Through the ANOVA, shown in Table 2, one can see that there is no evidence of lack of fit for the fitted models in the second factorial design, since the calculated F values (lack of fit/pure error) are lower than the critical F value ($F_{0.95,3,2}$ = 19.16) at 95% confidence for both models. Furthermore, the results show that the model for the MG concentration in the residue (MGR), Equation 5, is predictive in the experimental conditions studied, since the percent of explained variance is high (98.53%) and the calculated F value (regression/residual) is more than 13 times higher than the critical F

value at 95% of confidence ($F_{0.95,5,5} = 5.05$). As a practical rule, the regression can be considered useful to predict values when the calculated *F* value (regression/residual) is more than 10 times higher than the critical *F* value [19].

Table 3: Experimental data of the ratio D/F at different operating conditions[a].

	100 D/F (%)		
TEV (ºC)	Q = 5 mL/min	Q = 10mL/min	Q = 15mL/min
200	13.8	6.5	4.5
220	21.5	10.3	7.3
240	35.3	16.7	7.4
260	46.7	19.4	14.0
280	58.3	31.2	16.6
300	78.5	35.8	17.1

[a] D, mass of distillate stream obtained in the distillation; F, mass of starting material fed into the distillator; for other abbreviations see Table 1.

As can be seen in Figure 3, obtained from Equation 4, at low values of Q, the MGD starts decreasing at temperatures above 250ºC, owing to the significant amount of DG that leaves the distillator in the distillate stream under these conditions. Q is important because, at high values of Q, the residence time of the molecules on the evaporator surface is short and DG evaporation may not be high enough to dilute the MG in the distillate stream. Figure 3 shows that the maximum MG content obtained in the studied conditions, with just one distillation, is approximately 80%.

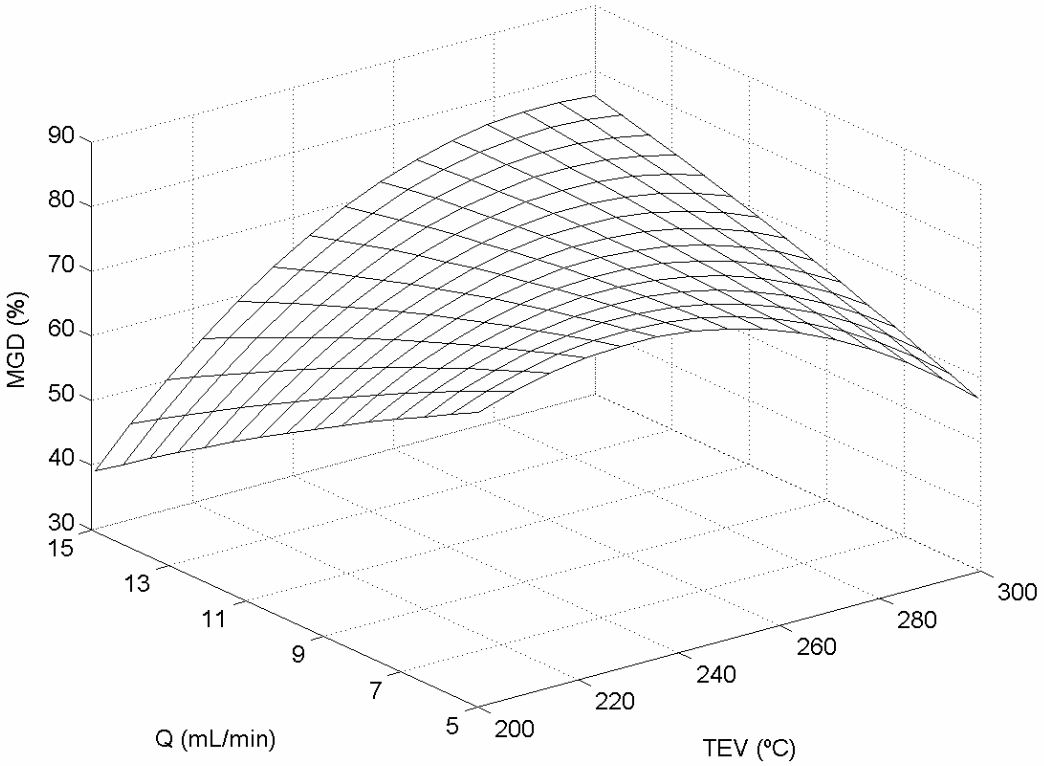

Figure 3: Response surface for the MG concentration in the distillate stream for the second factorial design.

2.3.2 *Strategy for the Distilled MG Production*

A strategy consisting of four distillation steps was developed to obtain distilled MG. In this strategy, the first step was based on the results given by the response surfaces. The other three steps were carried out as a refinement, to obtain highly concentrated MG. Actually, the best operating conditions for these three steps can not be obtained from the factorial design, since the feed concentrations of the components in these distillations are different from the starting material used in the factorial designs. However, the MG concentration surfaces give very important information about the experimental range of TEV and Q that must be explored.

This strategy is presented in Figure 4, where the distillate streams are represented by the symbol D and the residue streams are represented by the symbol R. The numbers 1, 2, 3 and 4 refer to the number of distillations carried out. The first distillation was carried out at TEV = 250ºC and Q = 5mL/min, since, as shown in Figure 3, maximal MG content in the distillate was obtained around this condition. Two subsequent distillations were carried out to decrease the GL concentration. A last distillation at TEV = 250ºC and Q = 5mL/min was made to obtain a final product containing 96.3% MGD.

Table 4 contains experimental data on the component concentrations, such as the individual MG recovery for each stream. In this table, the MG concentration obtained in the distillate and residue streams of the first distillation (streams 1D and 1R) are 82.6% and 31.4%, respectively. Comparing these values with the values predicted by the fitted models in the first and second factorial designs confirmed the good agreement between the experimental observations and the mathematical models. In the first factorial design, the predicted values for the MGD and MGR are 83.3% and 33.6%. In the second factorial design, the predicted values are 78.1% and 28.1%, respectively. In analyzing the MG recovery, it can be concluded that a product with a MG content higher than 90% (stream 2R) can be reached with a total MG recovery of 55.0 %.

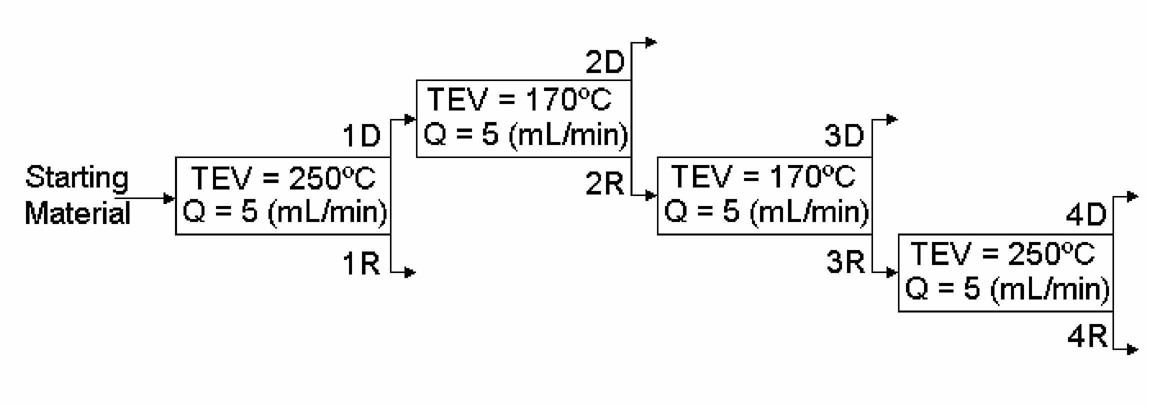

Figure 4: Scheme of the strategy adopted for the production of distilled MG.

Table 4: Component concentrations and the individual MG recovery for each stream[a].

Stream	TG (%)	DG (%)	MG (%)	FFA (%)	GL (%)	MG recovery
Starting Material	10.8	37.7	43.6	0.7	7.2	
1D	ND	2.6	82.6	1.5	13.4	0.609
1R	17.2	50.0	31.4	0.9	0.6	0.391
2D	ND	ND	36.8	4.9	58.2	0.096
2R	ND	5.3	90.2	1.0	3.6	0.904
3D	ND	ND	85.8	3.8	10.2	0.087
3R	ND	6.5	91.5	1.4	0.6	0.913
4D	ND	2.1	96.3	ND	1.6	0.436
4R	ND	12.1	87.1	0.3	0.6	0.564

[a] GL, glycerol, ND, not detected; D, distillate; R, residue.

2.4 References

1. Sakiyama, T., T. Yoshimi, A. Tanaka, S. Ozaki, and K. Nakanishi, Analysis of Monoglyceride Synthetic Reaction in a Solvent-Free Two-Phase System Catalyzed by a Monoacylglycerol Lipase from Pseudomonas sp. LP7315, *J. Biosci. Bioeng. 91*: 88-90 (2001).

2. Berger, M., M. Schneider, Regioisomerically Pure Mono- Diglycerols as Synthetic Building Blocks, *Fat. Sci. Technol. 95*: 169-175 (1993).

3. Bornscheuer, U. T., R. J. Kazlauskas, *Hydrolases in Organic Synthesis: regio- and stereoselective biotransformations*, Wiley-VCH, Weinheim, 1999, pp. 164-167.

4. Bailey, A. E., *Bailey's Industrial Oil & Fat Products*, 5th Edition, Edited by Y. H. Hui, John Wiley, New York, 1996, pp. 569-601.

5. Cvengros, J., Three-Stage Wiped-Film Molecular Evaporator: Design and Application, *Chem. Eng. Technol. 18*: 49-58 (1995).

6. Micov, M., J. Lutisan, and J. Cvengros, Balance Equations for Molecular Distillation, *Sep. Sci. Technol. 32*: 3051-3066 (1997).

7. Batistella, C. B., M. R. W. Maciel, R. Maciel Filho, Rigorous Modeling and Simulation of Molecular Distillators: Development of a simulator under conditions of non ideality of the vapor phase, *Comput. Chem. Eng. 24*: 1309-1315 (2000).

8. Batistella, C. B., E. B. Moraes, R. Maciel Filho, M. R. W. Maciel, Molecular Distillation Process for Recovering Biodiesel and Carotenoids from Palm Oil, *Appl. Biochem. Biotechnol. 98*: 1149-1159 (2002).

9. Moraes, E. B., C. B. Batistella, M. E. T. Alvarez, R. Maciel Filho, M. R. W. Maciel, Evaluation of Tocopherol Recovery through Simulation of Molecular Distillation Process, *Ibid. 113*: 689-711 (2004).

10. Xu, X., C. Jacobsen, N. S. Nielsen, M. T. Heinrich, D. Zhou, Purification and Deodorization of Structured Lipids by Short Path Distillation, *Eur. J. Lip. Sci. and Technol. 104*: 745-755 (2002).

11. Breivik, H., G. G. Haraldsson, B. Kristinsson, Preparation of Highly Purified Concentrates of Eicosapentaenoic Acid and Docosahexaenoic Acid, *J. Am. Oil Chem. Soc. 74*: 1425-1429 (1997).

12. Schoenfelder, W., Determination of Monoglycerides, Diglycerides, Triglycerides and Glycerol in Fats by Means of Gel Permeation Chromatography, *Eur. J. Lip. Sci. and Technol. 105*: 45-48 (2003).

13. Ferreira-Dias, S., A.C. Correia, F.O. Baptista and M.M.R. da Fonseca, Contribution of Response Surface Design to the Development of Glycerolysis Systems Catalyzed by Commercial Immobilized Lipases, J. *Mol. Catal B: Enzymatic. 11*: 669-711 (2001).

14. Khuri, A.I., J. A. Cornell, *Response surface design and analyses*, Marcel Dekker Inc, New York, 1987.

15. Carvalho, C. M. L., M. L. M. Serralheiro, J. M. S. Cabral, M. R. Aires-Barros, Application of Factorial Design to the Study of Transesterification Reactions Using Cutinase in AOT-Reversed Micelles, *Enzyme Microb. Technol. 21*: 117–123 (1997).

16. Box, G. E. P., W. G. Hunter, J. S. Hunter, *Statistics for Experimenters*, Wiley, New York, 1978, pp. 510-539.

17. Burkert, J. F. M., F. Maugeri, M. I. Rodrigues, Optimization of Extracellular Lipase Production by *Geotrichum* sp. Using Factorial Design, *Bioresour. Technol. 91*: 77-84 (2004).

18. Batistella, C. B., M. R. W. Maciel, Recovery of Carotenoids from Palm Oil by Molecular Distillation. *Computers Chem. Engng. 22*: S53-S60 (1998).

19. Barros Neto, B., I. S. Scarminio, and R. E. Bruns, *Como Fazer Experimentos*, 2nd Ed., Editora da UNICAMP, São Paulo, Brazil, 2003, pp.251-266.

CAPÍTULO III

Optimization of Distilled Monoglycerides Production

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Optimization of Distilled Monoglycerides Production

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Abstract: Monoglycerides (MG) are emulsifiers widely used in food and pharmaceutical industries. Current industrial processes for MG production consist on the interesterification of triglycerides (TG) with glycerol (GL), in the presence of inorganic catalysts at high temperatures (>200°C). This reaction is known as glycerolysis and produces a mixture of approx 50 % of MG. This level of concentration is suitable for many applications, although, for some specific uses like margarine, shortening, icing and cream filling, require distilled MG, which are purified MG (min. 90%) obtained by the molecular distillation process. Therefore, in this work, a 2^3 factorial design was employed to evaluate the effects of reaction parameters in the MG content after the interesterification reaction of refined soybean oil with GL in the presence of sodium hydroxide as catalyst. After that, the MG content in the reaction product was enhanced through the molecular distillation process in order to obtain distilled MG.

KEY WORDS: Glycerolysis; soybean oil; distilled monoglycerides; molecular distillation; short path distillation; factorial design.

3.1 Introduction

Many different types of lipid-based emulsifier can be applied to the food, cosmetic, and pharmaceutical industries. The manufacturer must select the one that is the most suitable for each particular product, considering the physicochemical properties of the final product, cost, and availability of the emulsifier and its compatibility with other ingredients [1].

Monoglycerides (MG) are the predominant type of emulsifier, representing about 70% of the synthetic emulsifiers produced [2]. Some researchers have developed three lipase-catalyzed routes to MG: (1) hydrolysis or alcoholysis of triglyceride (TG), (2) glycerolysis of TG, and (3) esterification or transesterification of glycerol (GL), considering the mild condition requirements of the lipases (low temperatures and near neutral pH). Furthermore, they can explore the lipase fatty acid selectivity and regioselectivity for the primary vs secondary positions in the GL [3].

However, industrially, MG are manufactured by batch or continuous reactions at temperatures greater than 200ºC, using inorganic catalysts. Products with around 50% of MG content are achieved by direct esterification reaction, when the starting material is fatty acid or, by interesterification when the starting material is TG. As the dominant part of the manufacturing cost is the price of the feed material, interesterification is preferred, because acids are more expensive than TG. Direct esterification is frequently used when MG with a specified acid distribution is required.

The MG content obtained in these chemical reactions is suitable for many applications, although for some specific uses such as cake or icing, the mouth-melt of the product is critical. The use of a commercially prepared MG emulsifier could impact texture or mouthfeel of the product [4], so that distilled MG are required, which are purified MG (min. 90%), normally obtained through the molecular distillation process.

Also known as short path distillation, molecular distillation is characterized by a short exposure of the distilled liquid to the operating temperature and high vacuum [5,6]. Because of these features, besides the concentration of MG, this process has been widely applied in lipid areas. Some of these applications include the recovering of carotenoids from palm oil [7], recovering of tocopherol from crude deodorizer distillate of soya oil [8], purification and deodorization of structured lipids [9], and the preparation of purified concentrates of polyunsaturated fatty acid [10].

The aim of this study is to find the best conditions for the glycerolysis of refined soybean oil in a batch reactor, carried out at relatively low temperatures (190 – 210ºC), and also to obtain distilled MG from the reaction products using molecular distillation process.

3.2 Materials and Methods

3.2.1 Determination of TG, Diglycerides, MG , Free Fatty Acids and GL

For the determination of TG, diglycerides (DG), MG, free fatty acids and GL, high-performance size-exclusion chromatography (HPSEC) was used according to Schoenfelder (2003) [11]. The chromatographic system consists of an isocratic pump, model 515 high-performance liquid chromatography (HPLC) Pump (Waters, Milford, MA), a differential refractometer detector model 2410 (Waters), and an oven for columns thermostatted at 40ºC by a temperature control module (Waters). The samples were injected using a manual injector (model 7725i; Rheodyne; Alltech, Deerfield, IL), with a 20-µl sample loop. Two HPSEC columns Styragel HR 1 and HR 2 (Waters), with dimensions of 7.8 x 300 mm and particule size of 5 μm, packed with styrenedivinylbenzene copolymer were connected in series. The mobile phase used was HPLC-grade tetrahydrofuran from Tedia (Fairfield, OH) and the flow rate was 1 ml/min. The typical pressure at this flow rate was 470 psi. All the standards were obtained from Supelco (Bellefonte, PA). The data processing was done by the Millenium software 2010 Chromatography Manager Software from Waters.

3.2.2 Analysis of Fatty Acid Composition

The fatty acid composition of the reaction products was determined by gas-liquid chromatography (GLC). Acylglycerols were converted into fatty acid methyl esters (FAME) according to Hartman (1973) [12]. The FAME mixture was analyzed by a Varian gas chromatograph model STAR 3600CX (Lexington, MA) equipped with a flame ionization detector and with a DB 23 column (30 m x 0.53 mm, J&W Scientific, Folsom, CA). Injector and detector temperatures were set at 250ºC and 300ºC, respectively. The carrier gas used was helium at 46 mL/min. Air and hydrogen flow rates were 334 and 34 mL/min, respectively. The program of the oven temperature was as follows: starting at 50 ºC for 2 min; from 50ºC to 180ºC at 10ºC/min; 180ºC was held for 5 min; from 180ºC to 240ºC at 5ºC/min. Identification of different FAME was based on a reference standard mixture F.A.M.E. Mix C4-C24 (Supelco, Bellefonte, PA).

3.2.3 Glycerolysis Reaction

In this work, to evaluate the effect of the mass ratio of GL to refined oil (GL/TG), and also the effects of the reaction temperature (T) and of the amount of catalyst (NaOH), a 2^3 factorial design with three central points was planned, as shown in Table 1. Experiments were carried out in a 250-mL glass-stoppered volumetric flask of 250 mL.

Initially, 50g of reactants consisting of commercial refined soybean oil and GL (Labsynth, SP, BRA) were fed in the batch reactor. Then, the mixture of reactants was heated by a stirring hot plate (Fisatom, SP, BRA) to a defined temperature, in nitrogen atmosphere, stirring the reaction mixture at 500 rpm. When the defined temperature was reached, a known amount of catalyst (NaOH, LabSynth, BRA) was added to the reactor (reaction time = 0). In order to monitor the conversion of TG into MG and also to verify whether the reaction reached the equilibrium condition, samples were withdrawn from the reactor at different times. The mass ratio (GL/TG) of each run, as well as the amount of catalyst (amount of NaOH) and the reaction temperatures (T) studied are shown in Table 1.

Table 1: Coded levels and real levels (in parentheses) of the variables studied and the results obtained in the glycerolysis reaction.

Runs	NaOH (g)	T (ºC)	GL/TG	% of MG[a] (t =90 min)
1	-1 (0.07)	-1 (190)	-1 (0.18)	41.0
2	1 (0.13)	-1 (190)	-1 (0.18)	41.8
3	-1 (0.07)	1 (210)	-1 (0.18)	41.8
4	1 (0.13)	1 (210)	-1 (0.18)	40.7
5	-1 (0.07)	-1 (190)	1 (0.30)	48.3
6	1 (0.13)	-1 (190)	1 (0.30)	51.8
7	-1 (0.07)	1 (210)	1 (0.30)	53.8
8	1 (0.13)	1 (210)	1 (0.30)	54.5
9	0 (0.10)	0 (200)	0 (0.24)	48.6
10	0 (0.10)	0 (200)	0 (0.24)	48.6
11	0 (0.10)	0 (200)	0 (0.24)	49.6

[a] Normalized peak area.

Manufacturers avoid oils rich in unsaturated fatty acids, such as soybean oil, because at temperatures >200ºC, they burn or polymerize causing a dark color, off-odor and burnt taste; so, usually, they use partially or fully hydrogenated fat. For these reasons, the experimental range of the reaction temperature was studied at relatively low levels, between 190ºC and 210ºC, and the fatty acid composition of the reaction products was accompanied. In case of significant degradation, the fatty acids composition of the reaction products may vary during the reaction time, what can be detected by the GLC analyses. Furthermore, if significant polymerization occurs, the molecules of high molecular weight formed in the reaction may be detected by the HPSEC analysis, since this method of analysis identifies components by their sizes.

Usually, in the factorial design, the variables levels are denoted by coded numbers. The superior levels are represented by +1 and the inferior levels by -1. The central points, which are used for the error estimation, are denoted by 0. They are replicates in the center of the experimental range that permit the evaluation of the repeatability of the experiments. The variation between them reflects the variability of whole design [13]. The response analyzed was the MG concentration at the equilibrium condition.

As GL is not totally soluble in the mixture, even in a system with good agitation, the percentage of GL varies considerable in different points of the reactor, causing sampling problem. To avoid this problem, the percentage of MG (in the equilibrium condition) reported in Table 1 was obtained by normalizing the peak areas of TG, DG and MG. Furthermore, this procedure permits the comparison among runs, with different initial GL concentration.

3.2.4 Molecular Distillation

Molecular distillation, also known as short path distillation, is a separation process characterized by a short exposure of its distilled liquid to the operating temperature, high vacuum in the distillation space (distance between the evaporator and condenser), and a small distance between these elements. The separation principle is the vacuum (enabling the molecules to evaporate from the evaporator to the condenser) and, in case of a centrifugal distillator, the centrifuge force (promoting a thin film on the evaporator surface). Two product streams are generated: Distillate (rich in the molecules that escape from the evaporator and reach the condenser) and Residue (rich in the heavier molecules, that remain in the evaporator).

In this work, the equipment used was a centrifugal distillator from Myers Vacuum Inc. (Kittanning, PA), with an evaporator area of 0.0046 m^2. The system was operated at a pressure of 1.6 x 10^{-4} bar and at the evaporator rotation velocity of 1350 rpm. The starting material was fed at 60ºC in the center of the evaporator (as indicated in Fig. 1), with defined flow rates (Q) and evaporator temperatures (TEV). The condenser temperature is fixed at 55ºC.

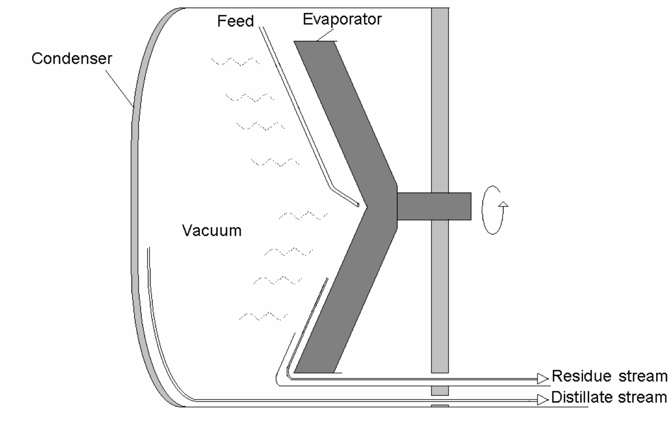

Figure 1: Simplified scheme of a centrifugal molecular distillator.

3.3 Results and Discussion

3.3.1 Glycerolysis Optimization

As can be seen in Fig. 2, after 1h, the system reached the equilibrium condition, for all the runs. It can be noted that the higher reaction yields were obtained in the runs with

GL/TG = 0.30 (runs 5–8). Analyzing the three central points (runs 9–11), the good repeatability of the experiments can be seen, as their results are very close.

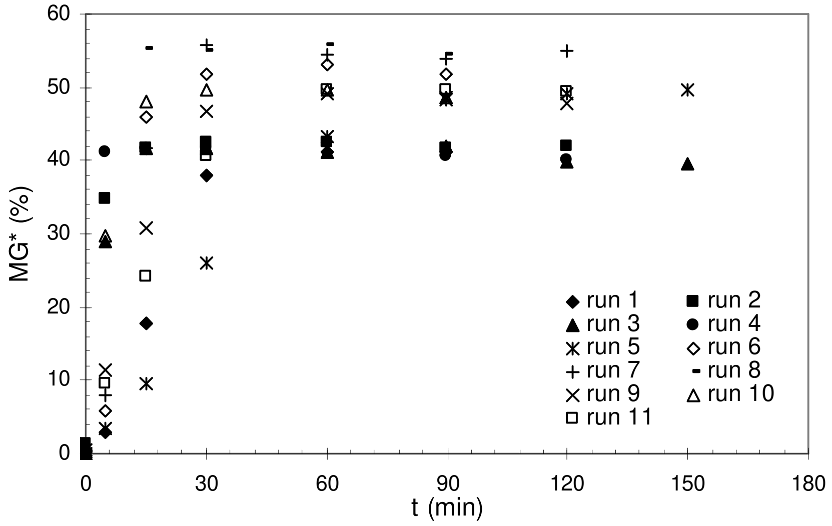

Figure 2: MG concentration during the glycerolysis reaction. *Normalized peak areas of TG, DG and MG

Figure 3a shows the time-course of the glycerolysis for run 2, representing the runs carried out with GL/TG = 0.18 and Fig. 3b shows the time-course of the glycerolysis for run 7, representing the runs carried out with GL/TG = 0.30. It can be seen that, in the experiments carried out with the mass ratio GL/TG = 0.30, the difference between the MG and DG concentrations at the equilibrium condition is approx 20%, whereas in the experiments carried out with GL/TG = 0.18, these concentration values are very close. Furthermore, it can be noted that the TG equilibrium concentration in the runs with GL/TG = 0.18 is approximately twice the TG equilibrium concentration when GL/TG = 0.30. This confirms that, at the experimental conditions studied, the higher yields was obtained with the GL/TG = 0.30.

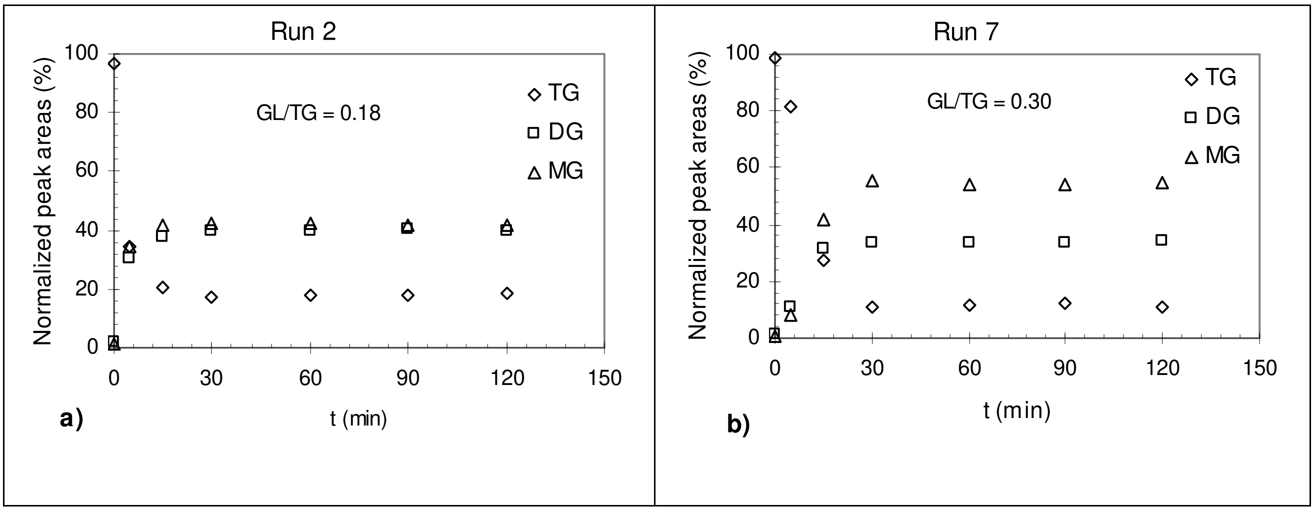

Figure 3: Comparison among the runs with GL/TG = 0.18 **(a)** and runs with GL/TG = 0.30 **(b)**.

The main effects of the three variables studied and the binary interaction effect involving these factors are shown in Table 2. It can be seen that, at 95% of confidence, GL/TG, T, and the interaction between T and GL/TG presented significant effects (*p*-value < 0.05). As shown before, the effect of the GL/TG is very relevant in the experimental condition studied, presenting an effect of 10.77%, what means that, on an average, the percentage of MG increases 10.77% when the level of the GL/TG is increased from -1 to +1.

Table 2: Main effects of GL/TG ,T, amount of NaOH and the binary interaction effect involving these factors.

	Effect (%)	Standard error	*t* (2)	*p*-value
(1)NaOH	0.96	0.204	2.388	0.1395
(2)T[a]	1.97	0.204	4.838	0.0401
(3)GL/TG[a]	10.77	0.204	26.393	0.0014
1 by 2	-1.20	0.204	-2.878	0.1025
1 by 3	1.17	0.204	2.756	0.1103
2 by 3[a]	2.13	0.204	5.205	0.0350

[a] Significant effects at 95% of confidence

The effect of T is positive and also significant, but much lower than the GL/TG effect. This may be owing to the narrow T experimental range studied. The interaction effect between T and GL/TG is significant at 95% of confidence, but also lower than the GL/TG effect. As expected, the main effect of the amount of catalyst (NaOH) is not significant at this level of confidence, as the catalyst concentration does not displace the equilibrium condition toward any side (product or reagent sides).

Because all the variables studied showed positive main effects, new experiments were carried out in order to explore a new experimental range, confirming the results obtained in the experimental design. Thus, higher levels of the mass ratio GL/TG were studied (Fig. 4) as its effect was significant at 95% of confidence level (the highest effect among the studied variables). The temperature was kept at 210ºC (the highest studied level in the experimental design). Although its effect is positive and significant at 95% of confidence level, in the experimental range studied, temperatures > 210ºC were not studied because it may cause considerable polymerization reactions. The amount of catalyst (NaOH) added in the system did not affect the equilibrium concentration, therefore it was fixed in 0.13g for 50g of reactants.

Figure 4 shows the MG concentration (normalized peak areas of TG, DG and MG) in the equilibrium condition as a function of the GL/TG ratio. It can be noted that, in this new experimental range explored (GL/TG values higher than 0.30), there is a small increase in the equilibrium MG concentration. However, it seems that for GL/TG values higher than 0.36, the equilibrium MG concentration remains the same. The maximum of MG concentration obtained (as normalized peak area) in the studied experimental range is around 57%.

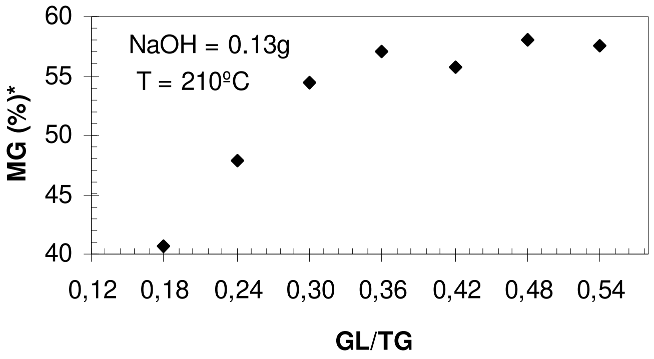

Figure 4: MG concentration in the equilibrium condition as a function of the GL/TG ratio.

*Normalized peak areas of TG, DG and MG.

Table 3 contains experimental data on fatty acid composition of acylglycerols at different times of reaction. One can see that, at the experimental conditions studied, the fatty acid composition changes lightly with time, indicating just a moderate occurrence of polymerization. The concentrations of linoleic acid and α-linolenic acid, both polyunsaturated, decrease because they are more susceptible to degradation. This partial degradation causes a change in the color of the oil, which becomes darker as well as a change in the odor. Despite the moderate degradation of the polyunsaturated fatty acids, HPSEC analysis did not detect polymers formed.

Table 3: Fatty acids composition of acylglycerols.

t	Fatty Acid Composition (%)[a]								
(min)	16:0	18:0	18:1	18:2	18:3	20:0	20:1	22:0	24:0
0	12.1	3.3	21.8	54.2	5.4	0.4	0.2	0.5	0.2
30	12.4	3.8	22.3	53.2	5.2	0.4	0.2	0.5	0.2
60	12.6	3.4	22.5	53.2	5.1	0.4	0.2	0.5	0.2
90	12.8	3.7	22.2	52.4	5.1	0.4	0.2	0.5	0.2

[a] 16:0 Palmitic acid; 18:0 Stearic acid; 18:1 Oleic acid; 18:2 Linoleic acid; 18:3 α-Linolenic acid; 20:0 Arachidic acid; 20:1 Eicosenoic acid; 22:0 Behenic acid; 24:0 Lignoceric acid. GL/TG=0.48, T=210ºC, NaOH=0.13g, mass of reagents=50g.

3.3.2 Molecular Distillation Optimization

Fregolente et al. (2005) [14] have shown a study to find optimized operating conditions of the molecular distillation in order to enrich the distillate stream in MG, starting from a commercial MG. Its properties are shown in Table 4. The composition of this commercial MG is similar to the composition of the products obtained in the glycerolysis products (40–50%).

Table 4: Properties of the commercial MG used as starting material.

Product name	Source	Acid value (mg KOH/g)	Iodine value (cg I 2/g)	MG content (%)	Physical form
BRAWAX MGS C	Vegetable	1.3	58.3	43.6	Waxy solid

The variables studied were the evaporator temperature (TEV) and the feed flow rate (Q), since they are very important process variables in the molecular distillation process. The experimental range of these variables was chosen according to previous experience. Values of feed flow rate < 4 mL/min may not be high enough to form a uniform thin film on the evaporator surface. This uniform thin film promotes efficient mass and energy transfers [15]. For feed flow rate values greater than 15 mL/min, it was noted that the system operated with low effectiveness, as the residence time of the molecules on the evaporator is too low. Therefore, the feed flow rate varied from 5 to 15 mL/min. The variation range of TEV was from 200 to 300°C (Table 5).

Table 5: Central composite design carried out to optimize the molecular distillation process.

TEV (ºC)	Q (mL/min)	MGD (%)	MGR (%)
-1(215)	-1(6.5)	78.1	37.5
+1(285)	-1(6.5)	70.9	25.7
-1(215)	+1(13.5)	56.3	41.8
+1(285)	+1(13.5)	77.7	36.1
-1.41(200)	0(10)	56.9	41.5
1.41(300)	0(10)	65.2	29.3
0(250)	-1.41(5)	74.8	26.8
0(250)	1.41(15)	68.8	41.0
0(250)	0(10)	75.2	37.4
0(250)	0(10)	77.5	36.6

To find the optimized operating conditions, response surface methodology (RSM) was applied, that is a set of mathematical and statistical methods developed for modeling phenomena and finding combinations of a number of experimental factors that will lead to optimum responses [16]. Usually, in the RSM, simple coded models such as linear and quadratic are fitted. In this work, independent and dependent variables were fitted to a second-degree polynomial equation (Eq. 1), where y is the estimated response (MG concentration in the distillate stream [MGD], or MG concentration in the residue stream [MGR]), b_0 is a constant, b_{ij} are the coefficients for each term and x_i are the independent factors in coded values (x_1 corresponds to the coded value for TEV and x_2 corresponds to the coded value for Q).

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{22} x_2^2 + b_{12} x_1 x_2 \qquad (1)$$

Analyzing Eq. 1, which is a quadratic model with two variables, it can be seen that it contains six parameters, so that the number of combinations of the independent variable levels must be >6, as it is not possible to predict values when the number of equation parameters is higher than the number of independent variable levels. Thus, a factorial design consisting of 2^2 trials plus a star configuration (four axial points) with three central points was carried out. The distance of the axial points from the central point is calculated from the equation, $\alpha = (2^n)^{1/4}$, where α is the distance of the axial points and n is the number of independent variables [17]. This kind of factorial design, also known as central composite design, is suitable for the fit of Equation 1, because for two independent variables, it contains nine different combinations of the independent variable levels.

The quality of the fitted models was evaluated by the analysis of variance (ANOVA), based on *F*-test [18] and on the percentage of explained variance, which provides a measurement of how much of the variability in the observed response values could be explained by the experimental factors and their interactions [19].

The fitted coded models for the MGD and MGR are shown in Eqs. 2 and 3, respectively, in which, all the coefficients of Eq. 1 were considered.

$$MGD = 75.27 + 3.25xTEV - 6.04xTEV^2 -2.94xQ - 0.66xQ^2 + 7.13xTEVxQ \qquad (2)$$

$$MGR = 36.88 - 4.37xTEV - 0.59xTEV^2 + 4.35xQ - 1.32xQ^2 + 1.51xTEVxQ \qquad (3)$$

Through the analysis of variance (ANOVA), shown in Table 6, it can be concluded that there is no evidence of lack of fit for the fitted models, since the calculated *F*-values (lack of fit/pure error) are lower than the critical *F*-value ($F_{0.95,3,2}$ = 19.16) at 95%

confidence, for both models. Furthermore, the results show that the model for the MG concentration in the residue (MGR), Eq.3, is predictive in the experimental conditions studied, because the percent of explained variance is high (98.53%) and the calculated *F*-value (regression/residual) is more than 13 times higher than the critical *F*- value at 95% of confidence ($F_{0.95,5,5} = 5.05$). As a practical rule, the regression can be considered useful to predict values when the calculated *F*-value (regression/residual) is more than 10 times higher than the critical *F*-value (*20*).

As can be seen in Figure 5, obtained from Equation 3, at low feed flow rates, the MGD increases up to a maximum of 80%, approximately, and starts decreasing at TEV higher that 250ºC due to the significant amount of DG that leave the distillator in the distillate stream, at these conditions. It can be noted that, the feed flow rate (Q) is important, since at high Q, the residence time of the molecules on the evaporator surface is low, so that the DG evaporation may not be high enough to dilute the MG in the distillate stream (MGD).

Table 6: ANOVA for the fitted models [a].

Source of variation	Model	Sum of square	Degrees of freedom	Mean square	*F*-ratio
Regression	Eq. 2 (MGD)	570.002	5	114.000	10.57 [b]
	Eq. 3 (MGR)	323.592	5	64.718	66.93 [b]
Residual	Eq. 2 (MGD)	53.919	5	10.783	–
	Eq. 3 (MGR)	4.833	5	0.967	–
Lack of Fit	Eq. 2 (MGD)	44.262	3	14.754	3.06 [c]
	Eq. 3 (MGR)	4.373	3	1.458	6.34 [c]
Pure error	Eq. 2 (MGD)	9.657	2	4.829	–
	Eq. 3 (MGR)	0.460	2	0.230	–
Total	Eq. 2 (MGD)	623.921	10		
	Eq. 3 (MGR)	328.425	10		

[a] MGD, Percent of explained variance, 91.36; percent of explicable variance, 98.45;
[a] MGR, Percent of explained variance, 98.53; percent of explicable variance, 99.86 ;
[b] *F*-ratio (regression/residual)
[c] *F*-ratio (lack of fit/pure error)

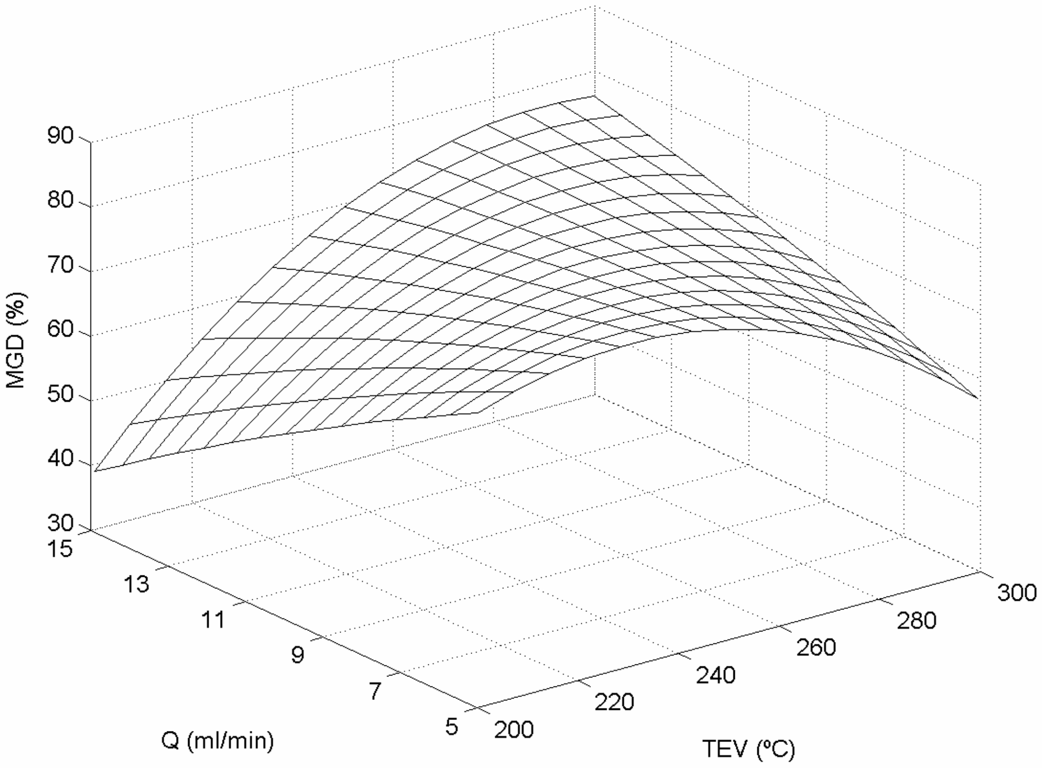

Figure 5: Response surface for the MG concentration in the distillate stream.

3.3.3 Distillation of the Glycerolysis Reaction Product

To obtain enough material for the distillation of the glycerolysis product in a optimized operating condition, the 50g experiments was scaled up to 500 g with the following conditions: GL/TG = 0.48, T = 210ºC and NaOH = 1.3 g. When the system reached the equilibrium condition, the reaction mixture was transferred to a separatory funnel in order to separate the insoluble GL. The composition of the two phases formed is shown in Table 7.

It is clear that the MG losses were small, as the MG concentration in the inferior phase is low (1.84%). Furthermore, it can be seen that the MG concentration level reached is 50.13%, a good value when it is compared with reactions carried out at higher temperatures.

The superior phase was submitted to a first distillation at TEV = 250ºC and Q = 5 mL/min, because according to Fig. 5, this is a suitable condition for the concentration of MG in the distillate stream. The MG concentration obtained in the distillate stream was 80.81% as shown in Table 7, with a MG recovery of 56%. It can be noted that the GL concentration in the distillate is high (15.17%). Therefore, a second distillation was carried out at TEV = 170ºC and Q = 5mL/min in order to remove the GL from the distillate stream. The MG concentration obtained in the residue stream of the second distillation is 90.88%, which can already be considered a commercial distilled monoglyceride (min. 90%).

Table 7: Composition of the two phases separated, after the glycerolysis reaction in the 500g system and the compositions of the streams obtained in the molecular distillations.

Material analyzed	TG (%)	DG (%)	MG (%)	AGL (%)	GL (%)
Superior phase (acylglycerols)	8.22	30.99	50.13	0.85	9.81
Inferior phase (GL)		0.34	1.84	0.9	96.91
Distillate stream of the first distillation		3.11	80.81	0.91	15.17
Residue stream of the second distillation		3.78	90.88	0.81	4.53

Besides the MG content, the color of the product, as well as odor and taste are essential properties to be considered. Therefore, it can be seen that the change in the color of the reaction products during the glycerolysis does not compromise the quality of the distilled MG obtained, as it is practically colorless. Furthermore, one can note that the odor was effectively removed by the molecular distillation process, as verified by Kuhrt et al. (1950) [21].

3.4 Concluding Remarks

This work represents an important contribution for the manufacturers of MGs, as it shows an optimization study of the MG production from soybean oil and also a study of the usual process for MG concentration.

After 60 min, the glycerolysis of the soybean oil reached the equilibrium condition for all the runs. Among the three variables studied (T, GL/TG, and NaOH), the GL/TG is the most relevant, in the experimental range studied. Its main effect is 10.77%. The maximum of MG concentration obtained in the glycerolysis reaction was around 50%, when the independent variables T and NaOH were fixed in the their superior levels studied and the GL/TG ratio was greater than 0.36.

For effective separation of the reaction products, careful attention must be given to feed flow rates (Q) and evaporator temperature (TEV). According to the results obtained in this work, with only one distillation step, the max. MGD was 80.81%, at TEV = 250ºC and Q = 5 mL/min. From this stream, a second distillation step was carried out in order to remove GL of the distillate stream (TEV = 170ºC and Q = 5mL/min), obtaining a colorless product with 90.88% of MG, which has the desired characteristics of Distilled MG.

3.5 References

1. Akoh, C. C., Min, D. B. (1998), Food Lipids: Chemistry, Nutrition, and Biotechnology, Marcel Dekker, New York.

2. Ferreira-Dias, S., Correia, A.C., Baptista, F.O., Fonseca, M.M.R. (2001), J. Mol. Catal B: Enzymatic, 11, 669.

3. Bornscheuer, U. T., Kazlauskas, R. J. (1999), Hydrolases in Organic Synthesis: regio- and stereoselective biotransformations, Wiley-VCH, Weinheim.

4. Bailey, A. E. (1996), *Bailey's Industrial Oil & Fat Products*, 5th ed., Edited by Y. H. Hui, John Wiley, New York, pp. 569-601.

5. Mikov, M., Lutisan, J.and Cvengros, J. (1997), *Sep. Sci. Technol*. 32, 3051-3066.

6. Batistella, C. B., Maciel, M. R. W., Maciel Filho, R.(2000), Comput. Chem. Eng. 24, 1309-1315.

7. Batistella, C. B., Moraes, E. B., Maciel Filho, R., Maciel, M. R. W. (2002), Appl. Biochem. Biotechnol., 98, 1149-1159.

8. Moraes, E. B., Batistella, C. B., Alvarez , M. E. T., Maciel Filho, R., Maciel, M. R. W. (2004), Appl. Biochem. Biotechnol., 113, 689-711.

9. Xu, X., Jacobsen, C., Nielsen, N. S., Heinrich,M. T., Zhou , D. (2002), Eur. J. Lip. Sci. and Technol., 104, 745-755.

10. Breivik, H., Haraldsson, G. G., Kristinsson , B. (1997), J. Am. Oil Chem. Soc., 74, 1425-1429.

11. Schoenfelder, W. (2003), Eur. J. Lip. Sci. and Technol., 105, 45-48.

12. Hartman, L., Lago, R. C. A., Laboratory Practice, 22, 475-476, 1973.

13. Carvalho, C. M. L., Serralheiro, M. L. M., Cabral, J. M. S., Aires-Barros, M. R. (1997), Enzyme Microb. Technol., 21, 117–123.

14. Fregolente, L. V., Batistella, C. B., Maciel Filho, R., Maciel, M. R. W. (2005), J. Am. Oil Chem. Soc., 82, 673-678.

15. Batistella, C. B., Maciel, M. R. W. (1998), Computers Chem. Engng., 22, S53-S60 .

16. Ferreira-Dias, S., Correia, A.C., Baptista, F.O., Fonseca, M.M.R. (2001), J. Mol. Catal B: Enzymatic., 11, 669-711.

17. Khuri, A.I., Cornell, J. A. (1987), Response surface design and analyses, Marcel Dekker Inc, New York.

18. Box, G. E. P., Hunter, W. G., Hunter J. S. (1978), Statistics for Experimenters, Wiley, New York, pp. 510-539.

19. Burkert, J. F. M., Maugeri, F., Rodrigues, M. I. (2004), Bioresour. Technol., 91, 77-84.

20. Barros Neto, B., Scarminio, I. S., Bruns, R. E. (2003), *Como Fazer Experimentos*, 2nd ed., Editora da UNICAMP, São Paulo, Brazil, pp.251-266 (in Portuguese).

21. Kuhrt, N. H., Welch, E. A., Kovarik, F. J. (1950), J. Am. Oil Chem. Soc., 27, 310-313.

CAPÍTULO IV

Effect of Operating Conditions on the Concentration of Monoglycerides Using Molecular Distillation

Artigo a ser submetido a um periódico internacional

Effect of Operating Conditions on the Concentration of Monoglycerides Using Molecular Distillation

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Abstract: In this work, experiments were carried out in order to study the effect of operating conditions on the monoglycerides (MG) concentration process using Molecular Distillation (MD) in laboratory scale. Therefore, producers of distilled MG can use the results obtained here to optimize industrial plants. Firstly, a 2^{4-1} factorial design was employed to select the most important operating variables of the process. Among the four variables studied, evaporator temperature (TE), feed flow rate (Q), feed temperature (TF) and condenser temperature (TC), just TE and Q are important at the experimental conditions studied. Furthermore, using empirical models and experimental data, it is shown the dependence of MG and diglycerides (DG) concentrations in the outlet streams to TE and Q, which were selected in the fractional factorial design.

KEY WORDS: Molecular distillation; Short path distillation; Monoglycerides; Fractional factorial design

4.1 Introduction

Molecular distillation (MD) is a gentle distillation method appropriate for separation and purification of thermally unstable materials as well as for liquids with low vapor pressure and high molecular weight [1].

Basically, there are two kinds of molecular distillators: falling film and centrifugal distillators [2]. In both models, the separation principle is the vacuum, enabling molecules to evaporate from the evaporator to the condenser, and the formation of a thin liquid film which promotes effective heat and mass transfers. Falling film distillators use gravity force to form the film on the evaporating cylinder (evaporator), usually with a wiping element that mixes and distributes the liquid over the whole evaporator surface [3], while centrifugal distillators use centrifuge force to promote this thin film. Two product streams are generated: distillate (D), rich in the molecules that escape from the evaporator and reach the condenser, and residue (R), rich in the heavier molecules that remain on the evaporator.

In the MD process, vapor molecules find a free path between the evaporator and the condenser, where the distance of these two components should be shorter than the mean free path of the evaporating molecules. In these conditions, theoretically, the return of the molecules from the vapor phase to the liquid phase should not occur and the evaporation rate should only be governed by the rate of the molecules that escape from the liquid surface [4]. However, in industrial plants, the distance between the evaporating and condensing surfaces is longer than the mean free path of the molecules. In this case, the process is called short path distillation [5].

The performance of the process depends on the design of the equipment, such as the geometry of the evaporation space [6], type of condenser [7], presence or not of a entrainment separator [8], and also on the operating variables of the process, like the operating pressure (P), evaporator temperature (TE), feed flow rate (Q), feed temperature (TF), condenser temperature (TC), etc.

In this work, experiments were carried out to determine the effect of operating conditions on the manufacturing process of distilled Monoglycerides (MG), which are concentrated MG that have been widely used in the food industry for many years to improve physical characteristics of shortenings [9], potato and pasta products [10]. Furthermore, experimental data were obtained to adjust empirical models which predict DG concentrations in the outlet streams. Thus, the models obtained in this work, as well as models obtained by Fregolente et al., 2005 [11] were validated with experimental data. Although the experiments were carried out in laboratory scale, producers of distilled MG may use the results obtained here to optimize their industrial plants.

4.2 Materials and Methods

4.2.1 Molecular Distillator

The model used in this work was a centrifugal distillator from Myers Vacuum Inc. (Kittanning, PA), with an evaporation surface area of 0.0046m^2, and the evaporator rotation velocity fixed at 1350 rpm. TC and TF were controlled by thermostatic baths, while TE was controlled by an electrical heater system and its control. A peristaltic pump (Masterflex, Vernon Hills, IL) was used to control Q. The typical P (16 Pa) was obtained by a vacuum system consisting of a diffusion and a mechanical pump configured in series.

4.2.2 Starting Material

The commercial MG that was fed in the molecular distillator was donated by Braswey S.A. (Pirapozinho, SP, Brazil). It is produced from partially hydrogenated vegetable oil and has the following composition: 10.8 % of triglycerides (TG), 37.7 % of diglycerides (DG), 43.6 % of MG, 0.7 % of free fat acids FFA and 7.2% of glycerol (GL). The composition of the starting material is similar to the typical composition of mixtures of TG, DG and MG produced industrially, by glycerolysis reaction at temperatures higher than 200ºC, using inorganic catalysts [12].

4.2.3 Method of Analysis

Gel-permeation chromatography, also called high-performance size-exclusion chromatography (HPSEC) was used for the acylglycerols, FFA and GL analyses [13]. The chromatographic system consists of an isocratic pump, model 515 high-performance liquid chromatography (HPLC) Pump (Waters, Milford, MA), a differential refractometer detector model 2410 (Waters), and an oven for columns thermostatted at 40ºC by a temperature control module (Waters). The samples were injected using a manual injector (model 7725i, Rheodyne, Alltech, Deerfield, IL), with a 20-µL sample loop. Two HPSEC columns Styragel HR 1 and HR 2 (Waters), with dimensions of 7.8 x 300 mm and particule size of 5 µm, packed with styrenedivinylbenzene copolymer were connected in series. The mobile phase used was HPLC-grade tetrahydrofuran from Tedia (Fairfield, OH) and the flow rate was 1 mL/min. The typical pressure at this flow rate was 450psi (3102kPa). All the standards were obtained from Supelco (Bellefonte, PA). The data processing was done by the Millenium software 2010 Chromatography Manager Software from Waters.

4.2.4 Screening of Operating Variables

Firstly, a set of experiments was designed to determine the effects of four operating variables (TE, Q, TF and TC) on the mass ratio (D/F). This mass ratio is calculated as:

$$D/F = (\text{mass of distillate})/(\text{mass of feed}) \qquad (1)$$

Different combinations of operating conditions impact in different D/F and, consequently, in different outlet stream compositions.

The half-factorial design that was employed to conduct this study is shown in Table 1. It is a 2^{4-1} experimental design, with three central points (runs 9, 10 and 11) [14]. These central points are important since they are replicates in the center of the experimental range. The variation between them reflects the variability of all design [15]. In Table 1, actual values (in parenthesis) of the operating variables are shown together with their coded values, where the superior levels of the coded values are represented by +1 and the inferior levels by -1. Central points are denoted by 0. The correspondence between the coded and actual values can be obtained using the following formula:

$$Z = (X - X^0)/\Delta X \qquad (2)$$

where Z is the coded value, X is the corresponding actual value, X^0 is the actual value in the center of the experimental range studied, and ΔX is the increment of X corresponding to one unit of Z. In this work, for example, the coded value of TC is given by Equation 3:

$$Z = (X-70)/20 \qquad (3)$$

Table 1. 2^{4-1} fractional design.

Run	TF(ºC)	TC(ºC)	TE(ºC)	Q(mL/min)	D/F
1	-1 (60)	-1 (50)	-1 (150)	-1 (5)	0.044
2	+1 (110)	-1 (50)	-1 (150)	+1 (10)	0.018
3	-1 (60)	+1 (90)	-1 (150)	+1 (10)	0.018
4	+1 (110)	+1 (90)	-1 (150)	-1 (5)	0.044
5	-1 (60)	-1 (50)	+1 (250)	+1 (10)	0.101
6	+1 (110)	-1 (50)	+1 (250)	-1 (5)	0.327
7	-1 (60)	+1 (90)	+1 (250)	-1 (5)	0.265
8	+1 (110)	+1 (90)	+1 (250)	+1 (10)	0.150
9	0 (85)	0 (70)	0 (200)	0 (7.5)	0.082
10	0 (85)	0 (70)	0 (200)	0 (7.5)	0.057
11	0 (85)	0 (70)	0 (200)	0 (7.5)	0.064

4.3 Results and Discussion

4.3.1. Screening of the Operating Variables

Figure 1 shows the effects of the operating variables on the mass ratio D/F, calculated from the results shown in Table 1. It can be seen that, in the experimental conditions studied, the most important variables are TE and Q. According to Figure 1, TE effect is approximately 1.8 times higher than the Q effect. The statistical analysis, Table 2, shows that at 95% of confidence, TF and TC do not present significant effects, i.e., *p*-value >0.05. The negative effect of Q means that, the higher the feed flow rate, the lower is the residence time of the molecules on the evaporator surface and, consequently, the lower is the mass ratio (D/F).

TF seems to have reduced effect on D/F, what may be due to the narrow TF experimental range studied (from 60ºC to 110ºC). Higher TF could impact in thermal damage since the material to be distilled would be exposed to increased temperatures for long time in the presence of oxygen. However, it is known that TF plays an important role in the MD process. When TF does not differ too much from TE, evaporation takes place at the very first moment the distilled liquid gets onto the evaporation surface [16].

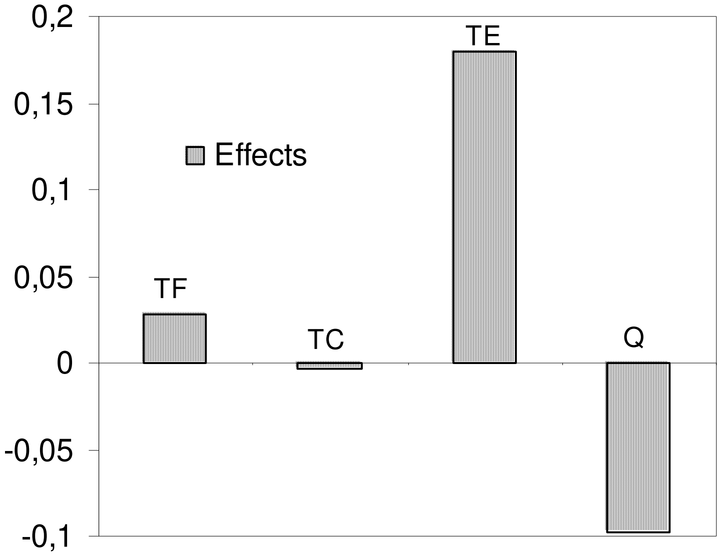


Figure 1. Effects of the operating variables on the mass ratio D/F.

Table 2. Statistical analysis of the operating variables effects on the mass ratio D/F.

Factor	Effect	Std. Err.[a]	*t*-Value	*p*-Value
TF	0.028	0.00898	3.1243	0.08898
TC	-0.0034	0.00898	-0.3824	0.73895
TE	0.18	0.00898	20.0170	0.00249[b]
Q	-0.098	0.00898	-10.9568	0.00823[b]

[a] Standard Error

[b] Significant factors (p-value<0.05)

To illustrate the influence of TE and Q on the mass ratio D/F, one-factor-at-a-time experiments were carried out, Figure 2. In these experiments, different TEs were studied at fixed Qs. For all these runs, TC and TF were kept at 55ºC and 60ºC, respectively. This figure confirms the high dependence of D/F in relation to TE and Q. It can be observed that the effect of TE is higher at low Q, since, at Q = 5mL/min, the ratio D/F increases from 0.14 to 0.79, when TE is increased from 200ºC to 300ºC. At Q = 15mL/min, the same TE increase gives just a D/F increase of 0.125 (from 0.045 to 0.17).

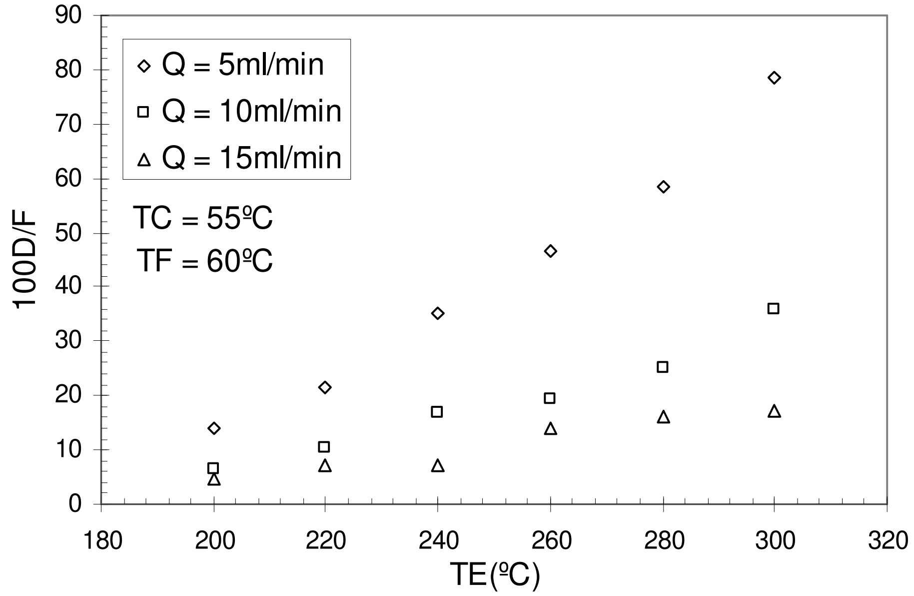


Figure 2. Influence of TE and Q in the mass ratio D/F.

4.3.2 Composition of the outlet streams

Based on the results obtained in the screening methodology, it was possible to identify the most important operating variables for the system studied, which are TE and Q, just analyzing the mass ratio D/F that is easily determined by weighing the streams after distillations. Although this measure has a direct relation to the composition of the outlet streams of the process, so far, nothing was told about composition. Then, in this section, through empirical models and experimental data, it is shown the dependence of the components concentration to the relevant operating variables identified in the fractional factorial design (TE and Q).

Firstly, experimental data on the DG concentration in the outlet stream were obtained, as shown in Table 3. These experiments were planed as a central composite design with three central points [17]. Symbol DGD represents DG concentration in the distillate stream and DGR represents DG concentration in the residue stream. Actual values (in parenthesis) of the operating variables are shown together with their coded values. From these results, empirical models were adjusted, Equations 4 and 5. The quality of these models was evaluated by the analysis of variance (ANOVA), shown in Table 4. One may conclude the models fitted the experimental data quite well, because the percent of explained variances are higher than 90% and the calculated *F*-values (regression/residual) are higher than the critical *F*- values at 95% of confidence ($F_{0.95,5,5} = 5.05$).

Table 3: Experimental data on the DG concentration in the outlet streams.

Run	TEV (ºC)	Q (mL/min)	DGD (%)	DGR (%)
1	-1 (215)	-1 (6.5)	3.4	47.3
2	+1 (285)	-1 (6.5)	20.8	51.3
3	-1 (215)	+1 (13.5)	1.7	43.8
4	+1 (285)	+1 (13.5)	8.3	48.6
5	-1.41 (200)	0 (10)	2.1	45.2
6	1.41 (300)	0 (10)	19.8	49.9
7	0 (250)	-1.41 (5)	9.4	53.0
8	0 (250)	1.41 (15)	1.8	46.1
9	0 (250)	0 (10)	5.2	46.5
10	0 (250)	0 (10)	7.3	49.0
11	0 (250)	0 (10)	4.8	47.9

$$DGD = 5.75 + 6.12xTE + 2.67xTE^2 – 3.12xQ – 0.014xQ^2 – 2.70xTExQ \quad (4)$$

$$DGR = 47.78 + 1.93xTE – 0.32xTE^2 – 1.99xQ + 0.70xQ^2 + 0.19xTExQ \quad (5)$$

To validate the models obtained in this work, and also to validate the models obtained by Fregolente et al., 2005, which predict MG concentration in the distillate stream (MGD) and MG concentration in residue stream (MGR), experiments were carried out in the same experimental range used to fit the parameters of the models. These data are shown in Table 5.

Table 4: ANOVA for the fitted models[a].

Source of Variation	Model	Sum of Square	Degrees of Freedom	Mean Square	*F*-ratio
Regression	Equation 4	450.5	5	90.1	81.56[b]
	Equation 5	66.2	5	13.2	10.05[b]
Residual	Equation 4	5.5	5	1.1	–
	Equation 5	6.6	5	1.3	–
Lack of Fit	Equation 4	1.7	3	0.6	0.30[c]
	Equation 5	3.4	3	1.1	0.71[c]
Pure error	Equation 4	3.8	2	1.9	–
	Equation 5	3.2	2	1.6	–
Total	Equation 4	466.0	10		
	Equation 5	72.7	10		

[a]Equation 4, Percent of explained variance, 98.79; percent of explicable variance, 99.17. Equation 5, percent of explained variance, 90.95%; percent of explicable variance, 95.62. [b]*F*-ratio (regression/residual). [c]*F*-ratio (lack of fit/pure error).

Table 5. Experimental data used for the validation of the models.

TE	Q	Distillate Stream				Residue Stream			
(ºC)	(mL/min)	MG		DG		MG		DG	
		exp.	model[a]	exp.	model	exp.	model[a]	exp.	model
200	5	59.5	75.7	1.7	1.4	38.2	38.5	45.7	49.0
220	5	82.2	79.6	4.4	3.6	32.6	34.0	48.4	50.4
240	5	76.2	79.6	12.3	7.5	26.2	29.9	51.1	51.5
260	5	66.0	75.7	19.3	13.2	23.5	26.3	47.1	52.4
280	5	60.5	68.0	28.7	20.5	22.0	23.0	47.2	53.2
300	5	49.8	56.4	37.4	29.5	21.3	20.1	41.2	53.7
200	10	54.4	58.6	1.5	2.4	40.9	44.2	44.0	44.4
220	10	65.6	68.2	2.2	2.5	39.6	41.0	45.2	45.9
240	10	79.5	73.9	5.7	4.2	34.8	38.2	47.7	47.2
260	10	75.0	75.7	8.0	7.7	35.8	35.7	46.5	48.3
280	10	73.9	73.7	11.3	12.9	32.7	33.6	48.7	49.2
300	10	66.5	67.8	19.2	19.7	30.0	31.9	47.6	49.9

[a] Model obtained by Fregolente et al., 2005.

Figures 3a, b, c and d compare values predicted by the models and the experimental data. It can be seen there is a good agreement between the experimental data and the predicted values. The best results were obtained for Q = 10mL/min, Figures 3b and 3d, since this flow rate is in the center of the experimental range (from 5 to 15mL/min) used to fit the parameters of the models. The data obtained at Q = 5mL/min are at the limit of the experimental range used in the model fittings, which is, frequently, the region of highest deviation between experimental and predicted values.

Figures 3a and 3b show that, considering the composition of the starting material, with just one distillation step, the maximum MGD obtained in the experimental conditions studied is around 80%. The TE used to obtain this level of concentration depends on Q. The higher Q, the higher the necessary TE. Furthermore, these figures confirm that the effect of TE is higher at low Q. At Q = 5mL/min, DGD increases significantly from 1.7% to 37.4% when TE is increased from 200ºC to 300ºC, consequently, MGD decreases up to 56.4%. At Q = 10mL/min, with the same TE increase, DGD just increases from 1.5% to 19.2%, thus MGD remains above 65%. Comparing Figures 3c and 3d, it can be seen that, when Q = 10mL/min, MGR and DGR are closer to the MG and DG concentrations of the starting material (43.6% and 37.7%, respectively).

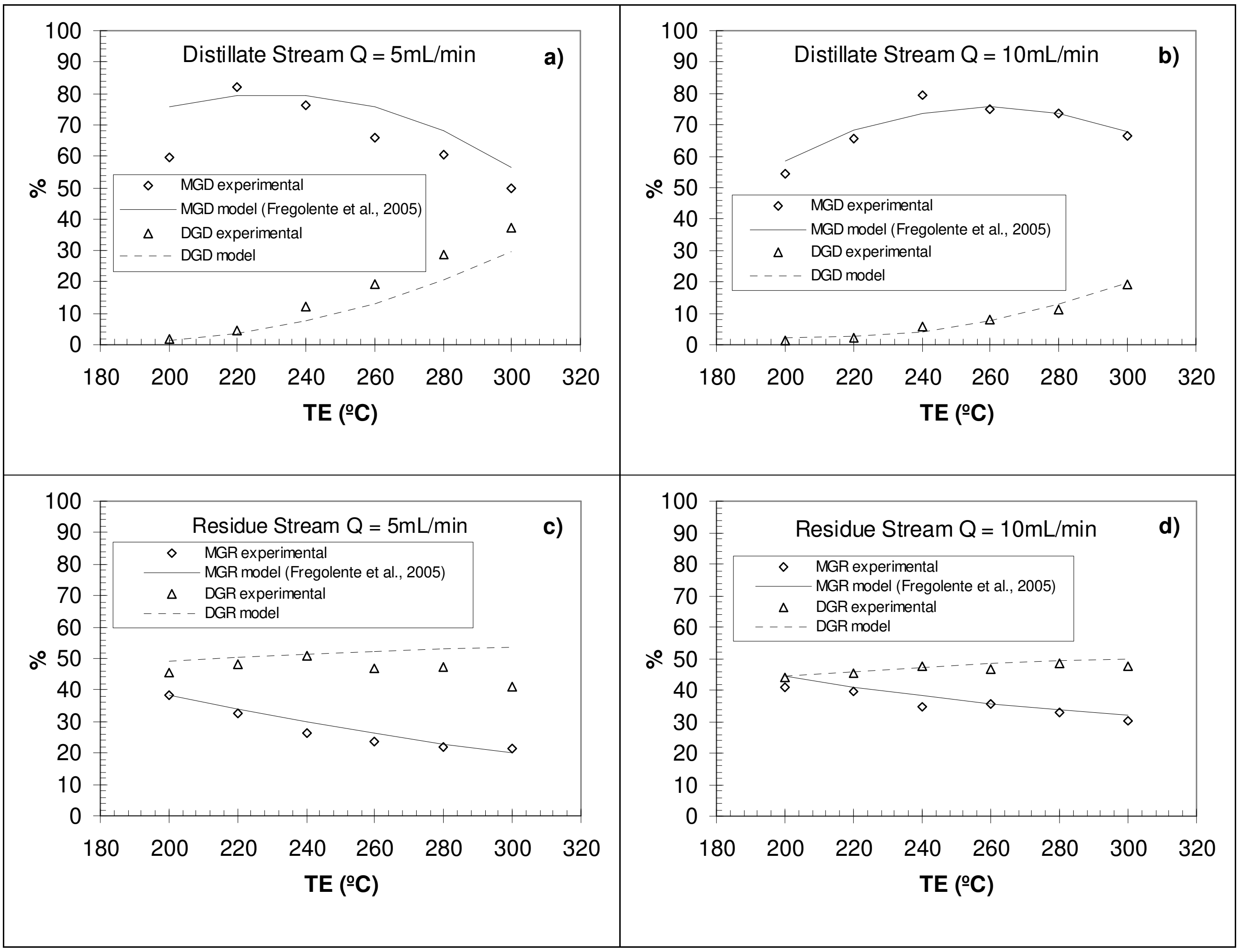


Figure 3. Experimental and predicted concentration of MG and DG in the outlet streams: **a)** Distillate stream at Q = 5mL/min, **b)** Distillate stream at Q = 10mL/min, **c)** Residue stream at Q = 5mL/min, **d)** Residue stream at Q = 10mL/min.

Figure 4 shows that the dependence of MG recovery (in the distillate stream) in relation to TE and Q is similar to the dependence of the mass ratio D/F in relation to these operating variables, which means that MG recovery is inversely proportional to Q and directly proportional to TE. Therefore, higher MG recoveries can be obtained at Q = 5 mL/min. Then, the best distillation condition depends on the MDG level desired. If a product with a minimum of 80% of MGD is desired, the best distillation condition obtained in the experimental range studied is: Q around 5mL/min and TE from 220ºC to 250ºC. At these conditions, the DGD is lower than 12% and the MG recovery is approximately from 50% to 60%.

4.4 Conclusions

This work shows that, for the system studied, the effects of TE and Q on the mass ratio D/F are much higher than the effect of TC and TF. TE effect is 1.8 times higher than the Q effect. Using experimental data, it was concluded that the empirical models obtained in this work represent quite well the DG concentration in the outlet streams. Furthermore, also using experimental data, it was shown that the models obtained by Fregolente, et al., 2005 are adequate to predict MG concentration in the outlet streams. Considering the composition of the starting material, with just one distillation step, the maximum of MGD obtained is around 80%, with DGD lower than 12%. To obtain these levels of concentration, the MG recovery ranges from 50% to 60%, approximately.

4.5 References

[1] M. Micov, J. Lutisan, J. Cvengros, Balance Equations for Molecular Distillation, Sep. Sci. Technol. 32 (1997) 3051-3066.

[2] C. B. Batistella, M. R. W. Maciel, Modeling, Simulation and Analysis of Molecular Distillators: Centrifugal and Falling Film, Comput. Chem. Eng. 20 (1996) S19-S24.

[3] J. Cvengros, S. Pollák, M. Mikov, J. Lutisan, Film Wiping in the Molecular Evaporator, Chem. Eng. J. 81 (2001) 9-14.

[4] C. B. Batistella, M. R. W. Maciel, R. Maciel Filho, Rigorous Modeling and Simulation of Molecular Distillators: Development of a simulator under conditions of non ideality of the vapor phase, Comput. Chem. Eng. 24 (2000) 1309-1315.

[5] F. Chen, T. Cai, G. Zhao, X. Liao, L. Guo, X. Hu, Optimizing Conditions for the Purification of Crude Octacosanol Extract from Rice Bran Wax by Molecular Distillation Analyzed Using Response Surface Methodology, J. Food Eng. 70 (2005) 47-53.

[6] Z. Kawala, P. Dakiniewicz, Influence of Evaporation Space Geometry on Rate of Distillation in High-Vacuum Evaporator, Sep. Sci. Technol. 37 (2002) 1877-1895.

[7] J. Cvengros, M. Mikov, J. Lutisan, Modelling of Fractionation in a Molecular Evaporator with Divided Condenser, Chem. Eng. Process. 39 (2000) 191-199.

[8] J. Lutisan, M. Micov, J. Cvengros, The Influence of Entrainment Separator on the Process of Molecular Distillation, Sep. Sci. Technol. 33 (1998) 83-96.

[9] N. H. Kuhrt, E. A. Welch, F. J. Kovarik, Molecularly Distilled Monoglycerides .1. Preparation and Properties, J. Am. Oil Chem. Soc. 27 (1950) 310-313.

[10] B. J. Bakels, Distilled Monoglycerides, Food Manuf. 2 (1976) 25.

[11] L. V. Fregolente, C. B. Batistella, R. Maciel Filho, M. R. W. Maciel, Response Surface Methodology Applied to Optimization of Distilled Monoglycerides Production, J. Am. Oil Chem. Soc. 82 (2005) 673-678.

[12] L. V. Fregolente, C. B. Batistella, R. Maciel Filho, M. R. W. Maciel, Optimization of Distilled Monoglycerides Production, Appl. Biochem. Biotech., Vol. 129-132 (2005) (in press).

[13] W. Schoenfelder, Determination of Monoglycerides, Diglycerides, Triglycerides and Glycerol in Fats by Means of Gel Permeation Chromatography, Eur. J. Lipid. Sci. Tech. 105 (2003) 45-48.

[14] B. Barros Neto, I. S. Scarminio, R. E. Bruns, Como Fazer Experimentos, second ed., Editora da UNICAMP, São Paulo, Brazil, 2003.

[15] C. M. L .Carvalho, M. L. M. Serralheiro, J. M. S. Cabral, M. R. Aires-Barros, Application of Factorial Design to the Study of Transesterification Reactions Using Cutinase in AOT-Reversed Micelles, Enzyme Microb. Tech .21 (1997) 117–123.

[16] J. Cvengros, J. Lutisan, M. Mikov, Feed Temperature Influence on the Efficiency of a Molecular Evaporator, Chem. Eng. J. 78 (2000) 61-67.

[17] A. I. Khuri, J. A. Cornell, Response surface design and analyses, Marcel Dekker Inc, New York, 1987.

Conclusões Gerais

Os resultados obtidos neste trabalho mostraram que, nas condições experimentais estudadas, a eficiência do processo de concentração de monoglicerídeos através da destilação molecular é altamente dependente da vazão de alimentação e da temperatura do evaporador. Já a temperatura do condensador e a temperatura de alimentação não apresentaram influência significativa sobre o processo.

Através da metodologia de análise de superfície de resposta, conseguiu-se mapear as regiões ótimas de operação do destilador molecular estudado, ou seja, com base no ajuste de modelos empíricos, foi possível identificar condições experimentais capazes de obter correntes de destilado com alta concentração de monoglicerídeos. Todos os modelos obtidos foram validados com dados experimentais. Estes modelos predizem a concentração de monoglicerídeos e diglicerídeos nas correntes de saída do processo.

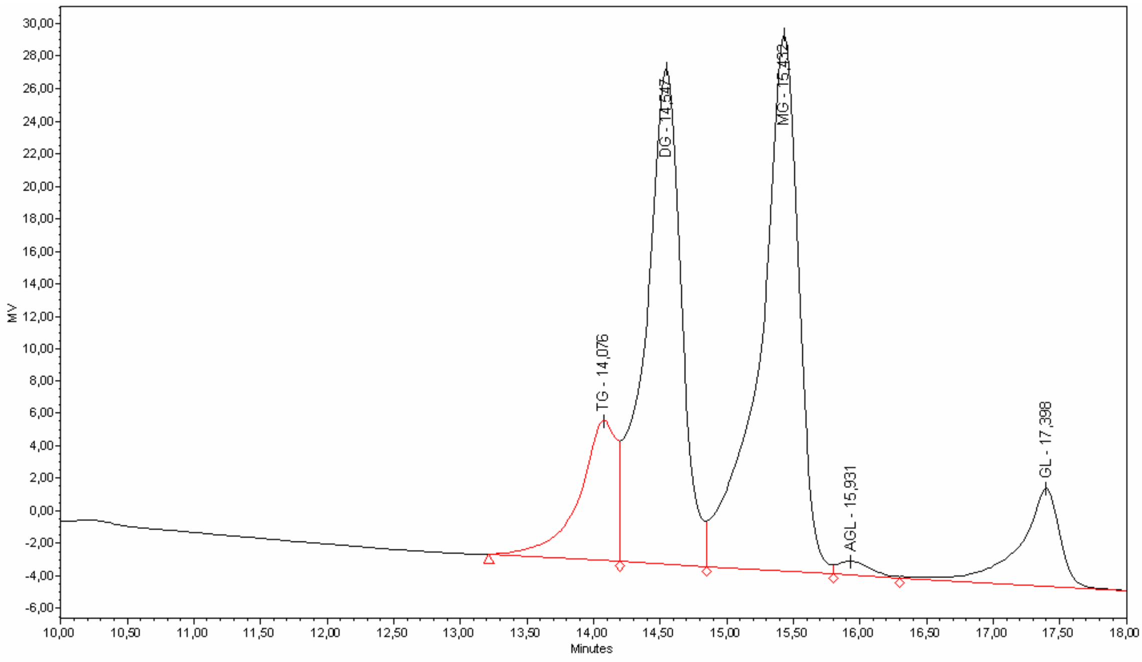
Partindo-se de uma mistura contendo 43,6% de monoglicerídeos, com apenas um passo de destilação, foi possível obterem-se experimentalmente teores de monoglicerídeos superiores a 80%, com recuperação em torno de 60%. Monoglicerídeos com teores acima de 96% foram obtidos utilizando-se quatro passos de destilação.

O estudo da síntese de monoglicerídeos através da glicerólise de óleo de soja mostrou que, dentre as variáveis estudadas, a razão mássica dos reagentes foi bastante significativa na composição de equilíbrio da mistura reacional. Através do acompanhamento da composição de triglicerídeos, diglicerídeos e monoglicerídeos, foi possível verificar-se que, após 60 min de reação, o sistema atingiu a condição de equilíbrio químico para todos os ensaios. Nas condições experimentais estudadas, foi possível a obtenção de monoglicerídeos com teores em torno de 50%.

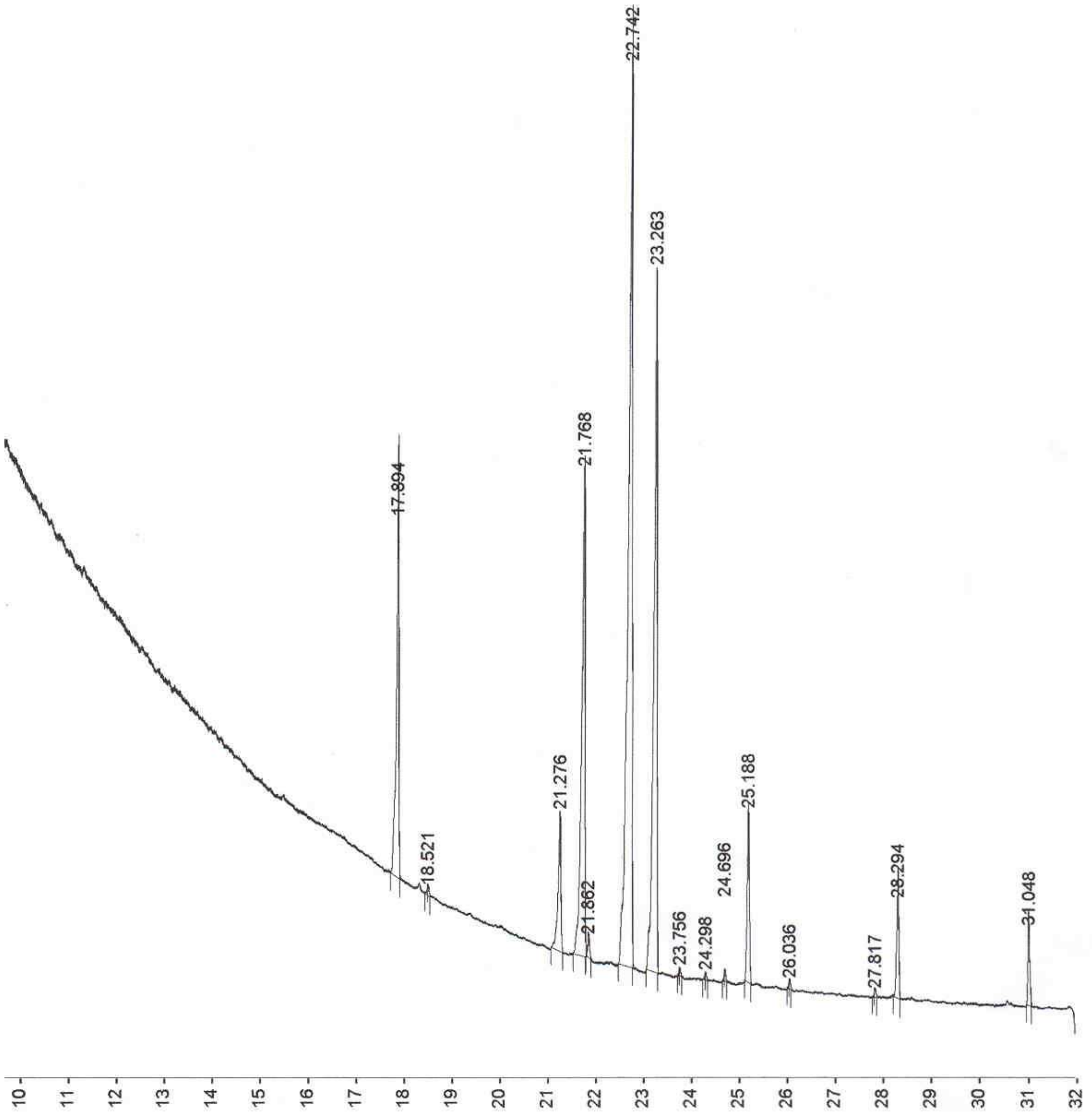
Através do acompanhamento da composição de ácidos graxos, foi verificada a ocorrência de degradação moderada de ácidos graxos poliinsaturados. Estas reações indesejadas conferiram aos produtos reacionais uma cor mais escura, a qual foi totalmente removida pelo processo de destilação molecular.

A partir do produto reacional da glicerólise, utilizando-se dois passos de destilação, foi obtido um produto com teores de monoglicerídeos acima de 90%, praticamente incolor e com odor característico de monoglicerídeos destilados.

Anexos



Cromatograma típico obtido através da cromotografia de permeação em gel.



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