Universidad de La Frontera
Facultad de Ingeniería Ciencias y Administración
Programa de Doctorado en Ciencias de Recursos Naturales

STUDY OF BIODIESEL PRODUCTION BY MEANS OF A CONTINUOUS SEPARATION SYSTEM BY CERAMIC MEMBRANES

Doctoral Thesis
In Fulfillment of the
Requirements for the Degree
Doctor in Sciences of Natural Resources
by

ISAAC REYES CANIUPAN

Temuco – Chile 2013

Abstract

Exploring new renewable resources for energy needs has been gaining great importance in recent years due to mounting crude oil prices, an irrevocable decrease in oil reserves, and increasing environmental degradation. Biodiesel has recently attracted considerable attention as a renewable and nontoxic fuel. However, conventional methods of biodiesel production have serious shortcomings that compromise the effectiveness of biodiesel as an energetic solution. Thus, the overall objective of this thesis work was: to implement and evaluate a biodiesel refining process by means of ceramic porous membrane for producing a high quality refined biodiesel. To achieve this objective, a literature review and two experimental chapters were developed and discussed in detail. The refining mechanism was clarified by analysis of miscibility multi-component and refining of synthetic emulsions at different operating conditions. Systematically, the results found during the development of this thesis provide useful information for the improvement of biodiesel production/refining process using membrane reactors at low methanol to oil molar ratio, condition not studied until now. Finally, a semi-continuous production/refining strategy of biodiesel under stoichiometric condition was implemented experimentally and discussed. The proposed strategy provides an inputs saving, especially methanol, representing a cost reduction. Additionally, could avoid the use of a sedimentation stage, simultaneously promoting a high permeate flux of biodiesel of low glycerides content was concluded.

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Study of biodiesel production by means of a continuous separation system by ceramic membranes

Esta tesis fue realizada bajo la supervisión del director de Tesis Dr. Rodrigo Navia Diez, perteneciente al Departamento de Ingeniería Química de la Universidad de La Frontera y es presentada para su revisión por los miembros de la comisión examinadora.

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Contents

Figure index

Table index

UNIVERSIDAD DE LA FRONTERA

PROGRAMA DE DOCTORADO Y MAGÍSTER EN CIENCIAS DE RECURSOS NATURALES

Title of the thesis

STUDY OF BIODIESEL PRODUCTION BY MEANS OF A CONTINUOUS SEPARATION SYSTEM BY CERAMIC MEMBRANES

Chapter I

Title

General Introduction

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ADVISOR THESIS: RODRIGO NAVIA DIEZ

1.1 Introduction

Exploring new renewable resources for energy needs has been gaining great importance in recent years due to mounting crude oil prices, an irrevocable decrease in oil reserves, and increasing environmental degradation (Ting et al. 2008). This added to fossil fuel resources deplete day by day because of rapidly increasing population and industrialization (Dizge et al. 2009). Biodiesel has recently attracted considerable attention as a renewable, biodegredable, and nontoxic fuel (Dizge et al. 2009). The main advantages of using biodiesel is that the amounts of CO, SO_2 and particulate matter, which are major contributors to environmental pollution in the exhaust gas, are much lower than those of petroleum diesel combustion (Yagiz et al. 2007).

Transesterification is one of the most commercially useable methods to produce fatty acid methyl esters (FAME or biodiesel). Biodiesel is produced from the direct transesterification of triglycerides (TG) source (vegetable oils, animal fats, and waste oils) in reaction with a short-chain alcohol in the presence of a chemical (alkali or acid) or enzymatic catalyst (Hama et al. 2006; Zhang et al. 2003). Different types of alcohols such as, methanol, ethanol, propanol and butanol have been used in transesterification. However, methanol and ethanol are the most widely used, particularly methanol owing to its low price and availability (Zabeti et al. 2009). Ideally, the products obtained by transesterification of triglycerides are methanol and glycerol (polar phase) and fatty acid methyl ester (non-polar phase). Nevertheless, the transformation of raw materials is never complete, because the transesterification reaction has three important limitations. First, the reaction is developed in a two-phase system, where the mass transfer is limited by the insolubility of reactants (oil and alcohol). Second, the TG transesterification is an equilibrium reaction. Therefore, it is not possible to drive the reaction to a complete TG conversion (Dubé et al. 2007). Third, the transesterification reaction yield depends on water and FFA content in raw material, especially when the alkaline-catalyzed method is used. A high water and fatty acid content in oil cause undesirable saponification reactions and catalyst consumption. The formed soaps retard the phase separation process, and additional washing steps to remove impurities are necessarily included in the refining process (Freedman et al., 1986; Veljkovic et al., 2006; Berchman and Hirata, 2008; Liu and Wang, 2009; Georgogianni et al. 2009). Consequently, the prevailing commercial process for

biodiesel production (alkaline-catalyzed batch configuration) involves long reaction and residence time, high alcohol/oil molar ratio and catalyst concentration.

High energy consumption is required in refining steps. Additionally, it is necessary to recover excess amount of alcohol and catalysts during downstream processing (Qiu et al., 2010). In addition, multiple water washing steps of the product are employed, which generate an abundant wastewater stream. This affects not only the production yield and cost, but also its environmental friendliness.

The biodiesel quality directly depends on the reaction control and process performance. In accordance with current international standards the glycerides content (MG, DG and TG) determines the biodiesel quality. High total glycerin content is associated with injector fouling in motors, decantation in tank storage and reduction of useful engines life, in general. Furthermore, the combustion of these components can lead to acrolein formation, a constituent part of photochemical smog. Additionally, oxidation in air is photolyzed forming CO, CO_2 and H_2O as well as unsaturated hydrocarbons (Cao et al., 2008; Cheng et al., 2009). Therefore, the study of configurations facilitating the mass- and heat-transfer and in-situ separation and recycling of products has been the focus of recent research. An option that grants the mentioned advantages is the membrane processes technology. This technology draws attention due to its easy and practical operation and more and more applications are being found in raw materials processing.

The general principle of an extractive membrane system applied to a reaction is based in the separation certain components from the reaction medium while reaction is achieving. In this way, it is possible to obtain an increase of the conversion yield in equilibrium-limited reactions by removing some products from the reactant stream using a permeable barrier. The separation is based on particle size (microfiltration) or the molecular size (in the case of ultra- and nano-filtration) from the reaction medium. According to Dube et al. (2007), it is possible to separate free components from a biphasic emulsion, when a hydrophilic component forms droplets of a determined size in hydrophilic environments. Therefore, using the capacity of oil/alcohol mixtures to form an emulsified system, FAME separation from a transesterification reaction medium would be possible (Cao et al. 2008). FAME extraction will move the equilibrium reaction close to complete TG conversion or will simply allow to refine biodiesel from other reaction components. In both cases, the effects of the reaction

reversibility will be avoided. With this information, this thesis project seeks to integrate a membrane refining process to the conventional process of biodiesel production by: one, diminishing the washing steps, two, diminishing the biodiesel neutralization step and three, facilitating the separation and purification of FAME. The determination of the conditions that generate a permanent emulsion with an adequate drop size will allow concentrating TG and a subsequent charge of methanol for a new productive cycle. Thus, the system could be projected as a continuous production system of biodiesel. The use of membrane technology could enhance the quality of the biodiesel and could diminishing or avoiding a final washing step. This will decrease the downstream process steps and the residual water generation.

1.2   Hypothesis

Using stoichiometric conditions in the oil transesterification is possible to achieve a single phase of refined Biodiesel by means a membrane process avoiding downstream processes.

1.3   General objective

To implement and evaluate a biodiesel refining process by means of ceramic porous membrane for producing a high quality refined biodiesel.

1.4   Specific objectives

1.4.1 To study the miscibility by ternary liquid–liquid phase equilibrium, applied to the refining of biodiesel.

1.4.2 To determine the influence of control variables in biodiesel refining using surface response methodology.

1.4.3 To propose and evaluate a sequential batch membrane reactor to increase fatty acid methyl esters quality at low methanol to oil molar ratio

1.5   References

1. Berchmans H.J., Hirata S., (2008). Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids, Bioresource Technology 99, 1716–1721.

2. Dizge N., Aydiner C., Imer D.Y., Bayramoglu M., Tanriseven A., Keskinler B., (2009) Biodiesel production from sunflower, soybean, and waste cooking oils by transesterification using lipase immobilized onto a novel microporous polymer Bioresource Technology, 100, 1983-1991.

3. Dubé M.A., Tremblay A.Y. & Liu J. (2007) Biodiesel production using a membrane reactor. Bioresource Technology 98, 639-647.

4. Freedman B., Butterfield R., and Pryde E., (1986). Transesterification kinetics of soybean oil, J. Am. Oil Chem. Soc. 63, 1375-1380.

5. Georgogianni K.G., Katsoulidis A.K., Pomonis P.J., Manos G. and Kontominas M.G., (2009). Transesterification of rapeseed oil for the production of biodiesel using homogeneous and heterogeneous catalysis. Fuel Processing Technology 90: 1016-1022.

6. Hama S., Tamalampudi S., Fukumizu T., Miura K., Yamaji H., Kondo A. & Fukuda H. (2006) Lipase localization in Rhizopus oryzae cells immobilized within biomass support particles for use as whole-cell biocatalysts in biodiesel-fuel production. Journal of Bioscience and Bioengineering 101,328–333.

7. Liu Y. & Wang L., (2009). Biodiesel production from rapeseed deodorizer distillate in a packed column reactor. Chemical Engineering and Processing 48, 1152–1156.

8. Ting W.-J, Huang Ch-M., Giridhar N and Wu W.-T., (2008). An enzymatic/acid-catalyzed hybrid process for biodiesel production from soybean oil. Journal of the Chinese Institute of Chemical Engineers 39 203–210

9. Veljkovic V.B., Lakicevic S.H., Stamenkovic O.S., Todorovic Z.B., Lazic M.L., (2006). Biodiesel production from tobacco (Nicotiana tabacum L.) seed oil with a high content of free fatty acids, Fuel 85, 2671–2675.

10. Yagiz F., Kazan D., Akin A. N., (2007). Biodiesel production from waste oils by using lipase immobilized on hydrotalcite and zeolites. Chemical Engineering Journal 134, 262-267.

11. Zabeti M., Wan Daud W. M. A., Aroua M. K., (2009). Activity of solid catalysts for biodiesel production: A review. Fuel Processing Technology, 90, 770-777.

12. Zhang Y., Dubé M., McLean D. & Kates M. (2003) Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresource Technology 90, 229–240.

UNIVERSIDAD DE LA FRONTERA

PROGRAMA DE DOCTORADO Y MAGÍSTER EN CIENCIAS DE RECURSOS NATURALES

Title of the thesis

STUDY OF BIODIESEL PRODUCTION BY MEANS OF A CONTINUOUS SEPARATION SYSTEM BY CERAMIC MEMBRANES.

Chapter II

Title

Membrane reactors in biodiesel production: A review

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Abstract

Biodiesel production has received considerable attention in the recent past as a biodegradable and nonpolluting fuel. Alkaline-transesterification has been accepted industrially for its high conversion and reaction rates. However, this industrial process has serious limitations and inefficiencies and is prone to undesirable by-product formation.

Recently, the FAME refining by membranes processes has attracted much attention on biodiesel production, since it achieves high purity and easy separation of products. Thus, the industrial implementation of the membrane technology is the objective of researcher community.

The present literature review aims to present the characteristics of membrane process, and also to report about the art state of application of membrane technology in the area of biodiesel refining.

Topics

2.1. Introduction

2.2. The Biodiesel or FAME and conventional production

2.3. Non-conventional technology and innovation in biodiesel production

2.4. The membrane reactor and its principle

2.5. Membrane reactor in Biodiesel production

    2.5.1. Theory of separation by membrane reactors in biodiesel production

    2.5.2. Reaction/refining performance of membrane reactors in biodiesel production

    2.5.3. Maintaining the membrane reactor applied to biodiesel production

    2.5.4. Control parameters of membrane reactors in biodiesel production

2.6. Conclusions

2.7. References

2.1   Introduction

The global economy has evolved within a paradigm reliant on fossil energy sources which provide the majority of the feedstock used in productive system for subsistence of human civilization. As demonstrated by studies by EIA (2010), the global energy consumption is governed by industrial and transportation sector. In fact, as is illustrated in Figure 1, the industrial sector, consisting of diverse industrial groups as manufacturing, agriculture, mining and construction, accounted for 52% of global energy used in 2007; the transportation sector, providing services, such as moving people and goods by road, rail, air, water and pipeline, uses 27%; the residential sector for household activities comprise 14% of the total; and the commercial sector, which consists of businesses, institutions, and organizations that provide services, comprises 7% (EIA, 2010). Although the global economic recession drove a reduction of energy consumption by 1.1% in 2009, the International Energy outlook 2010 (IEO, 2010) projections still predicted an increase of global energy consumption by 49%, or 1.4% every year until 2035 (EIA, 2010).
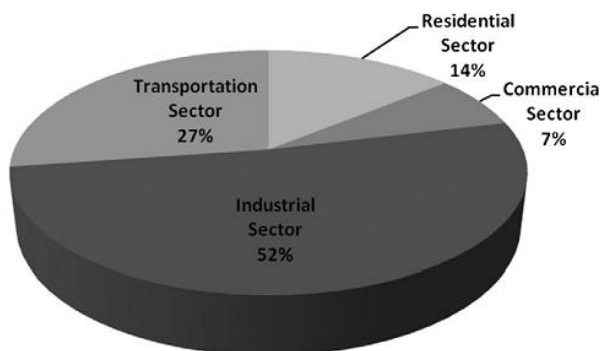
Figure 1. Global energy consumption in 2007 (EIA, 2010).
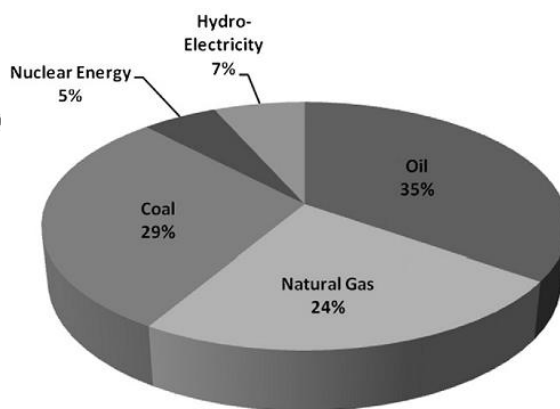
Figure 2. World energy production in 2009 (BP, 2009).

According to the statistical review conducted by British Petroleum (BP, 2009), global energy production depends heavily on oil (35%), coal (29%) and natural gas (24%) to satisfy the global energy demand, as shown in Fig. 2. The problem is that fossil fuels are the world's slowest-growing source of energy, and their supplies are decreasing daily. Thus, the long-term utilization of these depletable resources is unsustainable due to their limited reservoirs and non-renewable nature (Uihlein and Schebek, 2009). In fact, according to the estimates of the Oil and Gas Journal (O&GJ) released at December 6, 2010, the worldwide reserves of oil and natural gas were 1.47 trillion barrels and 6.6 quadrillion cubic feet, respectively (Radler, 2010). At the current consumption rates of around 84 million barrels per day of oil and 284.5 billion cubic feet per day of natural gas (BP, 2010), the reserves correspond to 48 years of oil supply and 64 years of natural gas supply. Thus, an increasing demand and an increase in the price of fossil fuels are expected. In addition, the growing emission of carbon dioxide, sulphur dioxide, hydrocarbons and volatile organic compounds (VOCs) from the combustion of fossil fuels could result in air pollution, global warming and climate change. These negative impacts on the environment are the target of current energy policies that

emphasis cleaner, more efficient and environmentally friendly technologies to increase the supply and usage of energy especially for industrial and transport sector (Hammond et al., 2008; Hoekman, 2008; Monni and Raes, 2008; Sawyer, 2009).

Thus, developments in alternative renewable energy sources have become indispensable for sustainable environmental and economic growth. Among the explored alternative energy sources, considerable attention has been focused on biodiesel as an alternative energy source to replace conventional petroleum-derived fuels because of biodiesel's clean and renewable nature. Additionally, it is widely available from inexhaustible feedstocks that can effectively reduce its production cost.

2.2 The Biodiesel or FAME and conventional production

Biodiesel or fatty acid methyl esters (FAME), is a mixture of monoalkyl esters of long-chain fatty acids derived from renewable lipid (biolipid) feedstocks. Biolipid feedstocks can be divided into four categories: virgin vegetable oils, waste vegetable oils, animal fats and non-edible oils. Virgin vegetable oil feedstock refers to rapeseed, soybean, sunflower and palm oil (Demirbas, 2008), while waste vegetable oil refers to these oils that have been used in cooking and are no longer suitable for human reutilization, as waste frying oils. (Azocar et al. 2010; Conservation ADoE, 2011; Lam et al., 2010). Animal fats include tallow, lard and yellow grease (Atadashi et al., 2010) while the non-edible oils include Jatropha (Shuit et al., 2010; Yee et al., 2009), neem oil, castor oil, tall oil (Demirbas, 2008) and microalgae (Ahmad et al., 2011).

Reduction of viscosity by Batch transesterification has been the most used strategy in FAME synthesis (Cao et al. 2008a; Qiu et al., 2010). The transesterification is a stepwise reaction based the alcoholysis of oil to produce FAME (Eq. 1, 2 and 3). The first step involves the conversion of triglycerides (TG) to diglycerides (DG) and later to monoglycerides (MG). Subsequently, the monoglycerides are converted to glycerol. The stoichiometric of the reaction requires 3 mol of alcohol and 1 mol of triglyceride (TG) to form 3 mol of FAME and 1 mol of glycerol. The overall reaction that occurs in transesterification is simplified by Equations 1, 2 and 3. Where R_1, R_2, and R_3 are long chain hydrocarbons (e.g., palmitic acid $-(CH2)_{14}-CH_3$)), sometimes called fatty acid chains (Cao et al. 2008).

$$
\underset{\text{DG}}{\left.\begin{array}{l} CH_2\!-\!OH \\ CH\!-\!OCOR_2 \\ CH_2\!-\!OCOR_3 \end{array}\right.} + \underset{\text{Methanol}}{CH_3\!-\!OH} \underset{K_4}{\overset{K_3}{\rightleftharpoons}} \underset{\text{MG}}{\left.\begin{array}{l} CH_2\!-\!OH \\ CH\!-\!OCOR_2 \\ CH_2\!-\!OH \end{array}\right.} + \underset{\text{FAME}}{CH_3\!-\!OCO\!-\!R_3} \qquad \textbf{(Eq.2)}
$$

$$
\underset{\text{MG}}{\left.\begin{array}{l} CH_2\!-\!OH \\ CH\!-\!OCOR_2 \\ CH_2\!-\!OH \end{array}\right.} + \underset{\text{Methanol}}{CH_3\!-\!OH} \underset{K_6}{\overset{K_5}{\rightleftharpoons}} \underset{\text{Glycerol}}{\left.\begin{array}{l} CH_2\!-\!OH \\ CH\!-\!OH \\ CH_2\!-\!OH \end{array}\right.} + \underset{\text{FAME}}{CH_3\!-\!OCO\!-\!R_2} \qquad \textbf{(Eq.3)}
$$
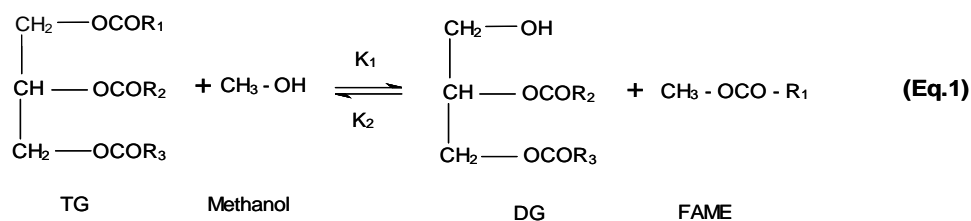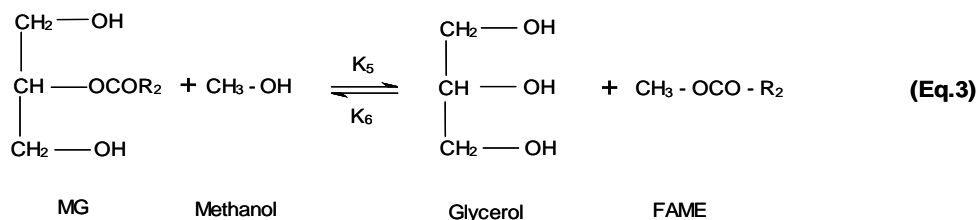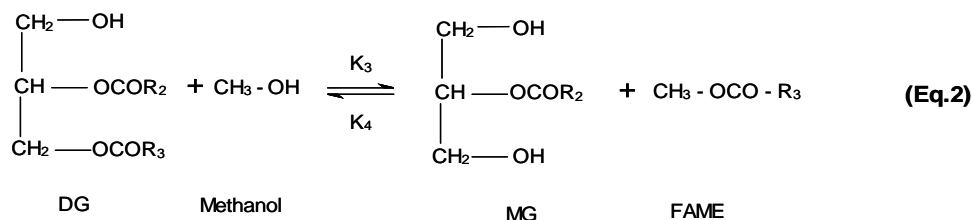
Different catalysis methods are used to run transesterification reaction to produce biodiesel includes homogeneous catalyzed transesterification, heterogeneous catalyzed transesterification, and enzymatic catalyzed transesterification (Marchetti et al., 2007). Each of these methods has its own disadvantages that eventually limit the energetic feasibility of the productive process and the biodiesel as energetic solution.

In this quest to improve conventional methods of biodiesel production, membrane technology has been recently used in the production process biodiesel showing to be a promising alternative for biodiesel production. Therefore, the aim of this chapter is to present the production of biodiesel via conventional methods and via membrane reactor, which includes the operation principles, and the effect of the process parameters of the transesterification reaction on the membrane reactor. Finally, the advantages offered by membrane technology in biodiesel production will be discussed.

A diagram of most commercial transesterification processes for biodiesel production is illustrated in Figure 3. The conventional process is usually based in a batch reactor where transesterification occurs at a single stage (Cao et al. 2008, Qiu et al. 2010). The reaction product is separated usually by decanting generating two phases, an upper biodiesel-rich phase (crude biodiesel) and a lower glycerol-rich phase (crude glycerin). After removing the excess alcohol, the crude biodiesel is neutralized (usually H_3PO_4) and washed with distilled water in several steps to remove soaps, catalyst residues and small amounts of glycerol, DG and MG. The washing step produces a large amount of waste water containing methanol; for each liter of biodiesel, 10 L of waste water are produced (Karaosmanoglu et al. 1996; Demirbas 2003). After washing, the separation of the FAME-rich phase from the water phase is usually difficult. Therefore, water content in FAME-rich phase is usually removed in a drying process by fractional distillation and finally refined biodiesel is obtained. On the other hand, glycerol-rich phase typically contains a mixture of glycerol, methanol, water, catalyst residue, free fatty acids, unreacted MG-, DG-, and TG-, FAME, and a variety of other non-glycerol organic compounds in varying quantities (Sdrula 2010).
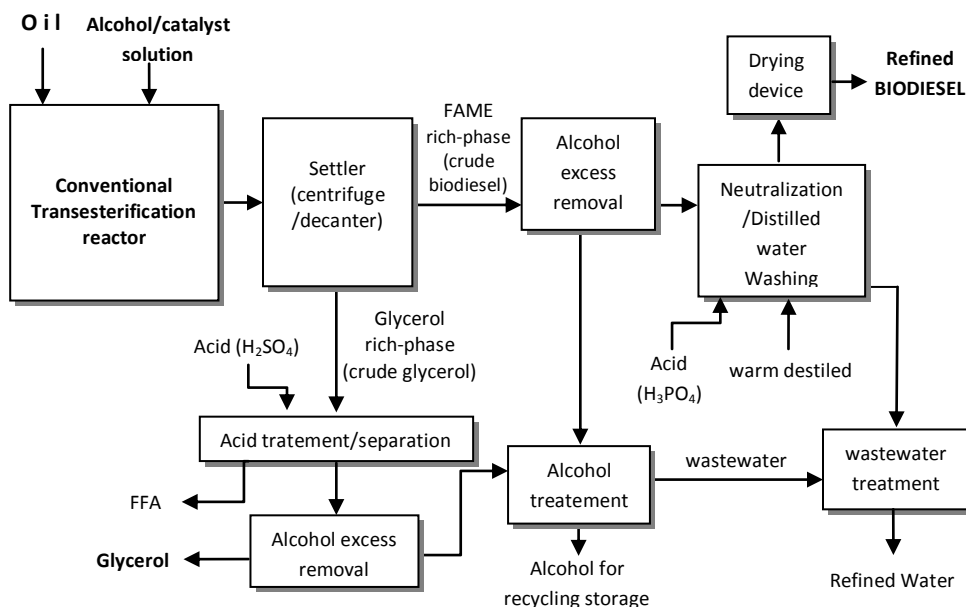
Figure 3: Conventional schematic diagram for FAME production and refining (adapted from Atadashi et al. 2010)

The residual catalyst dissolved in glycerol-rich phase is neutralized used an acid (usually H_2SO_4), while the alcohol excess is removed normally by fractional distillation and then is reused in a new batch transesterification. Both stream of excess alcohol from crude biodiesel line and crude glycerol line is recovered by distillation from the wastewater. Alcohol is recycled to the transesterification while the waste water with alcohol residues, glycerol DG, MG between others polar components, must be treated before disposal.

Due to the reversible character of the oil transesterification reaction, the FAME synthesis is highly dependent on the proportion of the reactant and the conditions of the transesterification. Thus, excess alcohol is normally used to increase TG conversion by shifting the reactions balance to products formation and increase the biodiesel production yiel d (Qiu et al., 2010; Keera et al. 2011). However, this alcohol consumption increases the production cost of FAME. This problem has been addressed by using acid or alkaline catalysts, which could improve the reaction rate and biodiesel yield. However, homogeneous acid solutions that catalyse transesterification processes, such as sulphuric (Sahoo et al., 2007), hydrochloric (Boucher et al., 2008), or sulphonic acids (Guerreiro et al., 2006) have been largely ignored because they increase the hydraulic retention time, require a higher reaction temperature and are corrosive by nature (Leung et al. 2010). Thus, alkaline catalysis is used more for commercial purposes because of its high yield and selectivity, shorter reaction time, as compared to acidic catalysis, low cost, and the possibility of reaction at low temperature and room pressure (Leung et al. 2010). Alkaline catalysts are preferable in industrial processes also because they are less corrosive (Ma and Hanna 1999; Ferrari et al. 2005; Gomes 2011). However, it has been reported that the alkaline catalysed reaction is strongly sensitive to the purity of the reactant, because water and free fatty acids (FFA) content in the raw feedstock could induce a saponification process as illustrated by equation 4 and 5 (Murugesan et al. 2009). In presence of water, TG and alkaline catalyst (usually NaOH) react to form soaps (Eq. 4).

At the same time, the FFA produced by the hydrolysis of TG could react with the alkaline catalyst to form more soap (Eq. 5). The catalyst consumption by saponification not only decreases the efficiency of reaction but also retards separation of FAME from glycerol-rich phase and the quality of biodiesel (Gomes 2011). In Fact, dissolved soap in the glycerol-rich phase would increase the solubility of FAME in the glycerol and complicate the subsequent separation and refining steps (Vicente et al., 2004; Gomes 2011). Also, the removal of either the homogeneous acidic or alkaline catalyst using hot distilled water would eventually result in the need to dispose more wastewater (Xie and Li, 2006).

Against the need to avoid catalyst efficiency loss via undesired saponification reactions and facilitate recovery of the catalyst from the glycerol-rich phase, Heterogeneous catalysis arises as an alternative. Solid catalysts such as $Ca(NO_3)_2/Al_2O_3$, CaO/Al_2O_3, $Sr(NO_3)_2/ZnO$, ZrO_2/SO_4^{2-}, zeolite HY, and zeolite X and enzymes (*Pseudomonas fluorescens, Rhizopus Oryzae, Candida rugosa* and *Pseudonas cepacia*) are applied for the production of biodiesel (Atadashi et al. 2011).

$$
\begin{array}{c}
CH_2-OCOR_1 \\
| \\
CH-OCOR_2 \;+\; 3\,NaOH \;\xrightarrow{+\,H_2O}\; 3\,R\text{-}CO\text{-}O\text{-}Na \;+\; \begin{array}{c} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} \qquad \textbf{(Eq.4)} \\
| \\
CH_2-OCOR_3
\end{array}
$$

$$\text{TG} \qquad\qquad \text{Catalyst} \qquad\qquad \text{Sodic soap} \qquad\qquad \text{Glycerol}$$

$$R\text{-}CO\text{-}OH \;+\; 3\,NaOH \;\xrightarrow{+\,H_2O}\; R\text{-}CO\text{-}O\text{-}Na \;+\; H_2O \qquad \textbf{(Eq.5)}$$

$$\text{FFA} \qquad\qquad \text{Catalyst} \qquad\qquad \text{Sodic soap} \qquad\qquad \text{water}$$
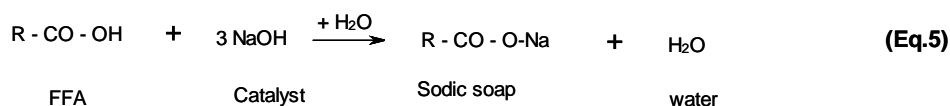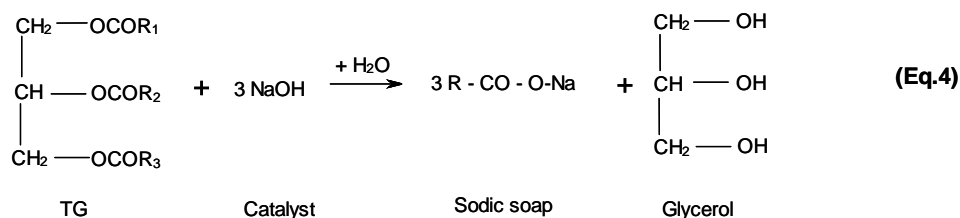
Solid catalysts provide a reduction of refining steps, and a non-corrosive and environmentally benign option. However, a three-phase reaction mixture formed by a solid catalyst, TG and alcohol strongly depends on pore diffusion process and active site availability for the catalytic reaction. Thus, heterogeneous catalysis faces a mass transfer resistance problem thereby decreasing the reaction rate (Mbaraka and Shanks, 2006). High surface areas offered by different catalyst supports have been the strategy for minimize the mass transfer limitation, but the active species in the supported catalyst can be corroded by alcohol, shortening the catalyst life-cycle (Liu et al., 2008). Numerous reports of FAME production using lipases have been published. Long reaction time and unfavorable reaction yields, in comparison to the alkaline catalyst are characteristics of FAME production by biocatalyst. The enzyme requires very specific reaction conditions in order to avoid enzymatic denaturation or deactivation (Dizge et al., 2009). On the other hand, one of the major obstacles to this process is the high cost of the enzyme. Therefore, biocatalyst of biodiesel is considered a commercially unviable process.

Using either homogeneous or heterogeneous catalysis, downstream processes based on biodiesel refining are necessary. Glycerol rich phase separation, catalyst neutralization and FAME refining

are included as the most used downstream processes. The refining of FAME rich phase involves the separation from others components of the reaction medium such as: dissolved glycerol, monoglycerides, diglycerides, FFA, soaps, catalyst, traces of alcohol and, nonreactive triglycerides (Atadashi et al. 2011). The multiple downstream processes are time-consuming and investments are considerably high (Wang et al. 2009; Gomes et al. 2010). In fact, Tai-Shung, 2007 reports that downstream processes constitutes over 60-80% of the total cost of a transesterification process plant.

Low refining yield of FAME creates infeasibility risks of use as biofuel in compression-ignition engines because may cause severe diesel engine problems, such as plugging of filters, coking on injectors, carbon deposits, excessive engine wear, oil ring sticking, engine knocking, and thickening and gelling of lubricant oil (Demirbas, 2007). Furthermore, the combustion of glycerides (TG, DG, MG, and glycerin) can lead to the formation of acrolein, a photochemical smog component (Cheng et al. 2009). Therefore, the removal of these impurities is essential to produce biodiesel that accomplishes international standard specifications. Currently, there are two main standards used for biodiesel quality control: ASTM D6751 standard for 100% pure biodiesel (B100) and DIN EN 14214 (European biodiesel standard). The former requires that the free and total glycerol content are <0.02 and 0.24 wt.%, respectively (Cao et al., 2008a); and the latter requires that monoglycerides (MG), diglycerides (DG) and triglycerides (TG) be less than 0.8, 0.2 and 0.2 wt.%, respectively (Cheng et al., 2009). In this context the industrial biodiesel production not only requires an efficient control of transesterification reaction but also an efficient refining process necessary to accomplish with the required standards quality.

2.3   Non-conventional technology and innovation in biodiesel production

The conventional batch production process of biodiesel must face a series of technical problems that can be summarized in the following points:

a) Reaction rate can be limited by mass transfer between the oil and alcohol because they are immiscible (Qiu et al. 2010). Therefore, high energy requirement for mixing is necessary (Yin et al., 2008).

b) Multiple downstream processing steps are necessary (Tai-Shung, 2007) to obtain a refined biodiesel. This also involves high wastewater generation and its treatment (Xie and Li, 2006).

c) Transesterification itself is a reversible reaction and in thermodynamic equilibrium (Cao et al., 2008b). Therefore there is an upper limit to raw materials conversion in the absence of product removal (Qiu et al. 2010).

The problems described above in biodiesel production can be improved by process intensification technologies. These technologies involve the use of novel reactors to enhance reaction rate and to reduce residence time (Qiu et al., 2010). Recently, novel reactors, such as the micro-channel reactor, oscillatory flow reactor, rotating/spinning tube reactor, cavitational reactor and microwave reactor, have been developed and applied to improve the mixing and mass/heat transfer between the oil and methanol in biodiesel production (Qiu et al., 2010). Table 1 shows a synthesis of the non-conventional technologies proposed for biodiesel production in the last seven years. Table 1 presents details of operating principles, advantages and disadvantages of each reactor in comparison to the conventional batch technology (stirred tank). As shown in Table 1, most of the developed technologies in these last years seek to intensify the transesterification reaction by either enhancing the mixing of oil and methanol or improving the heat transfer between the two liquid phases.

The reactors described in Table 1 propose directly or indirectly to solve problems of mixing and mass/heat transfer between reactants in conventional batch biodiesel production. However, none of the reactors mentioned aims to address problems of chemical equilibrium in transesterification, such as shifting the equilibrium of the reaction towards the formation of products by a partial separation/refining process. At this point specifically, the membrane reactor offers another interesting process intensification technology for biodiesel production.

2.4   The membrane reactor and its principle

Membrane reactor can be defined as a device that combines reaction and separation in a single unit (Caro, 2008). Basically, membrane reactors are configured by fusion or coupling between a conventional reactor and a membrane to obtain multifunctionality on same process. Thus, a membrane reactor can combine the reactor and membrane separator into a single unit as well as, membrane can operate as an external process unit. Some classifications have been proposed to membrane reactors according to different criteria, as:

1) membrane nature: organic, inorganic, porous or dense membrane.
2) membrane form: plate or tubular
3) membrane activity: inert or catalytic membrane reactor
4) reactor design utility: separator, concentration, extractor, distributor or contactor
5) type of reaction: dehydrogenation (Caro, 2008), esterification (Buonomenna et al., 2010; Caro, 2008), water dissociation (Caro, 2008) or wastewater treatment (Drioli et al., 2008).

However, in all cases, the operational principle is the same. The membrane acts as selective barrier to regulate the mass transfer rates of substances by permeability across the membrane (Böddeker, 2008). Membrane reactors can serve different purposes such as controlled diffusion of reactants to the reaction mixture so as well; selectively remove the products from the reaction mixture (Westermann and Melin, 2009). A selective diffusion of components achieved by membrane reactors makes such reactors are particularly useful to avoid the equilibrium conversion limits and improving the conversion of reversible reactions (Chmielewski et al. 1999). Nevertheless, the most important problem of this technology continues to be membrane fouling and concentration polarization. Both factors involve pretreatment or cleaning process, causing loss of productivity (Jagannadh & Muralidhara, 1996).

Table 1: Recently non-conventional technologies and innovation in biodiesel production

Reactor type	Principle	Advantage	Disadvantage
Micro-channels	Improvement the reaction rate increases the volume/surface ratio in the reactor by use micro-channels	- Fast and efficient heat dissipation and mass transfer (Qiu et al., 2010; Wen et al., 2009) - Because of the high heat transfer rate, consumed less energy than the conventional stirrer reactor (Qiu et al., 2010)	- Low production throughput, which is attributed to the limitations of the micro-fabrication technology that is used to produce the micro-channel. - High investment cost of the micro-channel reactor prohibits the addition of more reactors in parallel to amplify the production of biodiesel (Kalu et al., 2011).
Oscillatory flow	Improvement of radial mixing using a piston to produce oscillatory flow inside reactor equipped with plate baffles (Qiu et al., 2010).	- Increases in mass and heat transfer while maintaining plug flow (Phan et al., 2011; Qiu et al., 2010). - Improves the residence time distribution and suspension multi-phase reaction medium (Zheng et al., 2007). - Lower cost technology, reduced pumping cost and ease of control (Qiu et al., 2010).	- Hard temperatures control it can result in undesirable temperature gradients (Meeuwse et al. 2012). - Expensive maintenance in comparison to continuous stirred tank reactor (Meeuwse et al. 2012)
Rotating/spinning tube	Improvement of interfacial contact area using a shear reactor containing two tubes separated by a narrow annular gap, which produces Couette flow (laminar flow between two parallel plates)	- High reaction rate between the oil and the methanol. - Less mixing power and reaction time are required to produce biodiesel compared to a conventional reactor. - Suitable to handle feedstocks with high FFA because the residence time is short (Qiu et al., 2010).	- High investment and operational costs. Due to equipment costs, and a higher risk of mechanical failure - Not the best choice for large scale processes.
Cavitational	Enhancing mass transfer rate of the reaction by creating intense turbulence and liquid micro-circulation currents using cavities. It create a violent collapse, causing high local energy densities, temperatures and pressures (Gogate and Kabadi, 2009; Qiu et al., 2010).	- High effective for mixing immiscible liquids and consumes half of the energy required by conventional mechanical stirring (Pal et al., 2010; Colucci et al., 2005; Rokhina et al., 2009). - Temperature, pressure, reaction time and catalyst concentration, are significantly reduced (Deshmane et al., 2008; Kalva et al., 2008).	- Sonochemical reactors suffer from erosion and particle shedding at the delivery tip surface because of the high surface energy intensity (Gogate and Kabadi, 2009). - Scale-up of a sonochemical reactor is relatively more difficult than it is for a hydrodynamic cavitation reactor because the former relies on a source of vibration (Qiu et al., 2010).
Microwave	Improvement of energy transfer by irradiation directly into the reactants for accelerate the transesterification reaction.	- Efficient heating of reactants to the desired temperature because of the energy interactions at the molecular level (Barnard et al., 2007). - Compared to a conventional thermal heating reactor, a microwave reactor is able to achieve similar biodiesel conversion with a shorter reaction time and in a more energy-efficient manner (Qiu et al., 2010).	- The scale-up of a microwave reactor is difficult. - Microwave reactor offer a more energy-efficient alternative, but its installation and maintenance is difficult.

Fouling involves the adsorption or trapping of particles (foulant) by physical and/or chemical phenomenon. This can result of plugging or agglomeration by blocking membrane pores. The foulant may adsorb strongly to the membrane surface and, in some cases, chemically react with the polymeric membrane. Although several membrane materials such as polymeric, metal, or ceramic are presented, fouling is still a critical problem during any membrane processing (Jagannadh & Muralidhara, 1996). Different strategies have been proposed to keep the fouling under control as: pulses of negative transmembrane pressure or backflush (Sirkar, 1997) and desorption of foulant by solvent (Basso et al. 2009). On the other hand, concentration polarization is caused by the accumulation of retained solute at the membrane interface, forming a secondary layer that restricts the transport of the permeating species (Porter, 1972). Concentration polarization reduces the permeation rate of the more permeable component but favors the permeation of the less permeable components (Bakhshi et al., 2006). This hydrodynamic/diffusion phenomenon can be controlled using high shear on the membrane surface (Jagannadh & Muralidhara, 1996). An option used is increase the feed flow rate, the resulting turbulent flow will reduce the thickness of the boundary layer caused by the retained solute. Therefore, the mass transfer resistance at the boundary layer on the upstream of the membrane can be reduced, leading to an increase in the total permeation flux (Peng et al., 2007). The concentration polarization will always be present during membrane processing due to the fundamental limitations of mass transfer and the existence of a boundary layer (Jagannadh & Muralidhara, 1996).

2.5   Membrane reactor in Biodiesel production

The application of membrane reactors in biodiesel production has received attention in recent years. One reason is because the operating principle of membrane reactor fits very well to the requirements of the transesterification reaction of TG. Indeed, the objectives of the researches related to the subject seek to solve the reversibility of the reaction of transesterification of TG with partial separation of products. Thus, not only the priority is the product formation by moving the reversible reaction equilibrium but also, biodiesel is refined.

Recently, the membrane reactor has been applied as a promising technology in biodiesel production (Reyes et al. 2012; Baroutian et al., 2011; Wang et al. 2009; Cheng et al. 2009; Cao et al., 2008b; Dubé et al., 2007). A synthesis of recent work in the production of biodiesel by membrane reactors is shown in Table 2. The characteristics of the reactor used and the operating conditions in all cases are included in Table 2. As shown, tubular ceramic membranes with cut-off sizes between 0.02 and 0.12 μm have been preferably used in acid- and alkaline-transesterification of oil for a majority of cases. Also, reaction reactors, refining synthetic solutions and crude biodiesel have been proposed to study membrane reactors.

A schematic diagram for the transesterification reaction via membrane process is shown in Fig. 4 (Cao et al., 2008a, 2008b). Initial dissolution of methanol/catalyst is prepared into a feed tank. Then, the oil and methanol/catalyst dissolution are charged in a pre-mixing vessel to form the reaction mixture.
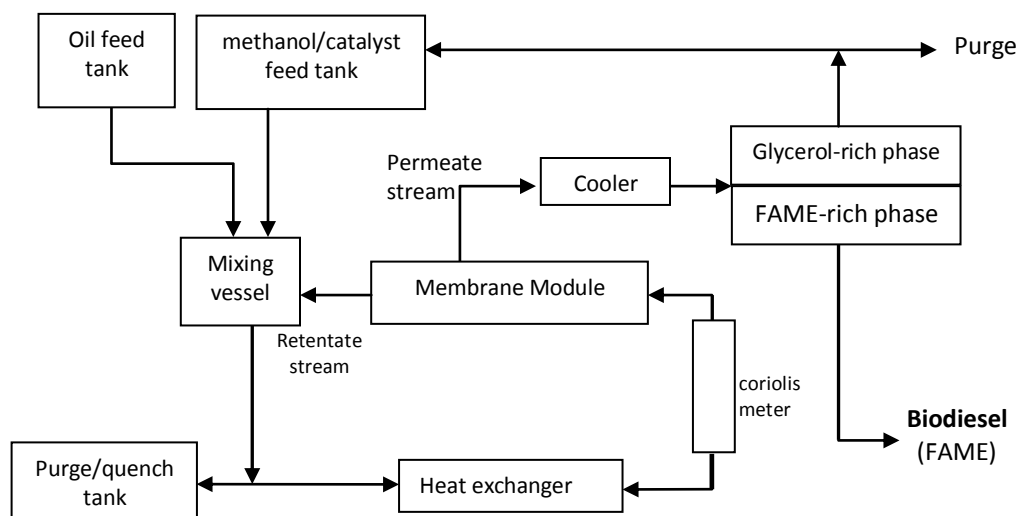
Figure 4: Schematic diagram of transesterification reaction via membrane reactor (adapted from Cao et al., 2008a, 2008b).

The oil/methanol/catalyst mixture is heated to the desired reaction temperature using a loop and heat exchanger before starting the process in membrane reactor. As stated, the application of membrane reactors for the production of biodiesel has been proposed for the selective separation of components of the reaction medium to shift the equilibrium of the reaction towards product formation. The development of the transesterification reaction begins with maximum concentrations of alcohol, TG and two clearly defined phases. Depending on turbulent mixing conditions and alcohol/TG ratio used in the transesterification, these phases form an emulsion of TG droplets embedded in an alcohol phase or alcohol drops embedded in a TG phase (Reyes et al. 2012). As TG and alcohol react, ideally FAME, glycerol and intermediaries (DG, MG) are formed according to Equations 1.2 and 3. At the end of transesterification two phases with different polarity are formed, a polar phase preferably rich in FAME and a non-polar phase preferably rich in glycerol. If the agitation conditions persist in the system, these phases will continue co-existing as an emulsion. Thus, the reaction medium is a complex biphasic mixture of reactants, products, further comprising soaps, water, FFA, and other impurities that promote an emulsion that forms the retentate (Atadashi et al. 2011). Depending of the operational conditions and oil/methanol molar ratio used, permeate stream can consist preferably of FAME and a minor content of methanol, MG, DG and catalysts (Cao et al., 2008a; Dubé et al., 2007, Wang et al. 2009) or may simply consist in the FAME-rich phase (Reyes et al. 2012). In order to comply with standards for biodiesel quality, further purification of the FAME-rich phase is conducted to remove methanol, MG, DG and catalysts (Cao et al., 2008a).

Table 2: Synthesis of recent work in the production of biodiesel by membrane reactors

Authors	Mixture	Characteristics of membrane rector			Operational conditions				FAME in permeate (Wt. %)
		membrane	pore size (µm)	total area contact (m^2)	Flow (mL/min)	Pressure (KPa)	PTM* (KPa)	T° (°C)	
Dubé et al. (2007)	Emulsion (commercial Canola oil/methanol/H_2SO_4 FAME, glycerol)	carbon tube	0.05	0.022	15.2	138	not reported	65	96
Cao et al. (2008b)	Emulsion (commercial canola oil/methanol/ H_2SO_4 FAME, glycerol mixture) with recirculation of phase methanol/ H_2SO_4	ceramic tube membrane	0.02	not reported	50	275,8	173.4	65	93
Wang et al. (2009)	Crude biodiesel from KOH-trans-esterification of refined palm oil	ceramic tube membrane	0.1	0.045	not reported	not reported	150	60	> 90
Cheng et al. (2009)	Biodiesel from NaOH-transesterification of canola oil	ceramic disc membrane	0.14	0.0013	400	not reported	66.7	40	60
Baroutian et al. (2011)	Crude biodiesel from heterogeneous KOH-trans-esterification of refined palm oil	ceramic tube	0.05	0.0201	not reported	100	not reported	70	95
Reyes et al. (2012)	Crude Biodiesel from NaOH-transesterification of canola oil	ceramic tube	0.1	0.09	517	41	not reported	55	79

(*)PTM: trans-membrane pressure

2. 5.1 Theory of separation by membrane reactors in biodiesel production

So far, the separation principle of a membrane processes applied to production of biodiesel is based on the drops size achieved in the reaction medium. The intra-membrane pressure is the driving force for membrane reactor separation (TakhtRavanch et al., 2008). According to Dubé et al. (2007) and Cao et al. (2008), oil droplets with diameters larger than the membrane pore size are retained while a continuous phase comprising FAME, methanol and glycerol, readily permeates through the membrane. Indeed, selectivity criterion proposal by Dubé et al., (2007) and Cao et al. (2008) does not consider the role in rejection aspect of reaction intermediaries (MG y DG) and other components, as FFA, water, or soaps formed. Also, this criterion does not address the composition change of the emulsion during transesterification. Unlike previous year publications, Wang et al. (2009) complements the membrane separation principle giving more attention and responsibility to other emulsion components formed during the transesterification as soaps and free glycerol. Wang et al. (2009) proposed that due to surface activity of soap formed and the immiscibility of glycerol into biodiesel, soaps exists in a reversed micelle form in biodiesel (FAME-rich phase). The hydrophilic ends of soaps are bond to the free glycerol droplets, while the hydrophobic ones are immersed into the crude biodiesel. The micelle size formed by soap and free glycerol with a mean size of 2.21 μm are larger than that of biodiesel. Therefore these "micelle complexes" are easily retained by microporous membrane. The theory of TG retention by these micelle complexes is not clear. Usually the authors cite previous reports about oil-water emulsions refining by membranes. Shu et al. (2006), who used a ceramic membrane process in the treatment of oil-water micro-emulsions, attribute the permeation of TG to deformations experienced by the oil droplets, even when the oil droplet diameter are larger than membrane pores. Other authors explain the incomplete rejection of TG by the coalescence of the oil droplets on the membrane surface, which may have result in the formation of a continuous oil phase and permeation through the membrane (Gomes et al., 2010) and the less TG rejection rate have been associated with decrease of permeate flux even through a membrane of 0.2 μm pore size (Wang et al., 2000).

2. 5.2 Reaction/refining performance of membrane reactors in biodiesel production

Using the conditions specified in Table 2. Dubé et al. (2007) proposed a semi-batch membrane reactor for FAME production. A solution of methanol/H_2SO_4 was added at a rate of 6.1 mL/min for 6 hours in 100 g of Canola oil. As a large methanol:oil molar ratio was employed (24:1), an excess of methanol in reaction medium and in permeate was expected. In fact, a large non-reactive methanol was obtained as permeate. On the other hand, Dubé et al. (2007) found that membrane reactor could selectively hold TG in the retentate, while allowing FAME, methanol and glycerol permeation during transesterification. In fact, a 96 wt.% in FAME was achieved. Nevertheless, FAME concentration in permeate was not constant as the reaction progressed. Furthermore, the membrane system studied by Dube et al. (2007) showed good results, however the continuous permeation of methanol may limit its availability as a reactant of the reaction. Therefore, the system requires continuous pumping of large amounts of methanol to the reaction medium not favoring the reduction of production costs of FAME. On the other hand, as FAME and glycerol the permeate was obtained, the separation of FAME-rich phase and glycerol-rich phase was not achieved by the proposed system, thus sedimentation stage decanter is not avoided

Supplementing the results obtained by Dube et al. (2007) and with the aim of minimizing the use of methanol excess by recycling, Cao et al. (2008) experimented with a ceramic membrane reactor. They obtained a permeate in the range of 85-93 wt.% in FAME and a polar-rich phase (high methanol and glycerol content) using a ceramic membrane reactor. Differing form Dube et al., 2007, Cao et al. 2008 refer to the intermediaries content in permeate (FAME-rich phase), as "occasional trace amounts of DG". However, Cao et al. 2008 affirmed that this DG content can easily be transformed into FAME in a thermal step for industrial application. On the other hand, MG, TG, and glycerol were not detected in FAME-rich phase and water washing was not necessary. The authors conclude that continuous biodiesel production was successfully and a high purity FAME product, free of non-saponifiable materials was produced.

With the aim of refining crude biodiesel Wang et al. (2009) proposed a ceramic membrane process instead of a hot water washing step typically used in biodiesel production. Using the conditions specified in Table 2, crude biodiesel was directly micro-filtered to remove the residual glycerol, catalyst, soap, and some salts. Thus, a refined biodiesel with minimum concentration of glycerol (0.0108%), K (1.40 mg/kg), Na (1.78 mg/kg), Ca (0.81 mg/kg) and Mg (0.20 mg/kg) in permeate was obtained.

The polar phase obtained at the end of transesterification by membrane process can be recycled back to the membrane reactor in order to reduce the overall methanol to oil molar ratio (Cao et al., 2006). Two ways to recycle methanol back to the reactor have been reported: recycling of the methanol from the distillation of the FAME-rich phase (Baroutian et al., 2010) and direct recycling of the glycerin-rich phase (polar phase with high methanol content) (Cao et al., 2008b). In the first case, temperatures between 80-130°C were used in the recovery of methanol by distillation (Baroutian et al., 2010), therefore the process does not present significant energy savings. The second case may be of interest; because the glycerol-rich phase not only has alcohol but also an important FAME content to be recycled (Reyes et al. 2012). In addition, glycerol-rich phase can increase the FAME purity, as the glycerol-rich phase can help to reduce the interface tension making the formation of smaller droplets and aggregate complexes in the reaction medium easier (Yilmaz et al. 1999). Thus, it can reduce the amount of water required for FAME washing process (Cao et al., 2008b).

The experimental conditions that can favor TG permeation during transesterification in membrane reactors have not been reported in detail. Especially when low oil/methanol ratios are used or when TG is the continuous phase, for instance at the start of transesterification. Therefore, there are different challenges for biodiesel refining while the transesterification reaction is running. Considering this lack of information, it is impossible to know what specific time of the reaction is advisable to apply the refining stage: only at the beginning, only at the end or during the entire transesterification reaction time. An important approach was conducted by Cheng et al. (2009), under the hypothesis that an increase of the FAME concentrations can favor an increase of TG content in permeate. Therefore, Chen et al. (2009) postulated that to ensure TG rejection by the membrane, knowledge of the phase behavior for the typical system composed of TG/FAME/MeOH is necessary. In fact, in this paper, the liquid–liquid phase equilibrium for TG/FAME/MeOH using synthetic mixtures was experimentally studied using a disk ceramic membrane. The phase diagrams allowed estimate the mixture of TG/FAME/MeOH that favors TG permeation across the membrane

(as continuous phase) and which mixture form an emulsion can promote the TG retention. The results showed that a two-phase state as reaction medium is strictly necessary for TG retention by the refining membrane, as high FAME concentrations in the TG/FAME/MeOH mixture may form a permeable homogenous phase (non-emulsion). Thus, high concentrations of methanol and FAME can act as TG dissolvent and favor the permeation of TG through the membrane.

2.5.3 Maintaining the membrane reactor applied to biodiesel production

Effects of fouling in the production of biodiesel by membrane reactors have not been studied in detail. Pressure increases and decreased permeate flow are indicators that lead to assume the presence of fouling and concentration polarization on the surface. On the other hand, the biphasic equilibrium reaction and the use of alcohol in the transesterification forced to seek a practical solution and prevent fouling formation either to use a simple regeneration procedure of the membrane by a washing step. Thus, with the goal of proposing a cleaning process of the membrane used in biodiesel production, Wang et al. (2009) proposed the use of recycled methanol (after microfiltration of crude biodiesel) as membrane cleaning solution. In effect, they demonstrated that the soap and the free glycerol accumulated on surface or/and precipitating within the pores of membrane were easily removed by the methanol, due to its high solubility to these polar substances. Therefore, recycled methanol is demonstrated to be a good solvent for cleaning the membrane. This last aspect and the degree of refining achieved in crude biodiesel, simplify the refining steps used by conventional washing process. Consequently, not only the usage of water need is reduced but also wastewater generation. Indeed, 10 L of wastewater for each liter of biodiesel are generated by a conventional washing process (Karaosmanoglu et al. 1996; Demirbas 2003).

To avoid membrane fouling by the modification of reaction medium composition provoked by different transesterification/refining cycles, Reyes et al., 2012 proposed a semi-batch membrane reactor under the conditions described in Table 2. The FAME concentration (> 70%) as criterion to start a membrane refining stage was used. At the end of the refining stage a complete separation of FAME-rich phase (permeate) from glycerol-rich phase (retentate) was achieved. Then, the semi-batch membrane reactor was charged again with feed reactant solution to start a new transesterification/refining cycle. A new condition inside reactor was achieved in each cycle without decreasing the permeate flux. Increments of permeate flux in each transesterification/refining cycle can represent an indirect control of fouling and concentration polarization. The results of Reyes et al. 2012 suggest that the operational strategy proposed could diminish fouling and the cleaning stages of the membrane reactor.

2.5.4 Control parameters of membrane reactors in biodiesel production

The operation mode of a membrane reactor including chemical reaction and refining in a same process, (i.e. a "full process") are associated with the transesterification reaction and refining by membrane reactor. Some authors have addressed the entire process (Dubé et al., 2007; Cao et al., 2008; Baroutian et al. 2011; Reyes et al., 2012), while others have studied only the refining of crude biodiesel (Wang et al. 2009; Cheng et al., 2009).

As is shown in Table 2, temperatures in the range of 40-70°C have been used in membrane reactors. The conversion of oil to FAME was found to be positively affected by increasing the reaction

temperature (Dubé et al., 2007). However, these temperatures are lower than those used in conventional transesterification, as the reaction medium is based on a bi-phasic system and is strongly sensitive to interfacial tension (Yilmaz et al., 1999). Thus, temperatures higher than 70°C can destabilize the emulsion and transform the reaction medium in a homogeneous phase easily permeable across of membrane. Usually, an increase of TG content in permeate is coupled with the increase of temperature. Thus, temperatures of less than 60°C are recommended for a membrane reactor (Cheng et al. 2009).

Usually higher methanol/oil ratios have been used in membrane reactors (Cheng et al., 2010; Hamma et al., 2007; Zhang 2003). Methanol in membrane reactors fulfills functions in both the transesterification reaction and in the refining step. As transesterification is an equilibrium reaction, usually methanol excess is used to move the equilibrium of the reaction to the synthesis of FAME (Cheng et al., 2009). On the other hand, Dubé et al. (2007) and Cao et al. (2008) reported the use of methanol not only to maintain the dispersed phase droplets in retentate side but also as continuous phase, acting as a solvent and carrier of TG and FAME. Additionally, considering the constant extraction of methanol from the reaction medium (as permeate), excess available methanol as reactant is required. Some methanol/oil molar ratios used have been: 24:1 (Baroutian et al., 2011; Cao et al., 2008a; Cheng et al., 2010), 6:1 (Shi et al., 2010), 26:1 (Zhu et al., 2010), 106:1 (Guerreiro et al., 2006) and 254:1 (Guerreiro et al., 2010) 46:1 (Tremblay et al., 2008). However the molar stoichiometric ratio (3:1 methanol/oil) for transesterification using membrane reactors has not been addressed in detail

The pressure is considered the driving force able to mobilize permeable components across a membrane. Therefore, the permeate flux increases with higher transmembrane pressure (TMP) because a greater driving force is applied for separation (Gomes et al., 2010). However, the use of high pressures can cause the compacting of the boundary layer, increasing the fouling of the membrane (Hwang & Kammermeyer, 1998; Ribeiro et al. 2006). Additionally, in a biphasic reaction medium formed by micellar aggregates, high constant TMP may involve low selectivity of the species involved transesterification. In fact, less oil rejection rate for pressures higher than 200 kPa in oil-water emulsions have been reported (Wang et al., 2000), deformation of oil droplets effect (Shu et al. 2006) also, low retention of DG in the refining of biodiesel at 173 kPa has been reported (Cao et al. 2008b). On the other hand, coalescence effect of the oil droplets on the membrane surface have been reported (Gomes et al., 2010). Therefore, the TMP must be low enough to keep the membrane fouling control. When TMP is kept constant, the TMP profiles in the membrane reactor can act as an indicator to check the progress of the transesterification reaction. A sharp increase in the TMP indicates that transesterification is not occurring, and the oil has become a continuous phase within the membrane reactor. On the other hand, a constant and stable TMP profile for all operating times reveals that a sufficient amount of oil has been transesterified into FAME. Thus, permeation of lower viscosity products, as FAME, allows the continuous operation of the membrane reactor (Tremblay et al., 2008).

As the operating principle of membrane reactors for the production of biodiesel is based on the emulsified droplets size achieved, membrane pore size appears to be an essential factor in the production of biodiesel by membrane reactors. Cao et al., 2006 reported that average size of the oil droplets falls in the range of 12-400 μm, which is much larger than the membrane pore size used in

biodiesel production (Table 2). In fact, biodiesel with FAME content higher than 90 wt. % has been achieved using a membrane pore size between 0.02-0.1 µm (Baroutian et al., 2011; Wang et al. 2009; Cao et al. 2008b; Dubé et al. 2007). However, various effects as less TG retention even through a membrane of 0.2 µm pore size (Wang et al., 2000), deformations by oil droplets (Shu et al. 2006), and coalescence effect experienced by oil droplets on the membrane surface, which may have result in the formation of a continuous oil phase and permeation through the membrane have been reported (Gomes et al., 2010).

A research that included the membrane pore size as variable in biodiesel production, reported that contents of metals and free glycerol in permeates and the initial flux of different pore size of membrane microfiltration decreased when the pore size decreases (0.6, 0.2, and 0.1µm). However, retention of free glycerol in micro-filtrated crude biodiesel by membranes of 0.2 and 0.6 µm was over 90% (Wang et al. 2009). Therefore, for a successful biodiesel production/refining process, membrane pore size must be in the range between 0.02-0.2 µm and the mixture condition must maintain an emulsion size sufficiently high to favor TG retention and FAME permeation.

Considering high yield, high selectivity, shorter reaction time and low cost, alkaline catalysis have been prefered in biodiesel production as compared to acidic catalysis (Leung et al. 2010).. Because the concentrations of the catalyst used is usually selected based on the stoichiometric requirements of the reaction, a catalyst concentration of less than 1 wt.% in relation to the oil mass is recommended (Leung et al. 2010) Higher concentrations of alkaline catalyst are not used because the excess can react with water and FFA of oil to form soaps (Eq. 4 and 5). The soaps formed can promote the emulsion (Atadashi et al. 2011) but is not clear if these can increase the retention of other components of the reaction medium, such as TG, however, soap will be increase the risk of fouling or clogging of the membrane.

2.6   Conclusions

Currently, one of the main problems facing the biodiesel production process using membrane reactors is the retention of glycerides (TG, DG, and MG). Therefore, it is assumed that the separation mechanism is not entirely clear. Most authors agree that the separation depends on the droplet size achieved by the reaction medium consisting of oil/FAME/Me-OH, but other authors give prominence to micelle effect caused by other species involved in the reaction medium such as soaps and FFA. Despite the lack of knowledge, some authors conclude that transfer of TG and non-reacting lipids to the product stream will be diminished by maintaining a two-phase system in the membrane reactor. In this sense, the changes experienced by the emulsion composition during transesterification/refining should be studied extensively. Previous knowledge about the phase equilibrium of emulsion systems will induce not only a better understanding of the separation process for the biodiesel mixture but also to clarify the operation model of membrane reactors.

In recent years, the limitations of mass and energy transfer between immiscible reactants (alcohol and triglycerides) in transesterification has been mainly guided by the improvement of conditions due to changes in mixing reactors. Thus, improving the performance of the transesterification has been possible. However, these technologies do not consider the reversibility of the reaction nor the

decrease in downstream processes, aspects directly related to water use, wastewater generation and processing costs.

Through the bibliographical revision it is clear that membrane reactors represent a promising option for biodiesel production. Membrane reactors offer considerable advantages compared to conventional biodiesel production, including reduction of refining steps, decrease in the use of washing water, decrease in the generation of wastewater, reduction of the size of the reactor, increase in the biodiesel quality expressed in glycerol retention and intermediates, and finally decrease in production costs. These advantages not only make up a safe and more environmentally friendly process but are also competitive compared to distillation in maintaining product quality in the petroleum processing industries. Therefore, the production of biodiesel using membrane reactor could partially solve the energy requirements of the most demanding sectors such as industry and transportation.

2.7.   References

1. Atadashi IM, Aroua MK, Abdul Aziz A., (2011). Biodiesel separation and purification: a review. Renew Energy 36, 437–43.
2. Atadashi I.M., Aroua M.K. Abdul Aziz A., (2010). High quality biodiesel and its diesel engine application: A review. Renew. Sust. Energ. Rev. 14, 1999-2008.
3. Azócar L., Ciudad G., Heipieper H.J., Muñoz R., Navia R., (2010). Improving fatty acid methyl ester production yield in a lipase-catalyzed process using waste frying oils as feedstock, J Biosci. Bioeng. 109, 609–614.
4. Bakhshi A, Mohammadi T, Nik OG, Aroujalian, (2006). A. Effect of operating conditions on pervaporation of methanol–water mixtures: part 2. Membr Technol 7-11.
5. Barnard TM, Leadbeater NE, Boucher MB, Stencel LM, Wilhite BA., (2007). Continuous-flow preparation of biodiesel using microwave heating. Energy Fuel 21, 1777–81.
6. Baroutian S, Aroua MK, Raman AAA, Sulaiman NMN., (2010). Methanol recovery during transesterification of palm oil in a TiO2/Al2O3 membrane reactor: experimental study and neural network modeling. Sep Purif Technol 76, 58–63.
7. Baroutian S, Aroua MK, Raman AAA, Sulaiman NMN (2011). A packed bed membranereactor for production of biodiesel using activated carbon supported catalyst. Bioresour Technol 102, 1095-1102
8. Basso R.C., Gonçalves LAG., Grimaldi R. and Viotto LA., (2009). Degumming and production of soy lecithin, and the cleaning of a ceramic membrane used in the ultrafiltration and diafiltration of crude soybean oil. Journal of Membrane Science 330, 127–134.
9. Böddeker K.W., (2008). Liquid separations with membranes. Berlin: Springer-Verlag Berlin Heidelberg, p. 34.
10. Buonomenna MG, Choi SH, Drioli E., (2010). Catalysis in polymeric membrane reactors: the membrane role. Asia Pac J Chem Eng 5, 26–34.
11. Cao P, Tremblay AY, Dubé MA, Morse K., (2006). Effect of membrane pore size on the performance of a membrane reactor for biodiesel production. Ind Eng Chem Res;46:52–8.
12. Cao P, Dubé MA, Tremblay AY., (2008a) High-purity fatty acid methyl ester production from canola, soybean, palm, and yellow grease lipids by means of a membrane reactor. Biomass Bioenergy 32, 1028–36
13. Cao P, Dubé MA, Tremblay AY.,(2008b). Methanol recycling in the production of biodiesel in a membrane reactor. Fuel 87, 825–33.

14. Caro J. (2008). Catalysis in micro-structured membrane reactors with nano-designed membranes. Chin J Catal 29, 1169–77.
15. Cheng L-H, Cheng Y-F, Yen S-Y, Chen J., (2009). Ultrafiltration of triglyceride from biodiesel using the phase diagram of oil–FAME–MeOH. J Membr Sci 330, 156–65.
16. Chmielewski D, Zoe Z, Vasilios M. (1999). Conversion targets for plug flow membrane reactors. Chem Eng Sci 54, 2979–84.
17. Colucci J, Borrero E, Alape F., (2005). Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing.. J Am Oil Chem Soc 82, 525–30.
18. Conservation ADoE. How can I dispose of used cooking oils and fats? . Retrieved 13th March, 2011, fromhttp://www.dec.state.ak.us/eh/docs/fss/cooking.pdf.
19. Demirbas A. (2003). Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. Energy Convers Manage 44, 2093–109.
20. Demirbas A., (2007). Progress and recent trends in biofuels. Prog Energy Combust Sci 33, 1-18.
21. Demirbas A. (2008). New liquid biofuels from vegetable oils via catalytic pyrolysis. Energy Educ Sci Technol 21, 1-59.
22. Deshmane VG, Gogate PR, Pandit AB. (2008). Ultrasound-assisted synthesis of biodiesel from palm fatty acid distillate. Ind Eng Chem Res 48, 7923–7.
23. Dizge N, Aydiner C, Imer DY, Bayramoglu M, Tanriseven A, Keskinler B., (2009). Biodiesel production from sunflower, soybean, and waste cooking oils by transesterification using lipase immobilized onto a novel microporous polymer. Bioresour Technol 100, 1983–91.
24. Drioli E, Fontananova E, Bonchio M, Carraro M, Gardan M, Scorrano G. (2008). Catalytic membranes and membrane reactors: an integrated approach to catalytic process with a high effiiency and a low environmental impact. Chin J Catal 29, 1152–8.
25. Dubé MA, Tremblay AY, Liu J. Biodiesel production using a membrane reactor. Bioresour Technol 2007;98:639–47.
26. EIA. International Energy Outlook. Chapter 1: world energy demand and economic outlook. Retrieved 25th January, 2011, fromhttp://www.eia.gov/oiaf/ieo/pdf/world.pdf2010.
27. Ferrari R.A. Oliveira, V.S. , Scabio A. (2005). Biodiesel de soja–Taxa de conversão emésteres etílicos, caracterizacão físico-química e consumo em gerador de energia, Química Nova 28 19–23.
28. Gogate PR, Kabadi AM. (2009). A review of applications of cavitation in biochemical engineering /biotechnology. Biochem Eng J 44, 60–72.
29. Gomes MCS, Curvelo PN, Davantel de Barros ST. (2010). Separation of biodiesel and glycerol using ceramic membranes. J Membr Sci 352, 271–6.
30. Gomes MCS, Arroyo PA, Pereira NC., (2011). Biodiesel production from degummed soybean oil and glycerol removal using ceramic membrane. J Membr Sci 378,453–61.
31. Guerreiro L, Castanheiro JE, Fonseca IM, Martin-Aranda RM, Ramos AM, Vital J., (2006). Trans-esterification of soybean oil over sulfonic acid functionalised polymeric membranes. Catal Today 118, 166–71
32. Hama S., H. Yamaji, Fukumizu T., Numata T., Tamalampudi S., Kondo A., Noda H., Fukuda H., (2007). Biodiesel-fuel production in a packed-bed reactor using lipase-producing Rhizopus oryzae cells immobilized within biomass support particles. Biochemical Engineering Journal 34, 273-278
33. Hammond GP, Kallu S, McManus MC., (2008). Development of biofuels for the UK automotive market. Appl Energy 85:506–15.
34. Hoekman SK. (2008). Biofuels in the U.S. Challenges and opportunities. Renew Energy 34. 14–22.

35. Hwang S.T., Kammermeyer K., (1998). Membranes in Separations. New York: Wiley-Interscience, 1975. Apud: Ultrafiltration and Microfiltration Handbook, Lancaster, p.1.
36. International Energy Outlook (IEO, 2010). Chapter 1: world energy demand and economic out-look. Retrieved 25th January, 2011, fromhttp://www.eia.gov/oiaf/ieo/pdf/world.pdf
37. Jagannadh S.N. and Muralidhara H.S., (1996). Electrokinetics Methods to Control Membrane Fouling Ind. Eng. Chem. 35, 1133–1140.
38. Kalu EE, Chen KS, Gedris T., (2011). Continuous-flow biodiesel production using slit-channel reactors. Bioresour Technol 102, 4456–61.
39. Kalva A, Sivasankar T, Moholkar VS. (2008). Physical mechanism of ultrasound-assisted synthesis of biodiesel. Ind Eng Chem Res 48, 534–44.
40. Karaosmanoglu F, Cigizoglu KB, Tuter M, Ertekin S., (1996). Investigation of the refining step of biodiesel production. Energy Fuels 10:890–5.
41. Keera, S. T.; El Sabagh, S. M. y Taman, A. R. (2011). Transesterification of vegetable oil to biodiesel fuel using alkaline catalyst. Fuel, 90, 42-47.
42. Lam MK, Lee KT, Mohamed AR. (2010). Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. Biotechnol Adv 28, 500–18.
43. Leung DYC,Wu X, Leung MKH., (2010). A review on biodiesel production using catalyzed transesterification. Appl Energy;87:1083–95
44. Leung D.Y.C. , Wu X. , Leung M.K.H. (2010). A review on biodiesel production using catalyzed transesterification. Applied Energy 87, 1083–1095.
45. Liu X, He H, Wang Y, Zhu S, Piao X., (2008). Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. Fuel;87:216–21
46. Ma F., Hanna M.A., (1999) .Biodiesel production: a review, Biores. Tech. 70, 1–15.
47. Marchetti JM,Miguel VU, Errazu AF. (2007). Possible methods for biodiesel production. Renewable Sustainable Energy Rev 11, 1300–11.
48. Mbaraka IK, Shanks BH., (2006). Conversion of oils and fats using advanced mesoporous heterogeneous catalysts. J Am Oil Chem Soc 83, 79–91.
49. Meeuwse M., van der Schaaf J., Schouten J.C., (2012). Multistage rotor-stator spinning disc reactor. 58, 247—255
50. Monni S, Raes F., (2008). Multilevel climate policy: the case of the European Union, Finland and Helsinki. Environ Sci Policy 11,743–55.
51. Murugesan A., Umarani C., Chinnusamy T.R., Krishnan M., Subramaniam R.,.Neduzchezhain N, (2009) . Production and analysis of biodiesel from non edible oils - a review. Renewable & Sustainable Energy Reviews 13, 825–834.
52. Peng F, Hu C, Jiang Z., (2007). Novel ploy(vinyl alcohol)/carbon nanotube hybrid membranes for pervaporation separation of benzene/cyclohexane mixtures. J Membr Sci;297:236–42.
53. Phan AN, Harvey AP, Rawcliffe M., (2011). Continuous screening of base-catalysed biodiesel production using new designs of mesoscale oscillatory baffled reactors. Fuel Process Technol;92:1560–7.
54. Porter M. C., (1972). Concentration polarization with membrane ultrafiltration. Prod Res Dev 11, 234–48
55. Qiu Z, Zhao L, Weatherley L., (2010). Process intensification technologies in continuous biodiesel production. Chem Eng Process 49, 323–30.
56. Radler M, (2010). Total reserves, production climb on mixed results, Oil and Gas Journald 108
57. Reyes, I., Ciudad, G., Misra, M., Mohanty, A., Jeison, D., Navia, D. (2012) Novel sequential batch membrane reactor to increase fatty acid methyl esters quality at low methanol to oil molar ratio. Chemical Engineering Journal 197, 459–467

58. Ribeiro, A. P. B., Moura, J. M. L. N., Gonçalves, L. A. G., Petrus, J. C. C., & Viotto, L. A. (2006). Solvent recovery from soybean oil/hexane miscella by polymeric membranes. Journal of Membrane Science, 282, 328–336.

59. Rokhina EV, Lens P, Virkutyte J., (2009). Low-frequency ultrasound in biotechnology: state of the art. Trends Biotechnol 27, 298-306.

60. Sahoo PK, Das LM, Babu MKG, Naik SN., (2007). Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine. Fuel;86:448–54.

61. Sawyer RF., (2009). Science based policy for addressing energy and environmental problems Proc Combust Inst 45–56.

62. Sdrula N. (2010). A study using classical or membrane separation in the biodiesel process. Desalination 250, 1070-1072.

63. Shi W, He B, Ding J, Li J, Yan F, Liang X., (2010). Preparation and characterization of the organic- inorganic hybrid membrane for biodiesel production. Bioresour Technol 101, 1501–5.

64. Shu W., Liangyin C., Wenmei C., (2006). Fouling-resistance composite membranes for separation of oil-in-water microemulsions, Chinese Journal of Chemical Engineering 14 37–45.

65. Shuit SH, Lee KT, Kamaruddin AH, Yusup S., (2010). Reactive extraction and in situ esterification of Jatropha curcas L. seeds for the production of biodiesel. Fuel 89, 527–30.

66. Sirkar, K. K., (1997). Membrane separation technologies: current developments. Chemical Engineering Communications. 157; 145-184.

67. British Petroleum (BP), Statistical review of world energy (2009). Retrieved 10th February, 2011,from;http://www.bp.com/liveassets/bp_internet/globalbp/globalbp_uk_english/reports _and_publications/statistical_energy_review_2008/STAGING/local_assets/9_downloads/st atistical_review_of_world_energy_full_report_9.pdf.

68. Tai-Shung NC. (2007). Development and purification of biodiesel. Sep Purif Technol 20, 377–81.

69. TakhtRavanchi M, Kaghazchi T, Kargari A., (2008). Immobilized liquid membrane for propylene-propane separation. World Acad Sci Eng Technol, 79–81.

70. Tremblay AY, Cao P, Dubé MA., (2008). Biodiesel production using ultralow catalyst concentrations. Energy Fuel 22, 2748–55.

71. Uihlein A, Schebek L. (2009). Environmental impacts of a lignocellulose feedstock biorefinery system: an assessment. Biomass Bioenergy 33,793–802

72. Vicente G, MartínezM, Aracil J. (2004). Integrated biodiesel production: a comparison of different homogeneous catalysts systems. Bioresour Technol 92, 297–305.

73. Wang Y, Xingguo W, Yuanfa L, Shiyi O, Yanlai T, Shuze T. (2009). Refining of biodieselby ceramic membrane separation. Fuel Process Technol 90, 422–7

74. Wen Z, Yu X, Tu S-T, Yan J, (2009). Dahlquist E. Intensification of biodiesel synthesis using zig-zag micro-channel reactors. Bioresour Technol 100, 3054–60.

75. Westermann T, Melin T., (2009). Flow-through catalytic membrane reactors-principles and applications. Chem Eng Process 48, 17–28.

76. Xie W, Li H., (2006). Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. J Mol Catal A: Chem 255, 1–9.

77. Yee KF, Tan KT, Abdullah AZ, Lee KT. (2009). Life cycle assessment of palm biodiesel: revealing facts and benefits for sustainability. Appl Energy 86, 189–96.

78. Yilmaz G., Jongboom R.O.J., van Soest J.J.G., Feil H., (1999). Effect of glycerol on themorphology of starch-sunflower oil composites, Carbohydrate Polymers 38, 33-39.

79. Zhang Y., Dubé M., McLean D. & Kates M., (2003). Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresource Technology 90, 229–240.

80. Zheng M, Skelton RL, Mackley MR., (2007). Biodiesel reaction screening using oscillatory flow meso reactors. Process Saf Environ Prot 85, 365–71.

81. Zhu M, He B, Shi W, Feng Y, Ding J, Li J, (2010). Preparation and characterization of PSSA/PVA catalytic membrane for biodiesel production. Fuel 89, 2299–304.

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PROGRAMA DE DOCTORADO Y MAGÍSTER EN CIENCIAS DE RECURSOS NATURALES

Title of the thesis

STUDY OF BIODIESEL PRODUCTION BY MEANS OF A CONTINUOUS SEPARATION SYSTEM BY CERAMIC MEMBRANES.

Chapter III

Title

Ternary study of miscibility and effect of operating variables of a membrane process applied to biodiesel refining

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Abbreviations

ANOVA: analysis of variance

ASTM: American Society for Testing and Materials

CBR: Conventional Batch Reactor

CBR-MS: Conventional Batch Reactor coupled to Membrane System

DG: Diglycerides

EN14214: European norm14214

FAME: Fatty Acid Methyl Esters

LLE: liquid–liquid phase equilibrium

MG: Monoglycerides

Me-OH: methanol

SBMR: Sequential Batch Membrane Reactor

TG: Triglycerides

Chapter III. Ternary study of miscibility and effect of operating variables of a membrane process applied to biodiesel refining

Abstract

The alkaline-batch transesterification has been one of the most used methods in the production of biodiesel or FAME (fatty acid methyl ester). Despite this, this method has shown serious shortcomings, especially in the number of steps necessary to achieve a biodiesel quality under international standards. Membrane technology has been recently used for this purpose. In this context, this thesis has been developed. In the course of the thesis it has been shown that a membrane refining step is not suitable at the start of a transesterification reaction, because unreactive TG and FAME are miscible and form a single continuous phase. On the other hand, operational parameters for TG retention and FAME refining have not been reported in detail in literature. Therefore, the aim of this work was first to study the miscibility of TG-Glycerol-Methanol and FAME-TG-Methanol applied to the TG separation and FAME refining, and for further studying the effect of different operational variables of a membrane refining process.

The results showed that the miscibility between TG and FAME is not only dependent on the concentration of each in the mixture, but also is influenced by the concentration of methanol. Methanol plays a key role as a surfactant between triglycerides and transesterification products. Thus, in a TG/methanol/FAME mixture at 24°C , TG can be removed as a biphasic emulsion if the concentration of methanol is higher than 12 wt.%, TG is higher than 15 wt.%, and FAME is less than 73 wt.%.

The proposed design based in response surface methodology (RSM) demonstrated that the most significant variable in permeate flux during the FAME/glycerol (80/20 wt.%) mixture refining, was the temperature, followed by the recirculation flow and finally, the pressure. The best refining performance of a non-reactive synthetic blend of FAME/ glycerol was obtained using a temperature of 60 °C, a recirculation flow of 1200 mL/min and a pressure of 6 psi, where a maximum permeate flux of 58 L/(m^2*h) was obtained. This chapter clarifies the operation mode of biodiesel membrane refining. The results obtained offer some useful criteria in future membrane refining proposals.

3.1 Introduction

Considering that global energy consumption is governed by industrial and transportation sector, increased attention has received the production of renewable fuels (Hammond et al., 2008; Hoekman, 2008; Monni and Raes, 2008; Sawyer, 2009). Thus, the research has been focused on separation and refining process to produce biodiesel (fatty acid methyl ester or FAME), because a highly purified biofuel is necessary to achieve the stringent ASTM-D-6751 and EN-14214 quality standards for FAME production (Atadashi et al., 2010). Compounds such as water, free fatty acids (FFA), and free and bound glycerin (mono-, di-, and triglyceride molecules), must be kept to a minimum level, while the purity of the biofuel (FAME) must exceed 96% (Freedman et al., 1986; Veljkovic et al., 2006; Berchmans and Hirata, 2008; Liu and Wang, 2009; Georgogianni et al., 2009). Recently, membrane technologies have shown several advantages compared with the conventional separation and purification process in FAME production, since no additional devises are necessary to separate glycerol (settler), reducing the operation time (Cheng et al., 2009; Dube et al., 2007; Wang et al., 2009). According to Wang et al., (2009), the separation principle is related to the immiscibility of free glycerol and FAME, where free glycerol forms droplets joining to the hydrophilic ends of the soap. These droplets can be separated from FAME by size exclusion using membranes.

The glycerol separation by microfiltration membrane has taken interest and has been researched using non-reactive media (Gomes et al., 2010). However, due to methanol excess used in transesterification, the solubilization of glycerides (TG, MG, DG and glycerol) in the non-polar FAME-rich phase remains a problem in the FAME membrane refining (Cheng et al., 2010; Hamma et al., 2007; Zhang 2003). In fact, in the course of current thesis, has shown that a membrane process is not suitable at the start of a transesterification because unreactive TG and FAME are miscible and form a single permeable phase. Furthermore, the operating conditions of a membrane refining are still not clear. Therefore, the aim of this chapter was first to study the ternary miscibility of TG-Glycerol-Methanol and FAME-TG-Methanol by making phase diagrams of solubility, applied to the glycerol separation and FAME refining, and then to study the effect of different operational variables on FAME refining process. With the aim of achieving an operating condition that get permeate fluxes as high as possible. The knowledge of the behavior of permeate flux under different operating conditions will allow not only optimize operating parameters that govern the process, but also to get control of membrane fouling and get a better fit in the future scaling process.

3.2   Materials and methods

3.2.1 Liquid–liquid phase equilibrium of FAME-TG-Me-OH and TG-Glycerol-Me-OH blends

With the goal of to study the ternary miscibility of TG-Glycerol-Methanol and FAME-TG-Methanol applied to the refining of biodiesel, a couple of phase diagram of solubility were made.

3.2.1.1 Materials

Crude canola oil was obtained by mechanical seed processing by Molino Gorbea Co. (IX Region of La Araucanía, Chile), and it was used as TG source. Methanol (99.9% purity), NaOH anhydrous pellets, and glycerol (99.8% purity) were supplied by Winkler Co.

3.2.1.2 Analytical procedures

3.2.1.3 Titration
The titration experiments were carried out in vessel flasks (50 mL) using a hot plate and a magnetic stirrer. The total volume was 50 mL, which was distributed in different ratios under isothermal conditions and at atmospheric pressure. These ratios were 1:1, 1:2, 1:5, 1:6 for all blends studied. The titrant used for FAME-TG-Methanol and TG-Glycerol-Methanol blends, was methanol.

3.2.1.4 Ternary liquid–liquid phase equilibrium (LLE) modeling

The titration data obtained were used to build the ternary liquid–liquid phase equilibrium (LLE) using the ProSim Software (ProSim S.A. Labege-France)

3.2.2 Refining of FAME to different conditions

With the goal to evaluate the effect of the variables: temperature, pressure, and recirculation flow on FAME refining, a non-reactive synthetic blend of FAME /glycerol (80/20 wt.%) was studied by a membrane refining process using response surface methodology (RSM). The response was measured as the permeate flow obtained in each experimental run.

3.2.2.1 Experimental design

 The experimental design based on the RSM and used to evaluate the effect of three operating variables of a membrane refining process in the flow of permeate is summarized in Table 1. The experimental design corresponded to a central composite design of face-centered with three variables represented by "X1" (temperature), "X2" (pressure) and "X3" (recirculation flow). The variables were studied by three working levels each (0, 1 and -1), (see Table 1). The answer "Y", was represented by measuring the permeate flux obtained under each experimental condition. The total number of experimental runs and detail of the operating conditions for each run are summarized in Table 2. A total of 25 experimental runs were studied (including duplicates) and three measurements of permeate flux (Y_1, Y_2 and Y_3) were performed for each experimental run.

Table 1: variables and different work levels of experimental design based on the RSM

	Variables	work levels		
		-1	0	1
X_1	temperature (°C)	40	50	60
X_2	pressure (psi)	6	10	30
X_3	recirculation flow (mL/min)	800	1000	1200

Table 2: Experimental runs and operating conditions for experimental design based on SRM

Run N°	Variables			Run N°	Variables		
	X_1 (°C)	X_2 (psi)	X_3 (mL/min)		X_1 (°C)	X_2 (psi)	X_3 (mL/min)
1	50	10	800	**14**	40	6	800
2	60	6	1200	**15**	50	30	1000
3	40	6	800	**16**	50	6	1000
4	50	30	1000	**17**	50	10	1000
5	60	30	800	**18**	40	10	1000
6	50	10	1000	**19**	50	10	800
7	40	30	1200	**20**	60	10	1000
8	50	6	1000	**21**	50	10	1000
9	50	10	1000	**22**	60	6	1200
10	60	10	1000	**23**	60	30	800
11	50	10	1200	**24**	50	10	1000
12	50	10	1200	**25**	40	10	1000
13	40	30	1200				

In table 2: X_1, X_2, and X_3 are variables: temperature, pressure, and recirculation flow, respectively.

3.2.2.2 Statistical analysis

Regression analysis was carried out with the aid of Design Expert 6.0.6 software (STAT-EASE Inc., Minneapolis, USA). The experimental data obtained (Table 3) were fitted to a second-order polynomial equation. This equation describes the relationship between the predicted response (Y, permeate flux obtained) and the independent variables (X_1, X_2, and X_3). The polynomial model for Permeate flux obtained may be written as follows:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_1^2 + \beta_5 X_2^2 + \beta_6 X_3^2 + \beta_7 X_1 X_2 + \beta_8 X_1 X_3 + \beta_9 X_2 X_3 \quad \text{(Eq. 1):}$$

Where:

Y: is the response measurement as permeate flux obtained in L/m^2*h, X_1: is temperature variable (°C), X_2: is pressure variable (psi) and, X_3: is the recirculation flow variable, and $\beta_0, ..., \beta_9$: are model regression coefficients.

With the fitted quadratic polynomial equation, contour plots were developed to analyze the interaction between terms and their effects on Permeate flux obtained.

For each variable was considered the variation in linear, quadratic and interaction with other variables. These interactions were verified through an inferential statistical analysis, for which it was done for hypothesis testing approach as follows:

- Null hypothesis (H_0): $\beta_i = 0$, i.e. none of the control factor contributes to the explanation of the response.
- Alternative hypothesis (H_1): $\beta_i \neq 0$, i.e. at least one control factor contributes to some extent to the prediction of the response.

For ANOVA decision was considered a significance level of $\alpha = 0.05$ (5%).

3.2.2.3 Materials and Methods

The biodiesel used was obtained by alkaline transesterification of rapeseed oil, using NaOH to 1 wt.%. and methanol-oil to molar ratio 3:1 in reaction mixture. After the transesterification, the glycerol rich-phase was removed and the biodiesel rich phase was washed with deionized water then neutralized with sulfuric acid 1M and then was heat treated for moisture content removal and to get a 99.9 wt% of Biodiesel. Glycerol used was 99.8% and supplied by Winkler Co. (GL- 0825).

3.2.2.4 Analytical procedure

Before biodiesel refining experiments FAME content was verified by spectrophotometer using a (Perkin Elmer Co., Clarus 600) chromatograph coupled to a (Perkin Elmer Co, Clarus 500T) mass spectrometer. An Elite-5ms capillary column with a length of 30 m, thickness of 0.1 μm and internal diameter of 0.25 mm was used. The following temperature program was used: 50 °C for 1 min and then increasing temperature at a rate of 1.1 °C/min up to 187 °C. Both the injector and detector temperatures were 250 °C and He was used as the carrier gas.

3.2.2.5 Refining experiments

For experiments refining of biodiesel were used synthetic blends biodiesel/glycerol (80/20 wt.%) simulating the product of a transesterification reaction. The biodiesel refining was performed in a recirculation system consisting of a multichannel ceramic membrane (Ceramfil CMF-19033 Jiangsu, China) packed in a recirculation steel module and coupled to a batch reactor (Fig. 1). The membrane uses was made of alumina/zirconia with a cut-off size of 0.1 μm and an effective surface area of 0.09 m². Trans-membrane pressure in the module was verified by two manometers, one on the permeate side and another on the retentate side (Fig. 1). The pressure was regulated by a valve and varied between 6 and 30 psi consistent with the experimental design. The temperature in the reactor was controlled by a thermostatic bath (Fig. 1) and a thermometer was used as indicator inside reactor. The temperature was varied between 40 to 60°C consistent with the experimental design. A peristaltic pump (Masterflex L/S model 900-1255) was used to raise the pressure and for recirculated the biodiesel-glycerol blend in all system. The pump was operated between 800 and 1200 L min⁻¹ according to the experimental design specified in Table 1.

The system was operated with complete recirculation of permeate flux to the reactor (see Fig. 1). The permeate flux was measured using a flowmeter (McMillan 1791 - 5T) and monitored using the software Labview 8.6 (National Instrument Co.). Each refining experiment was performed by 30 min. The permeate flux was recorded automatically every 3 seconds during refining. Thus, an average permeate flow was calculated every 10 min, generating three responses: $Y_{10\,min}$, $Y_{20\,min}$, Y_{30min}, respectively (See Table 3).
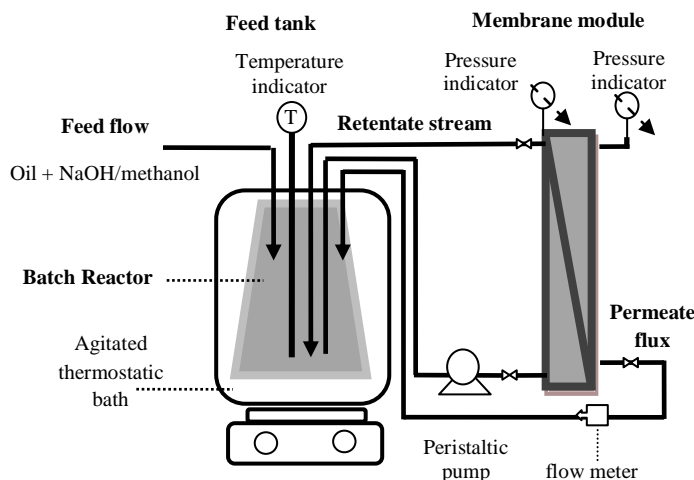
Figure 1: Settings used for the refining of synthetic blends of FAME/glycerol (80/20 wt.%) through a membrane system coupled to a batch reactor.

3.3. Previous antecedents

Synthetic emulsions studies for FAME refining by optical analysis

In order to supply information about the conditions of the emulsion in the retentate as size drops and FAME permeation, different binary mixtures of TG-methanol, TG-FAME, FAME-methanol, and FAME-glycerol were observed under optical microscopy. The results showed that droplets greater than 3 µm diameter in average were observed in all mixtures and concentrations studied. On the other hand, higher content of FAME in the mix resulted in general in smaller droplets with less size distribution in all mixtures studied. By contrast, the decrease of glycerol in the mixture increased the size and distribution of the drops. Thus, an excess of FAME, (at the end of the transesterification, e.g.), would homogenize the emulsion and maintain a droplet size useful for retaining the glycerol or glycerol agglomerates in retentate and facilitate it separation by a membrane process. For TG-FAME mixture that showed no emulsion in any of the proportions studied. Therefore, FAME and TG completely permeated through the membrane. The permeation of these components may be even more favored in a transesterification where an excess of methanol is used. In fact, the results for TG-methanol mixture showed that an excess of methanol causes a separation of easy phases and consequently TG permeation through a ceramic membrane of 0.1 µm

cutoff size. This showed the importance of the emulsion formation for apply the membrane filtration, since when there is no formation, the membrane can not to separate the mixture components. Thus, this chapter results took to conclude that efficiency of the separation and refining of biodiesel depends on the evolution of the emulsions formed during the transesterification.

3.4   Results and discussion

3.4.1 Ternary liquid–liquid phase equilibrium (LLE) study

With the objective to study the behavior of the miscibility between the different components involved in the transesterification reaction the LLE were studied.

3.4.1.1 Phase diagram of FAME -TG - Methanol system.

The Fig. 2 shows the behavior of the solubility of three components at different proportion in mixture. The points on the curve show the different ratios where the system begins to form a homogeneous phase. Thus, mixtures upper to curve, the system is a single homogeneous phase and under the curve, the mixture form a biphasic system. Therefore, when the content of the FAME is 73 wt.% and TG is 25 wt% and methanol is 10 wt%, (top point of curve in Fig. 2) the blend forms a homogeneous phase. However, at less percent of FAME and higher percents of methanol and TG (under this curve) the system forms two phases (Fig. 2).Therefore to achieve immiscibility between TG and FAME is require a concentration in the mixture less than 73 wt.% in FAME and 10 wt. % in methanol. This result makes a critic point for get an efficient separation of FAME-TG at 20°C during a transesterification reaction. For example, a product reaction consisting in 70 wt. % of FAME, a 16 wt. % of unreacted TG and a 14 wt. % of unreacted methanol (as end of reaction) can be easily separated by forming two phase. Similar LLE results were found by Chen et al., (2008) for FAME-TG-Methanol system at 20°C. They demonstrated an increasing of miscibility of the TG-FAME-Methanol system with increasing the amount of FAME and temperature. Thus a 70 wt.% of FAME was needed to achieve a homogeneous phase at 20 °C while a 50 wt. % of FAME is needed at 60 °C. According to Chen et al., (2008) results, the two phase area at 60 °C is much reduced than at 20°C. Therefore, the study and projection of the phase diagram at 20°C is representing an unfavorable but interesting condition for concludes.

The distribution of each component in the different phases formed can be estimated tracing a tie line (blue line, Fig. 2). Thus, a mixture of Methanol-TG-FAME of 14:16:70wt.%, respectively has an upper phase with a content of 15:14:71 wt.% (point A, Fig. 2), and a lower phase with a content of 11:20:69 wt.% in Methanol-TG-FAME, respectively (point B).
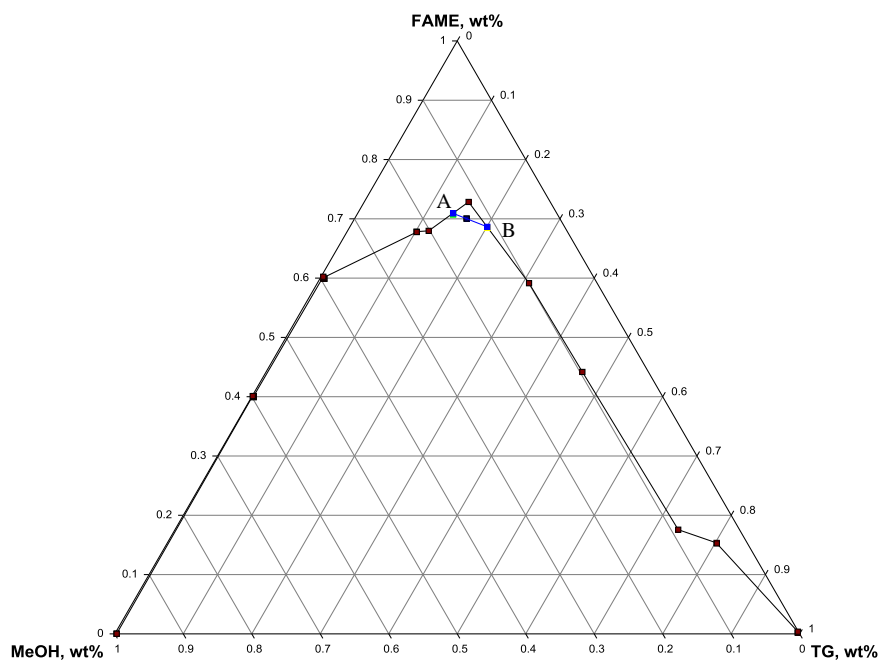
Figure 2: Phase diagram of Methanol-TG-FAME at 24°C and tie line proposal (line from point A to B)
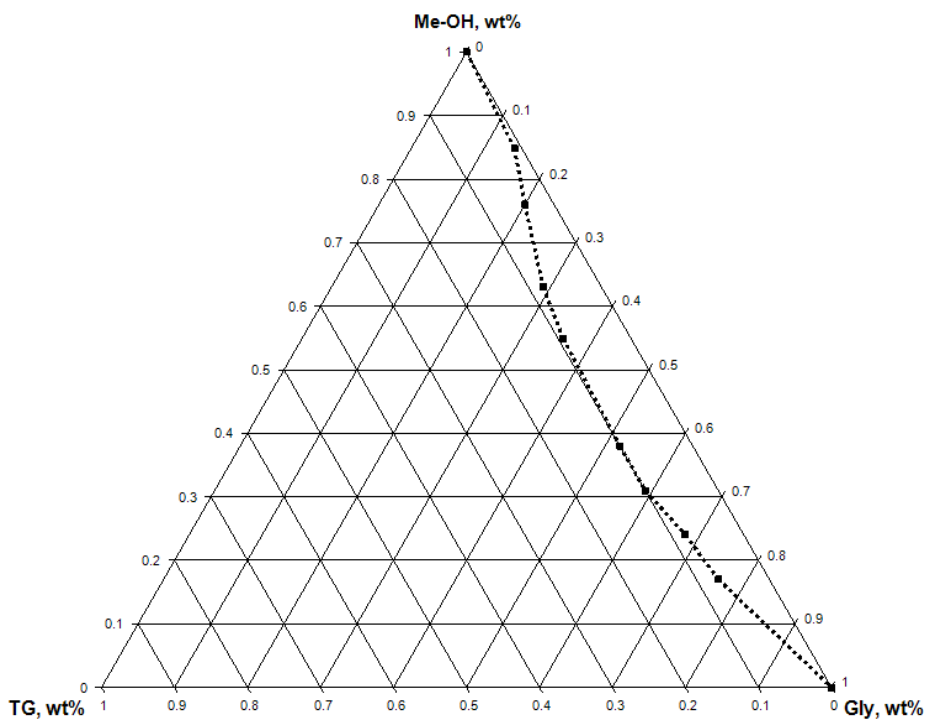

Figure 3: Phase diagram of TG - glycerol - methanol system

3.4.1.2 Phase diagram of TG -Glycerol- Methanol system.

The phase diagram of TG -Glycerol- Methanol system is show in Fig. 3. Considering the differences in polarity of the mixture (methanol/glycerol) vs. TG, the system will be preferably heterogeneous. The lower left zone shows different ratios where the system forms two phases. A high area indicates the surfactant effect of methanol (Gomes et al., 2010). The alcohol reducing the surface tension between the non-polar phase and glycerol, maximizing their superficial contact area and causing the formation of small droplets of the disperse phase (Yilmaz et al., 1999, Gomes et al., 2010). Thus a decrease in the interfacial tension makes it easier to break down the glycerol droplets into smaller ones. However, TG retention by a membrane not will be a problem if TG concentration exceeds 10 wt.% (left zone in Fig.3) in comparison to other components (methanol/glycerol). When the TG concentration is less than 10 wt.%, mixture methanol/glycerol form a homogenous phase in all cases (upper right zone in Fig.3). Thus, a retentate with a TG concentration less than 10%, glycerol 80% and methanol 10%, under favorable operating conditions may be perfectly permeable through the membrane. This could increase because, methanol is distributed in the glycerol-rich phase, and the up FAME-rich phase (Van Gerpen et al., 2004).

In the transesterification/refining context, the complete separation of methanol and un-reactive TG from the products is important especially at the end of the transesterification. The system studied (Fig. 3) could be useful to explain the permeation possibilities of retentate after a transesterification/refining membrane process, where there will be a low concentration of nonreactive TG, low concentration of unreacted methanol, and high concentration of glycerol.

3.4.2 Statistical analysis of proposal experimental design

3.4.2.1 Permeate flux in time

As each refining experiment was performed by 30 min and permeate flux was recorded automatically every 3 seconds by flow meter software during refining. An average permeate flow was calculated every 10 min, generating $Y_{10\,min}$, $Y_{20\,min}$, and $Y_{30\,min}$. Thus, a statistic analysis of significance between responses was done using SPSS Statistics 17.0 software (IBM Co. N.Y. USA).

The statistic analyses of results by Student T-test are showing in Table 4. A decreasing of flux in time after the beginning of the process was expected for each experiment. However, non-significative differences between $Y_{10\,min}$, $Y_{20\,min}$, and $Y_{30\,min}$ were obtained (Table 4). Thus, a mean value was considered for ANOVA ($Y_{mean\,flux}$, Table 3).

The different responses indicated that there not trend for the membrane to clog up in range of variables considered and during the time studied (30 min), discarding drastic flux reduction caused by the concentration polarization or other "incrustation" phenomena, such as pore blocking or molecule adsorption on the membrane surface (Gomez et al., 2010).

Table 3: Experimental runs, combination of variables according to RSM and responses obtained

Run N°	Variables			Responses (L/h*m^2)			Mean response
	X_1 (°C)	X_2 (psi)	X_3 (mL/min)	$Y_{10\ min}$	$Y_{20\ min}$	Y_{30min}	$Y_{mean\ flux}$ (L/h*m^2±std. dev.)
1	50	10	800	38	37	37	37.3 ± 0.6
2	60	6	1200	58	57	58	57.7 ± 0.6
3	40	6	800	29	28	28	28.3 ± 0.6
4	50	30	1000	43	41	40	41.3 ± 1.5
5	60	30	800	48	47	46	47.0 ± 1.0
6	50	10	1000	46	45	45	45.3 ± 0.6
7	40	30	1200	38	36	36	36.7 ± 1.2
8	50	6	1000	45	45	47	45.7 ± 1.2
9	50	10	1000	47	43	43	44.3 ± 2.3
10	60	10	1000	55	58	55	56.0 ± 1.7
11	50	10	1200	49	50	52	50.3 ± 1.5
12	50	10	1200	50	52	50	50.7 ± 1.2
13	40	30	1200	36	35	37	36.0 ± 1.0
14	40	6	800	30	28	28	28.7 ± 1.2
15	50	30	1000	42	38	41	40.3 ± 2.1
16	50	6	1000	44	44	45	44.3 ± 0.6
17	50	10	1000	47	46	46	46.3 ± 0.6
18	40	10	1000	38	37	37	37.3 ± 0.6
19	50	10	800	38	36	38	37.3 ± 1.2
20	60	10	1000	58	56	55	56.3 ± 1.5
21	50	10	1000	46	45	46	45.7 ± 0.6
22	60	6	1200	56	58	58	57.3 ± 1.2
23	60	30	800	45	46	45	45.3 ± 0.6
24	50	10	1000	45	45	46	45.3 ± 0.6
25	40	10	1000	39	39	37	38.3 ± 1.2

Table 4: Analysis of significance between $Y_{10\,min}$, $Y_{20\,min}$, and $Y_{30\,min}$ by Student T-test

Comparison	F value	Significance level	Confidence interval of difference
$Y_{10\,min}$ - $Y_{20\,min}$	0.268	0.607*	0.05
$Y_{10\,min}$ - $Y_{30\,min}$	0.16	0.691*	
$Y_{20\,min}$, -$Y_{30\,min}$	0.16	0.899*	

(*) non-significative difference at 5% level

3.4.2.2 ANOVA: analysis of variance of proposal experimental design

Table 5: ANOVA for response surface quadratic model for mean response

Source model	Sum of squares	DF	Mean square	F Value	Prob>F	Adjusted R-squared	Predictive R-squared	Adequate precision
Model	1549.2	9	172	393.8	<0.0001*	0.9933	0.9883	69.358
A (X_1)	336.7	1	336.7	770.4	<0.0001*			
B (X_2)	17.6	1	17.6	40.3	<0.0001*			
C (X_3)	174.2	1	174.2	398.6	<0.0001*			
A^2 (X_1^2)	7.9	1	7.9	18	0.0007*			
B^2 (X_2^2)	40.3	1	40.3	92.3	<0.0001*			
C^2 (X_3^2)	16.8	1	16.8	38.5	<0.0001*			
AB (X_1X_2)	8.64	1	8.6	19.7	0.0005*			
AC (X_1X_3)	4	1	4	9.1	0.0085*			
BC (X_2X_3)	0.7	1	0.7	1.6	0.2143			
Residual	6.56	15	0.44					
Lack of Fit	0.47	1	0.47	1.09	0.3145			
Pure error	6.08	14	0.43					
Cor total	1555.7	24						

(*) significant component of model at 5% level.

The result for ANOVA in Table 4 showed a model F-value of 393.8 that implies the model is significant and there is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. In Table 4, the "Prob > F" values less than 0.05 (α value) indicate model terms are significant. Thus, A, B, C, A^2, B^2, C^2, AB, AC are significant model terms. Therefore, is possible reject the null hypothesis (H_0) and accept the alternative hypothesis (H_1) proposed for ANOVA, because at least one control factor contributes to some extent to the prediction of the response. According to "Prob > F", the interaction BC is a not significant term at 5% (α value). Thus, BC can be eliminated in the model equation.

The Predictive R-Squared for the model was of 0.9883 (Table 5) and was reasonable agreement with the Adjusted R-Squared of 0.9933. As Adequate precision measures the signal to noise ratio and must be greater than 4 for to be desirable. I this case a ratio of 69.358 indicated an adequate signal. Therefore, this model can be used to navigate the design space.

The "Lack of Fit F-value" of 1.09 (Table 5) implies the Lack of Fit is not significant relative to the pure error. There is a 31.45% (Table 5) chance that a "Lack of Fit F-value" this large could occur due to noise. As lack of fit is non-significant the model can to be to fit.

Table 6: Estimated coefficient by regression model

regression coefficient	variable associated	coefficient value
β_0	constant	45.6
β_1	X_1	9.2
β_2	X_2	-2.1
β_3	X_3	6.6
β_4	X_1^2	1.3
β_5	X_2^2	-2.8
β_6	X_3^2	-1.8
β_7	X_1X_2	1.8
β_8	X_1X_3	-1.2

According to regression significant coefficient (see Table 6), the model proposal for described the comportment of permeate flux at different condition of temperature, pressure and recirculation flow studied is as following:

$$Y = 45.6 + 9.2X_1 - 2.1X_2 + 6.6X_3 + 1.3X_1^2 - 2.8X_2^2 - 1.8X_3^2 + 1.8X_1X_2 - 1.2X_1X_3$$

Where:

Y: is the response measurement as permeate flux obtained ($L*m^{-2}h^{-1}$), X_1, X_2, and X_3 are the temperature, pressure, and recirculation flow variables respectively in terms of factor -1, 0, and 1.

3.4.2.3 Interaction analysis between variables studied by model graphs

Interaction Temperature/pressure

Figure 4: Interaction recirculation pressure /temperature in permeate flux (Y, blue line in L/h*m^2).
A: 3D interaction graph, B: basal detail of 3D interaction graph

Interaction recirculation flow /pressure

DESIGN-EXPERT Plot

Y prom
X = B: pressure
Y = C: recirculation flow

Actual Factor
A: temperature = 55

DESIGN-EXPERT Plot

Y prom
X = B: pressure
Y = C: recirculation flow

Actual Factor
A: temperature = 55.41

Figure 5: Interaction recirculation flow /pressure in permeate flux (Y, blue line in L/h*m^2). A: 3D interaction graph, B: basal detail of 3D interaction graph

DESIGN-EXPERT Plot

Y prom
X = A: temperature
Y = C: recirculation flow

Actual Factor
B: pressure = 6.00

A

DESIGN-EXPERT Plot

Y prom
◆ Design Points

X = A: temperature
Y = C: recirculation flow

Actual Factor
B: pressure = 6.00
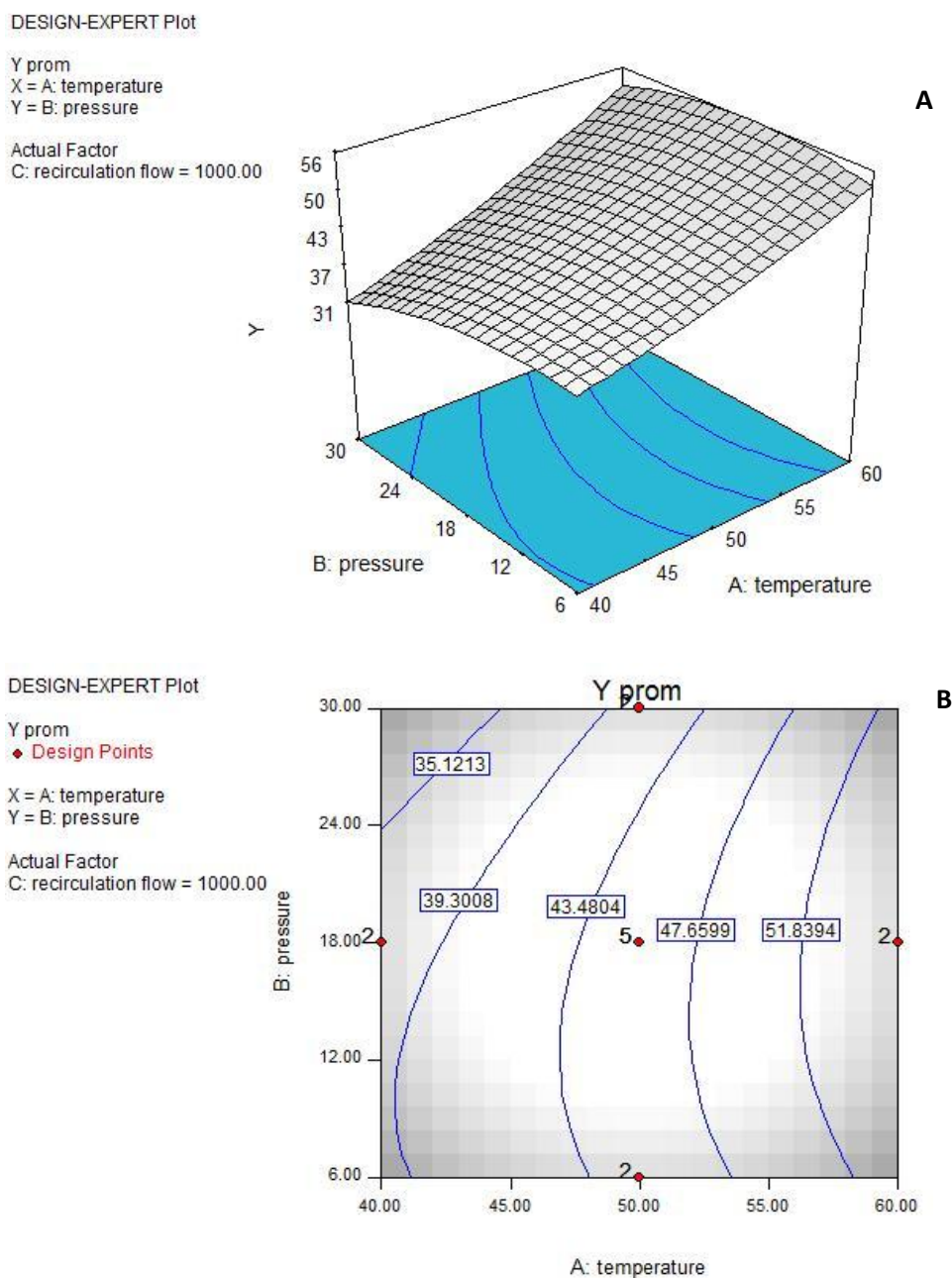
B

Y prom

51.8394

47.6599

43.4804

39.3008

35.1213
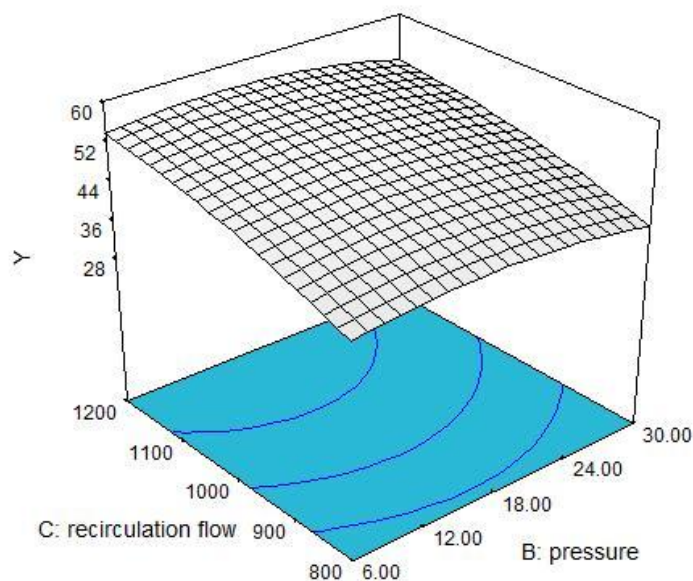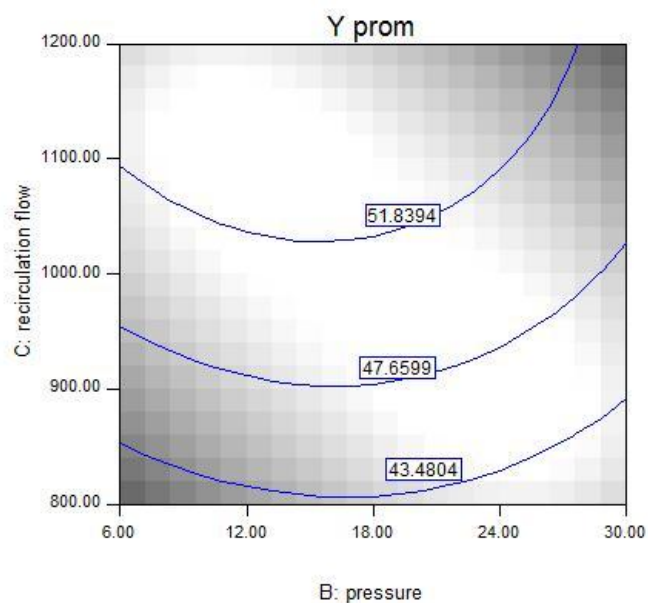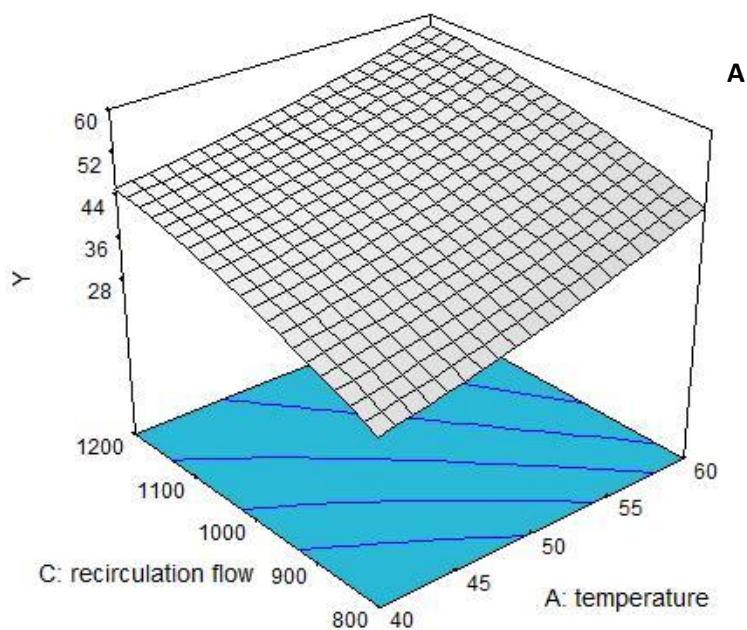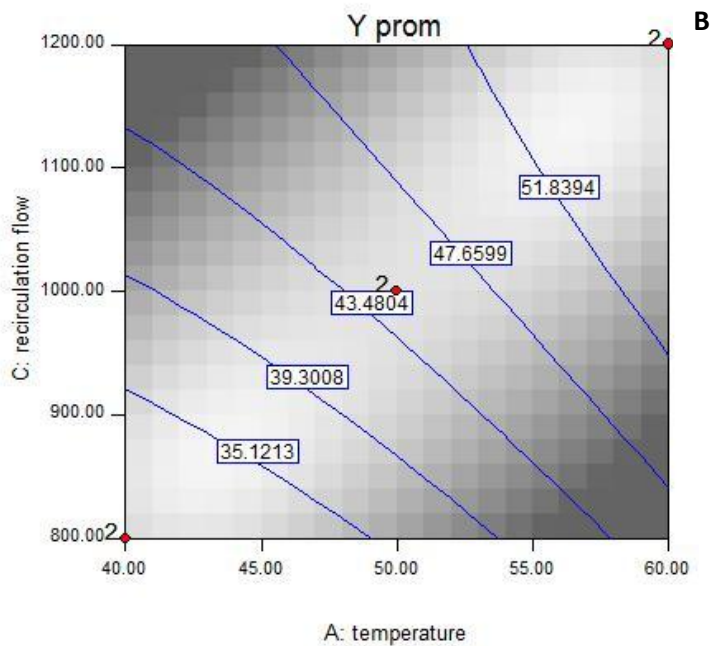
Figure 6: Interaction recirculation flow /temperature in permeate flux (Y, blue line in L/h*m^2).
A: 3D interaction graph, B: basal detail of 3D interaction graph

3.4.2.4 Refining experiment, analysis of results

Consistent with the proposed experimental design, maximum and minimum flux values were obtained at 6 psi. Thus, a maximum permeate flux (58 L/h*m^2) was obtained when the recirculation flow was 1200 mL/min and the temperature was 60 °C and a minimum value (28 L/h*m^2) was obtained when the temperature was 40°C and the recirculation flow was 800 mL/min. Similar results for range of permeate fluxes were achieved by Gomez et al., (2010), (see Fig 7), they got values of 25 and 56 L/(h*m^2) for a biodiesel, glycerol, ethanol mixture at 60 °C (80:10:10% mass) after 75 minutes operation of a membrane system of 0.2 µm cut-off membrane at 1.0 and 3.0 bar (14.5 to 43.5 psi), respectively. These are similar condition in comparison with used here. Also considering, they worked with a complete recirculation of permeate.
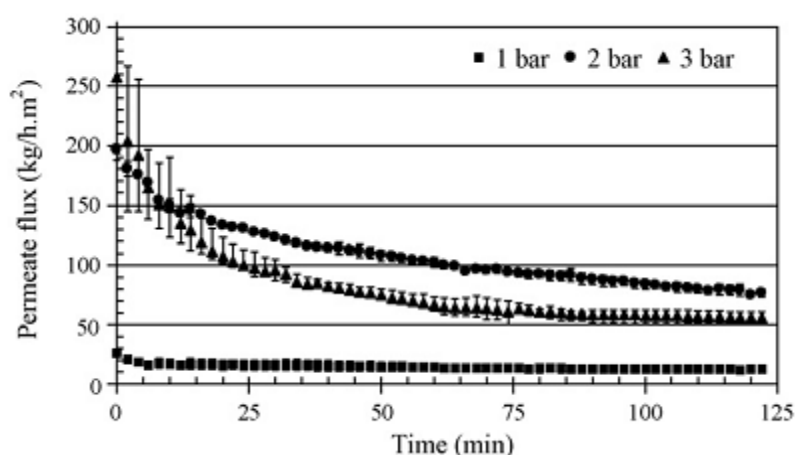
Figure 7: Permeate flux (kg/h*m^2) of the 0.2 membrane as a function of the filtration time for the biodiesel, glycerol, ethanol mixture (80:10:10% mass) at 1.0, 2.0, and 3.0 bar (14.5, 29, and 43.5 psi, respectively) and T=60°C (Gomez et al., 2010)

Temperature effect

Consistent with the F-value of A (associated to X_1), which indicates the significance of the temperature in the probabilistic model (Table 5), temperature is one of the most significant variables in the explanation of permeate flux behavior of the different conditions of pressure and recirculation flow studied. This is represented by curve slope of the Figs. 4 and 6, which correlates the pressure versus temperature and the recirculation flow, respectively. This increased flow of permeate is due to changes in viscosity experienced by FAME/glycerol mixture with increasing temperature (Gomes et al., 2010). The increase in viscosity with temperature of the mixture can be explained by Arrehenius relationship (LnU = LnB+ E/RT, where U is the viscosity and B is a constant).

As any glycerol precipitate was visible in the samples of permeate flux was assumed that the size reached by the drops of glycerol in the continuous phase (FAME) are sufficiently large to be retained by the membrane even using 60 °C and 1200 mL/min. In Fact, according to previous results of membrane refining experiment (Fig 8), concentration of 74% FAME in the

FAME/glycerol mix (recirculated at 55 °C, under pressure) resulted in droplets higher to 3µm, but with less size distribution. Thus, the FAME concentration used here, (80wt%, as end of the transesterification), can homogenize the emulsion and maintain a droplet size useful for retaining the glycerol (or glycerol agglomerates) in retentate and facilitate the separation of FAME in a membrane process. However, concentration measurements of free glycerol and intermediates are necessary.
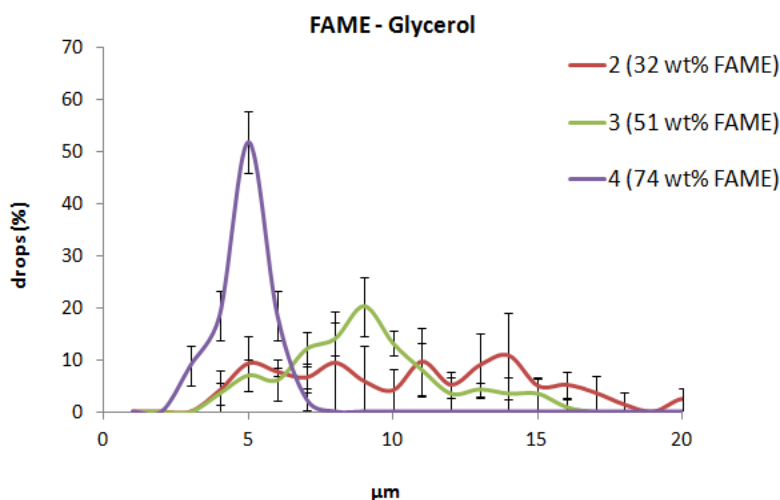

Figure 8: Distribution of drops sizes of FAME–glycerol synthetic mixture measurement from retentate flow and analyzed by optical microscope (55°C), (previous results, see 3.1 section)

Pressure effect

Consistent with the F-value of B (associated with X_2), which indicates the significance of the variable in the probabilistic model (Table 5), the pressure is the least significant variable in explaining the behavior of permeate flux at different conditions recirculation flow and temperature studied. As shows Fig 9, the experimental results showed no a drastic difference between permeate fluxes values obtained using 6 psi and 30 psi of pressure in refining process. However, permeate fluxes to medium pressures (18 psi) can be slightly greater.

The slight decrease in permeate flow using 30 psi can be attributed to the first indications of membrane fouling. At high pressure is expected that the drops of glycerol in dispersed phase to achieve a greater contact area with the continuous FAME-rich phase due to reduction in size of the droplets. Thus, the boundary layer, formed by FAME on the surface of the membrane, will be reduced, also reducing the FAME permeation.

This pressure effect on the permeation of emulsions has been discussed by Wang et al., (2000), they reported a permeate flux decrease associated to a less oil retention rate for pressures higher than 2.0 bar (29 psi) for the ultrafiltration of oil/water emulsions, indicating the oil permeation through the membrane of 0.2 µm. On the other hand, Gomes et al., 2010 concluded that a higher pressure may force the permeation of glycerol through the membrane pores, reducing the filtration area because of pore blocking and thus reducing the permeate flux. Thus, is possible conclude that using high pressure can not only decrease the permeate flux but also affect the quality of permeate rich in FAME.
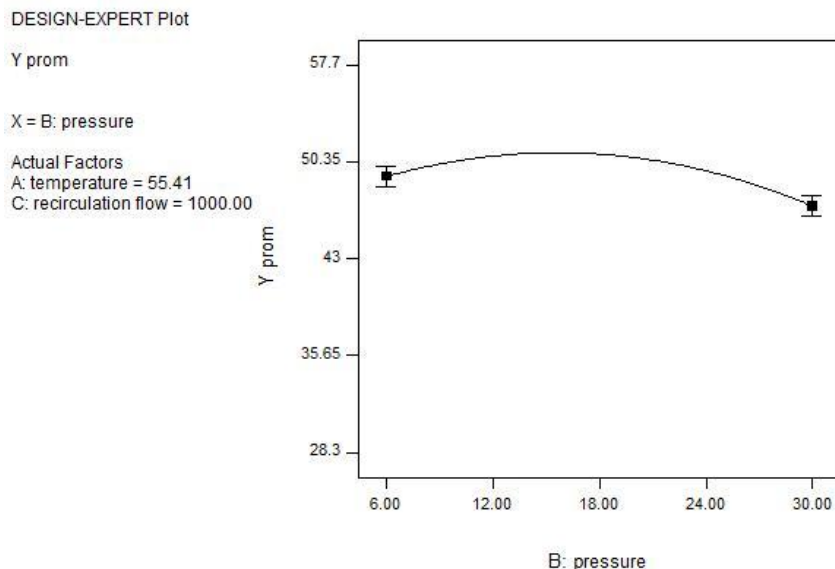
Figure 9: variation of permeate flux at different pressure studied according to experimental design based in SRM.

Recirculation flow effect

Consistent with the F-value of C (associated to X_3), which indicates the significance of C in the probabilistic model (Table 5), the recirculation flow is the second most significant variable in the explanation of permeate flux behavior at different temperature and pressure conditions studied.

In Figs. 5 and 6, was analyze the interaction between the recirculation flow versus pressure and temperature variables, respectively, and their effect on permeate flux. As Figures 5 and 6 show, the permeate flows increased with increasing recirculation flow in all cases. A more pronounced effect can be seen in the interaction of pressure with temperature for the reasons mentioned above.

Is possible to assume that the increase of permeate flux this favors a rheological condition which allows to maintain a uniform size glycerol as the disperse phase, avoiding the agglomeration of glycerol on the surface and keeping the boundary layer of FAME as continuous phase.

3.5 Conclusions

The behavior study of the different components involved in the transesterification by the phase equilibrium diagrams (LLE) leads to a better understanding of the separation process for the biodiesel blend. In the membrane refining context at 24°C, the TG in mixture with methanol and TG can be removed if methanol is greater than 12 wt.%, TG is greater than 15 wt.%, and FAME is less than 73 wt.% . On the other hand, for TG in mixture with glycerol and methanol, TG can be removed by a membrane process if it is greater than 51 wt.%, glycerol is greater than 35 wt.%, and methanol is less than 14 wt.%. Therefore, an operation mode of membrane refining according must be proposed.

The permeate flux behavior during refining of a FAME/glycerol mixture, is influenced by variables: temperature, pressure and recirculation flow. The most significant variable in permeate flux behavior within the operating range studied, was the temperature, followed by the recirculation flow and finally, the pressure. At higher temperatures ($\geq$60 °C) and recirculation flows ($\geq$1200 mL/min) results in higher permeate fluxes. On the other hand, higher permeate fluxes are obtained at pressures under 18 psi.

According to probabilistic model studied, the best refining performance measurement by permeate flux of a non-reactive synthetic blend of FAME/glycerol (80/20 w.%) was obtained using a temperature of 60 °C, recirculation flow of 1200 mL/min and a pressure of 6 psi, where was possible obtain permeate flux of 58 L/(m^2*h). However, the TG effect in mixture was no included in this experimentation.

3.6 Acknowledgments

3.7 References

1. Atadashi, I.M.; Aroua, M.K. & Abdul Aziz, A. (2010) Biodiesel separation and purification:A review. *Renewable Energy*. 36, 437- 443
2. Berchmans H.J., Hirata S., (2008). Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids, Bioresource Technology 99, 1716-1721.
3. Cheng L., Cheng Y., Yen S., Chen J. (2009) Ultrafiltration of triGlycerolceride from biodiesel using the phase diagram of oil–FAME–Methanol, *R&D* Center for Membrane Technology and Department of Chemical Engineering, Chung-Yuan Christian University, 330 (2007), 156–165.
4. Dubé M.A., Tremblay A.Y. & Liu J. Biodiesel production using a membrane reactor. Bioresource Technology 98 (2007), 639-647.
5. Freedman B., Butterfield R., and Pryde E., (1986). Transesterification kinetics of soybean oil, J. Am. Oil Chem. Soc. 63, 1375-1380.
6. Georgogianni K.G., Katsoulidis A.K., Pomonis P.J., Manos G. and Kontominas M.G., (2009). **T**ransesterification of rapeseed oil for the production of biodiesel using homogeneous and heterogeneous catalysis. Fuel Processing Technology 90, 1016-1022
7. Gomes M.C.S., Pereira N.C., Davantel de Barros S.T., (2010) Separation of biodiesel and glycerol using ceramic membranes, J. Membr. Sci. 352, 271-276.
8. Hama S., Tamalampudi S., Fukumizu T., Miura K., Yamaji H., Kondo A. & Fukuda H. Lipase localization in Rhizopus oryzae cells immobilized within biomass support particles for use as whole-cell biocatalysts in biodiesel-fuel production. Journal of Bioscience and Bioengineering 101(2006) 328–333.

9. Hammond GP, Kallu S, McManus MC., (2008). Development of biofuels for the UK automotive market. Appl Energy 85:506–15.
10. Hoekman SK. (2008). Biofuels in the U.S. Challenges and opportunities. Renew Energy 34. 14–22.
11. Liu Y. and Wang L., (2009). Biodiesel production from rapeseed deodorizer distillate in a packed column reactor. Chemical Engineering and Processing 48, 1152-1156.
12. Monni S, Raes F., (2008). Multilevel climate policy: the case of the European Union, Finland and Helsinki. Environ Sci Policy 11,743–55.
13. Sawyer RF., (2009). Science based policy for addressing energy and environmental problems Proc Combust Inst 45–56.
14. Van Gerpen J, Shanks B., Pruszko R., Clements D., Knothe G. Biodiesel Production Technology. National Midwest Research Institute, first ed., Renewable Energy Laboratory, Colorado (2004).
15. Veljkovic V.B., Lakicevic S.H., Stamenkovic O.S., Todorovic Z.B., Lazic M.L., (2006). Biodiesel production from tobacco (Nicotiana tabacum L.) seed oil with a high content of free fatty acids, Fuel 85, 2671-2675.
16. Wang Y., Wang X., Liu Y., Ou , S., Tan Y., Tang S., (2009). Refining of biodiesel by ceramic membrane separation. Fuel Processing Technology 90, 422-427.
17. Wang P., Xu N., Shi J., A piloty study of the treatment of waste rolling emulsion using zirconia microfiltration membranes, Journal of Membrane Science 173 (2000) 159–166.
18. Yilmaz G., Jongboom R.O.J., van Soest J.J.G., Feil H., Effect of glycerol on themorphology of starch-sunflower oil composites, Carbohydrate Polymers 38 (1999) 33-39.
19. Zhang Y., Dubé M., McLean D. & Kates M. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresource Technology 90 (2003), 229–240.

UNIVERSIDAD DE LA FRONTERA

PROGRAMA DE DOCTORADO Y MAGÍSTER EN CIENCIAS DE RECURSOS NATURALES

Title of the thesis

STUDY OF BIODIESEL PRODUCTION BY MEANS OF A CONTINUOUS SEPARATION SYSTEM BY CERAMIC MEMBRANES.

Chapter IV

Title

Novel sequential batch membrane reactor to increase fatty acid methyl esters quality at low methanol to oil molar ratio

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ADVISOR THESIS: RODRIGO NAVIA DIEZ

Abstract

This work improved the fatty acid methyl esters (FAME) quality produced using a stoichiometric methanol to oil molar ratio, removing monoglycerides (MG), diglycerides (DG) and glycerol by using a ceramic membrane. This work improved the conventional biodiesel batch reactor (CBR) performance, adding a refining stage using a ceramic membrane according to two different operational strategies: a batch reactor membrane system (CBR-MS) and a sequential batch membrane reactor (SBMR). The SBMR strategy showed the best results with an 87 wt. % FAME conversion yield and a 99.9 % glycerol removal efficiency. SBMR was based on the operation of consecutives cycles of charge, transesterification, and discharge of permeate by operating the membrane only when a 70% FAME conversion was reached. This allowed both to work with a low viscosity product, increasing the permeate flux during the filtration process, and to diminish MG and DG content in the permeate. The application of the SBMR strategy improved a 34% the FAME content in the final product, in comparison to the CBR and 13% in comparison to CBR-MS. In addition, MG content was reduced a 79% in the final product in comparison to the CBR and a 20% compared to the CBR-MS. Finally, the DG content was reduced a 78% in comparison to the CBR and a 50% compared to the CBR-MS system when applying the SBMR strategy. It is proposed that the biodiesel successful separation-refining performance depends on the evolution of the emulsion during transesterification, as the ceramic membrane cannot remove MG and DG, but using the adequate strategy, their removal is possible from the biofuel stream.

Keywords: biodiesel (FAME), sequential refining, membrane reactor, alkaline transesterification, glycerides.

Abbreviations

ASTM: American Society for Testing and Materials

CBR: Conventional Batch Reactor

CBR-MS: Conventional Batch Reactor coupled to Membrane System

DG: Diglycerides

FAME: Fatty Acid Methyl Esters

FAEE: Fatty Alkyl Ethyl Ester

FFA: Free Fatty Acids

GC-FID: Gas Chromatography with Flame Ionization Detection

HRT: Hydraulic Retention Time

MG: Monoglycerides

SBMR: Sequential Batch Membrane Reactor

TG: Triglycerides

WFO: Waste Frying Oils
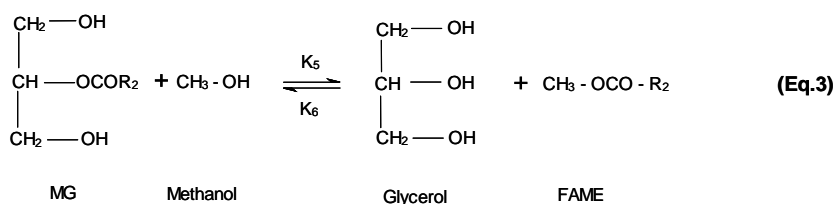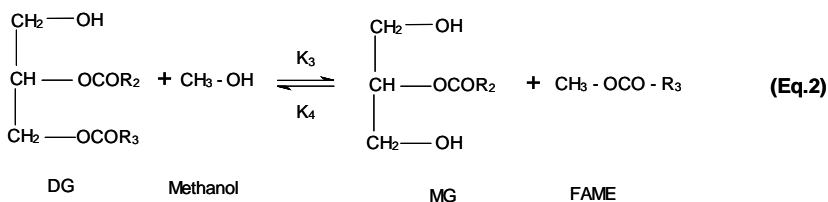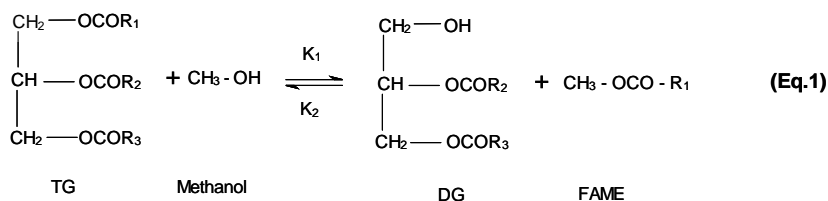
4.1. Introduction

Increasing attention has been focused on biodiesel (fatty acid methyl esters, FAME) separation and refining process, because a highly purified biofuel is necessary to achieve the stringent ASTM-D-6751 and EN-14214 quality standards for FAME production [1]. Compounds such as water, free fatty acids (FFA), and free and bound glycerin (mono-, di-, and triglyceride molecules), must be kept to a minimum level, while the purity of the biofuel (FAME) must exceed 96% [2-6]. High total glycerin content in FAME is associated with injector and valves fouling in motors, reduction of useful engines life by corrosion, and hydrolysis of monoglycerides (MG) and diglycerides (DG) in tank storage. Furthermore, the combustion of these components can lead to the formation of acrolein, a constituent part of photochemical smog [7, 8].

Alkaline-transesterification in batch reactors has been the most used strategy in FAME production [9]. Transesterification is a stepwise reaction described by Equations 1, 2 and 3. Reaction stoichiometry requires 3 mol of alcohol and 1 mol of triglyceride (TG) to form 3 mol of FAME and 1 mol of glycerol. However, due to the reversible character of the transesterification reaction and batch configuration, excess alcohol is normally used to increase TG conversion by shifting the reactions balance to products formation [9]. During alkaline transesterification for FAME production, water and FFA presence, characteristic in alternative raw materials such as waste frying oils (WFO), microalgae oils and jatropha oil, are responsible for undesirable saponification reactions and catalyst consumption in parallel reactions [6, 10].

After transesterification, usually glycerol is separated by conventional sedimentation from biodiesel. However, emulsions and soap presence decreases separation efficiency [11, 12]. This process is normally followed by a FAME washing step to remove free glycerol, soap, alcohol excess and residual catalyst. In this step, large water volumes are used, generating a wastewater stream that must be treated [13, 14].

Membrane separation technology is largely used in oil emulsions processing; however, its application in FAME purification processes is still under development [15].

$$CH_2-OCOR_1 \qquad\qquad CH_2-OH$$
$$| \qquad\qquad\qquad\qquad\qquad |$$
$$CH-OCOR_2 \; + \; CH_3\text{-}OH \; \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \; CH-OCOR_2 \; + \; CH_3\text{-}OCO\text{-}R_1 \qquad \textbf{(Eq.1)}$$
$$| \qquad\qquad\qquad\qquad\qquad |$$
$$CH_2-OCOR_3 \qquad\qquad CH_2-OCOR_3$$

TG   Methanol   DG   FAME

$$CH_2-OH \qquad\qquad\qquad CH_2-OH$$
$$| \qquad\qquad\qquad\qquad\qquad |$$
$$CH-OCOR_2 \; + \; CH_3\text{-}OH \; \underset{K_4}{\overset{K_3}{\rightleftharpoons}} \; CH-OCOR_2 \; + \; CH_3\text{-}OCO\text{-}R_3 \qquad \textbf{(Eq.2)}$$
$$| \qquad\qquad\qquad\qquad\qquad |$$
$$CH_2-OCOR_3 \qquad\qquad CH_2-OH$$

DG   Methanol   MG   FAME

$$CH_2-OH \qquad\qquad\qquad CH_2-OH$$
$$| \qquad\qquad\qquad\qquad\qquad |$$
$$CH-OCOR_2 \; + \; CH_3\text{-}OH \; \underset{K_6}{\overset{K_5}{\rightleftharpoons}} \; CH-OH \; + \; CH_3\text{-}OCO\text{-}R_2 \qquad \textbf{(Eq.3)}$$
$$| \qquad\qquad\qquad\qquad\qquad |$$
$$CH_2-OH \qquad\qquad\qquad CH_2-OH$$

MG   Methanol   Glycerol   FAME

Research regarding the use of membranes in oil refining has been mainly focused on the removal of phospholipids by micelle-enhanced ultrafiltration technique (degumming) in which surfactants are used to adsorb undesirable components, thus forming large and complex aggregates of about 20 kDa molecular mass [16, 17]. Recently, membrane technologies have shown several advantages compared to the conventional separation and purification process in FAME production, since no additional devises are necessary to separate glycerol (settler), reducing the operation time [8, 18, 19]. According to Wang et al. [19], the separation principle is related to the immiscibility of free glycerol and FAME, where free glycerol forms droplets joining to the hydrophilic ends of the soap. These droplets can be separated from FAME by size exclusion using membranes.

According to their resistance to chemical attack and thermal stability, inorganic ceramic membranes have received broad interest in FAME production by transesterification [7, 8, 19]. However, the experience of using ceramic membranes to refine FAME has been mainly related to the use of synthetic emulsions and high methanol to oil molar ratio. Moreover, there is no information about the different configurations or operational strategies for membrane modules to improve the separation and refining efficiency for FAME production. Therefore, the aim of this work was to evaluate the application of microfiltration by means of a ceramic membrane to reduce the presence of intermediary

products (MG and DG) and glycerol during an alkaline-transesterification performed at low methanol to oil molar ratio. In addition, two different membrane reactor operational strategies were explored to further improve FAME refining efficiency.

4.2. Materials and methods

4.2.1 Materials

Crude canola oil was obtained by mechanical seed processing by ENERGROW INC. (Newton, ON, Canada). The moisture content of Canola oil was 0.2 wt.%. The acid value and FFA content were 0.83 ± 0.04 mg KOH/g and 0.42 ± 0.02 wt.%, respectively. The acid value was quantified by titration with KOH using phenolphthalein as an indicator according to the method described by ASTM D-974 [20]. FFA value was determined according to the acidity values and oleic acid was used as reference [21]. Methanol (99.9% purity), and sodium hydroxide anhydrous pellets from Fisher Scientific Co. (Nepean, ON, Canada) were used as acyl acceptor and catalyst, respectively. Methyl heptadecanoate (Cat. N° 51633), 1,2,3-butanetriol (Cat. N° AMS000454), 1,2,3-tricaprinoylglycerol (Cat. N° T7517) from Sigma-Aldrich Co. were used as internal standards and were chromatographically pure. In addition, monolein (Cat. N° 44893-U), diolein (Cat. N° 44894-U), triolein (Cat. N° 44895-U), glycerin (Cat. N° 44892-U), N-methyl-N-(trimethylsilyl) trifluoroacetamide (Cat. N° 394866) and pyridine (Cat. N° 270407) were used in gas chromatography and obtained from Sigma-Aldrich Co.

4.2.2 Analytical procedures

Detection and quantification of diglycerides (DG), monoglycerides (MG), FAME and glycerol was carried out by gas chromatography in accordance with ASTM 6584 [22]. A GC-FID Shimazdu Model 2014 with a DB-5ht column of (5% phenyl) methylpolysiloxane (Chromatographic Specialties Inc. Canada) with a thickness of 0.5 μm and an internal diameter of 0.32 mm was used. The following temperature program was used for the GC-FID: 15°C for 1 min and three consecutive ramps of 15°C/min to 180°C, 7°C/min to 230°C and 380°C for 15 min. The detector temperature was 380°C. Quantification of FAME, glycerol, DG and MG was performed in the FAME-rich non-polar phase and in the glycerol-rich polar phase.

4.2.3 Operational strategies for FAME production in a membrane reactor

To diminish the presence of intermediary products and glycerol during the transesterification of TG, two different refining strategies by using a ceramic membrane for FAME production were applied as described below.

4.2.3.1 Conventional batch reactor (CBR) for FAME production

The most used industrial configuration for FAME production, i.e. the conventional batch reactor (CBR), was studied as control. The CBR consisted of a closed Erlenmeyer flask of 125 mL. CBR operational conditions are summarized in Table 1. NaOH was dissolved in methanol and added to the reactor with oil, previously conditioned at 55 ± 2 °C to obtain a 3:1 methanol to oil molar ratio. Transesterification reaction was then performed in an orbital incubator shaker.

Samples of 100 µL were taken using a micro-pipette every 0.08 h and then analyzed by GC-FID to quantify FAME, MG, and DG content in the FAME-rich non-polar phase, while glycerol content was determined in the glycerol-rich polar phase. All batch assays were performed in duplicate. All samples were previously centrifuged at 5000 rpm for 5 min to simulate a sedimentation process.
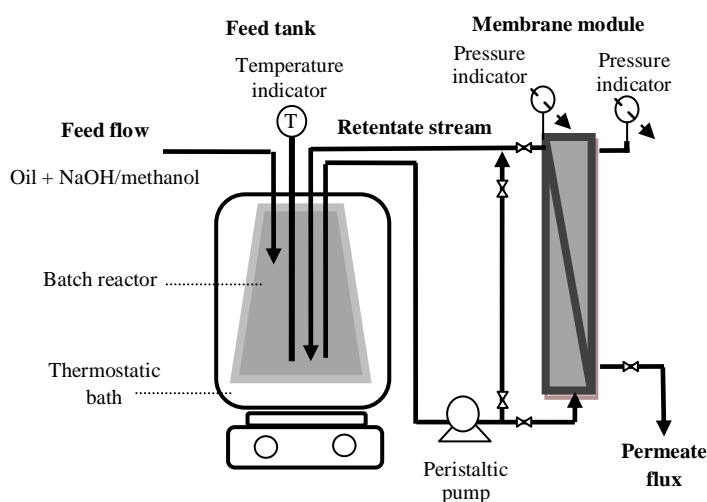

Figure 1: Configuration of the transesterification reaction tank coupled to a membrane module used for CBR-MS and SBMR strategies.

4.2.3.2 Conventional batch reactor coupled with a membrane system (CBR-MS) strategy

To improve both FAME quality (including glycerol, mono and di-glycerides removal) and CBR performance, a ceramic membrane separation and purification process was used. The refining process consisted of a CBR coupled with a membrane system (CBR-MS). One single refining stage was applied during FAME production process. The operational conditions of the CBR-MS system are summarized in Table 1 and a scheme of the reactor is illustrated in Fig. 1. Alkaline transesterification process was performed in a recirculation system consisting of a multichannel ceramic membrane (Ceramfil CMF-19033 Jiangsu, China) packed in a stainless steel module. The ceramic membrane used in this study was made of Alumina/Zirconia with a pore size of 0.1 µm and an effective surface area of 0.09 m^2. The trans-membrane pressure in the module was checked by two manometers, one on permeate side and another one on the retentate side. The pressure was selected according to the pressure capacity of the peristaltic pump and the permeate flow obtained in previous filtration experiments of synthetic mixtures of glycerol (30 wt.%) and biodiesel (70 wt.%). The temperature in the reactor was controlled by a thermostatic oil bath (Fig. 1). A reflux condenser on the reactor was used to control the evaporation of methanol and a thermometer was used to check the internal temperature. Temperature and pressure were maintained at 55 ± 2 °C and 6 psi, respectively. The reaction medium was recirculated using a peristaltic pump (Masterflex L/S model 900-1255) operated at 31 L/h. This same pump was used to maintain the internal pressure. The reactor was charged in a single stage with oil and a methanol-NaOH solution previously conditioned at 55 ± 2 °C. To quantify FAME, glycerol, MG and DG, a set of samples from retentate and permeate were taken during the reaction and analyzed by GC methods. The permeate flux was calculated considering the effective surface area (0.09 m^2) of membrane and measured manually every 4.8 min (0.08 h) using a 50 mL graduated cylinder and a stopwatch.

To evaluate the emulsion change during the reaction, three binary synthetic mixtures of TG-methanol (70-30 wt.%), FAME-glycerol (70-30 wt.%), and FAME-TG (60-40 wt.%), were recirculated in the setup (Fig. 1) at the same conditions used in the CBR-MS system (Table 1). Three samples of retentate flow (of approximately 2 µL) of each synthetic mixture were taken from a stopcock made of silicon tubing. The emulsion samples were

directly put in the microscope slide and immediately analyzed by an electronic microscope (Olympus CX31) with the objective lenses previously focused. To obtain the diameter of the drops of the dispersed phase, some representative images obtained by the microscope were analyzed by the software Micrometrics SE 2.8

4.2.3.3 Sequential batch membrane reactor (SBMR) strategy

An innovative semi-continuous reactor strategy was developed to decrease the presence of intermediary products based on the application of a ceramic membrane refining stage (SBMR). To achieve this purpose, the refining stage was operated only when at least 70 % of FAME content was measured in the reactor. The strategy consisted of three consecutive transesterification reactions coupled with a separation-refining stage by using the ceramic membrane. Thus, 3 cycles of transesterification-refining were performed. In each cycle, the reactor was first charged with oil and the methanol-NaOH solution. Each transesterification process performed during 0.5 h, according to the results obtained in the CBR-MS process. Once a 70% of FAME formation was achieved, a pressure gradient of 6 psi was applied to separate the FAME rich-phase. Each refining stage was stopped when a significant increase in pressure and a decrease in permeate flow was observed. Thus, it was assumed that the FAME rich-phase permeation was completed leaving only the glycerol rich-phase in the reactor as retentate. Subsequently, the reactor was loaded again with a new charge of oil and methanol-NaOH solution to complete the next transesterification process until completing 3 cycles. The permeate flux was measured manually every 1.8 min. (0.03 h) during each refining step using a 50 mL graduated cylinder and a stopwatch. Permeate samples of 100 μL were taken every 1.8 min (0.03 h) to quantify FAME, MG, DG and glycerol. Retentate samples of 100 μL were taken every 3 min (0.05 h) with the same goal.

4.2.4   FAME yield for the CBR, CBR-MS and SBMR strategies

To compare FAME yield, a mass balance was performed for CBR, CBR-MS, and SBMR strategies according to the reaction model described by Eq. 1 to 3. The total weight of the FAME-rich and glycerol-rich phases was measured at the end of each experiment also determining FAME, DG, MG and glycerol content. The purity of crude FAME was defined as the percentage of FAME in permeate (M_{FAME}), and the yield was defined as the

percentage of FAME obtained per mass of canola oil used. The yield for each system was defined according to Eq. 4.

$$Yield: \frac{M_B * M_{FAME}}{M_o} \qquad \text{(Eq. 4)}$$

Where:

$Yield$: Mass of FAME produced per mass of Canola oil used by each strategy (kg/kg)

M_{FAME}: Mass of FAME per mass of non polar biodiesel-rich phase obtained (kg/kg)

M_B: Mass of non polar biodiesel-rich phase (permeate for membrane strategies) obtained per mass of raw material used (kg/kg)

M_o: Mass of canola oil per kg of total raw material used (oil plus methanol) (kg/kg)

Table 1: Operational conditions and FAME yields for CBR, CBR-MS, and SBMR strategies.

Parameter	CBR	CBR-MS strategy	SBMR strategy
Reactor			
Total volume (L)	0.125	1.48	1.48
Useful volume (L)	0.023	0.970	0.970
Temperature (°C)	55 ± 2	55 ± 2	55 ± 2
Stirring rate (rpm)	200	-	-
Transmembrane pressure (psi)	-	6	6
Recirculation flow (L/h)	-	31	31
Transesterification stages (number)	1	1	3
Refining stages (number)	no	1	3
Refining stage duration (h)	0	0.65	0.15 *
Transesterification			
NaOH (wt. %)	1	1	1
Oil/methanol ratio (mol/mol)	1:3	1:3	1:3
Reaction time (h)	0.55	0.65	1.85
Coefficient			
M_B **	0.73	0.75	0.76
M_o **	0.9	0.9	0.9
M_{FAME} **	0.59	0.70	0.79
Yield (kg FAME/kg oil)	0.48	0.59	0.66

(*): Each refining stage

(**): Coefficient of Eq. (4)

4.3. Results and discussion

To evaluate the effect of two different separation-refining strategies by a ceramic membrane on FAME quality produced at low methanol to oil molar ratio, CBR-MS and SBMR strategies were compared with the conventional batch reactor (CBR).

4.3.1. Conventional batch reactor (CBR) for FAME production

Fig. 2A shows FAME production during transesterification for the CBR, reaching a 60 % of FAME at 0.2 h approximately. After 0.3 h, FAME content did not show any variation, indicating that methanol was a limiting reactant (Fig. 2A). The low FAME conversion was probably caused by the low methanol to oil ratio. Normally a 100 % excess methanol is needed to achieve higher TG conversions to FAME [8]. In fact, Meher et al., [23] found an optimal methanol to oil molar ratio of 9:1 and Liu et al. [24] reported an optimal methanol to oil molar ratio up to 12:1 for alkaline transesterification using vegetable oils in a batch reactor. Fig. 2A shows the evolution of MG, DG and glycerol measured in samples of the biodiesel-rich phase. MG content varied between 3 and 5 wt.%, while DG increased during the reaction from 3 to 8 wt.%. DG and MG accumulation in the biodiesel-rich phase indicates a low CBR efficiency to transform the intermediary products into FAME. Glycerol content in the non-polar FAME-rich phase was always lower than 0.49 wt.%. However, even applying centrifugation (simulating a sedimentation stage to remove glycerol), MG and DG content exceeded the maximum allowed for B-100 biodiesel requirements (0.8 and 0.2 wt.% for MG and DG, respectively) [25]. These results indicate that separation and refining stages for CBR process are necessary to remove of DG, MG and simultaneously separate glycerol from FAME. Therefore, the separation by a membrane system could allow the retention of the intermediary products and glycerol, improving FAME quality.
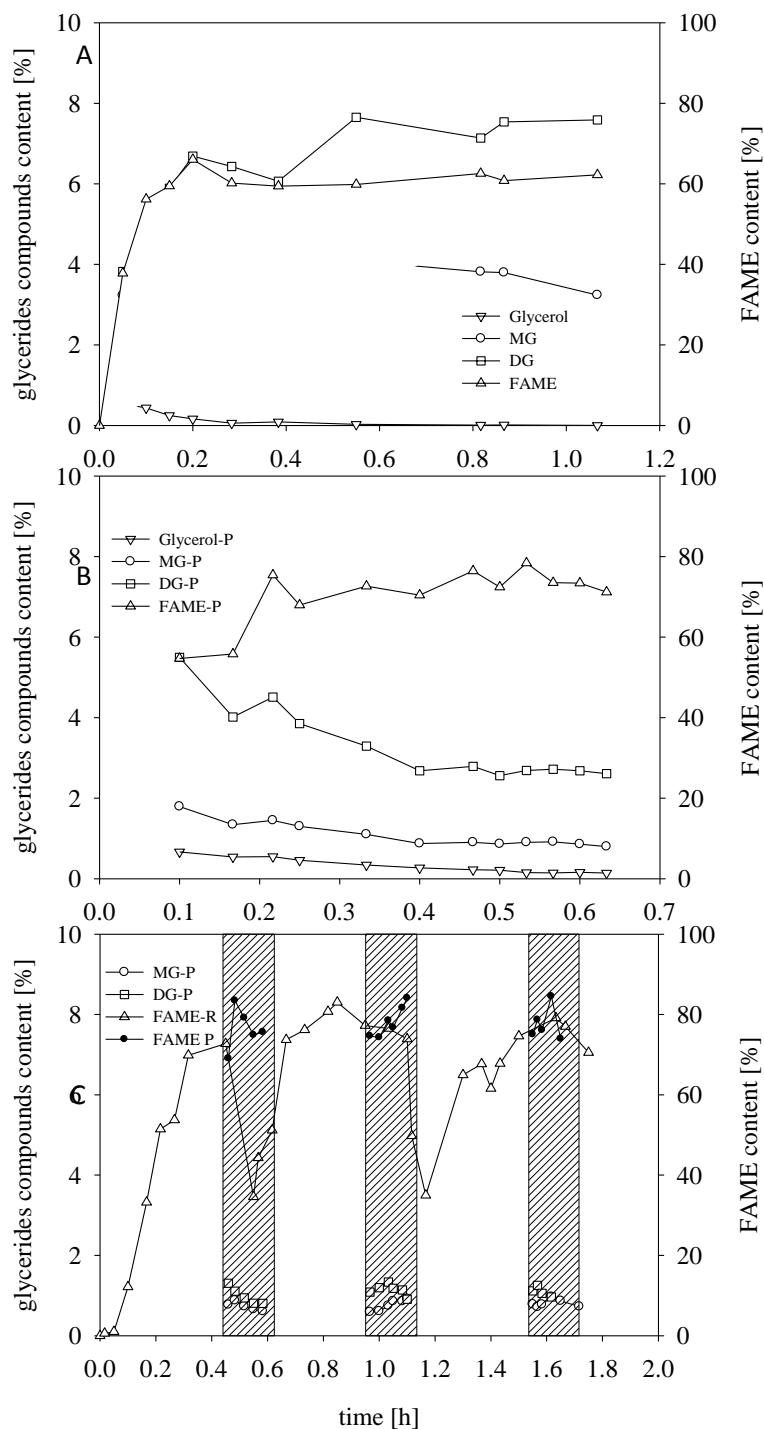
Figure 2: (A) DG, MG, FAME and glycerol kinetics measured in the non-polar biodiesel-rich phase during transesterification by CBR strategy. (B) DG, MG, FAME and Glycerol kinetics measured in the permeate stream (DG-P, MG-P, FAME-P, and Glycerol-P) during transesterification by CBR-MS strategy. (C) DG, MG, FAME content in permeate (DG-P, MG-P, FAME-P) and FAME content in retentate (FAME-R) obtained by SBMR strategy. Hatched bars indicate the application of the refining stages.

4.3.2. Conventional batch reactor coupled with a membrane system (CBR-MS) strategy

To improve the removal of intermediary products and glycerol from FAME, a continuous single refining stage was coupled to the CBR. As a result, a single phase of FAME without precipitate was obtained as permeate product. Fig. 2B shows FAME, DG, MG and glycerol content in permeate for the CBR-MS. FAME content reached 78 wt.% after 0.2 h (12 min). Low FAME content was detected in the permeate at the beginning of the transesterification, indicating that CBR-MS strategy not only favored the passage of FAME through the membrane, but also that of intermediate products and TG. In fact, in Fig. 2B DG and MG concentrations showed higher values in the permeate during the first 0.4 hours (24 min). At the beginning of the reaction, DG showed concentrations close to 6 wt.%. Then, a consumption of DG was observed during the first 0.5 hours (30 min). In the case of the retentate a maximum of 78.4 wt.% FAME was detected at 32 min (0.53 h). The concentration of MG was less than 1 wt.%, while DG concentrations ranged between 3 and 6.5 wt.% and for glycerol less than 0.2 wt.%. DG values showed more variation in comparison to MG. According to the DG kinetic model proposed by Noureddin and Zhu [26], this behavior was expected as the kinetic of DG conversion at 50 °C depends on K_1 (0.05 mol/min), K_2 (0.11 mol/min), K_3 (0.215 mol/min) and K_4 (1.228 mol/min), being K_4 much higher than K_1, K_2, and K_3 (see Eq. 1 to 3). Therefore, the accumulation of DG is explained by this fact. After 0.5 h MG and DG content tend to stabilize in the CBR-MS.

Fig. 3 shows the permeate flux obtained at 6 psi for the CBR-MS. The permeate flux increased continuously during the process. The flux through the membrane is function of the trans-membrane pressure and is inversely correlated with the permeate viscosity [27]. Therefore, the flux increment shows the progress of the transesterification reaction and consequently the viscosity reduction caused by TG transformation into FAME.

At the beginning of the transesterification, methanol droplets are dispersed in the vegetable oil phase (Fig. 4A). However, during the reaction progress the emulsion changes to glycerol droplets dispersed in a continuous FAME phase (Fig. 4B). As FAME and TG are miscible and form one single phase (Fig. 4C), for an efficient separation-refining of FAME the formation of an emulsion or agglomerates between glycerol and less polar components as non reactive TG, DG and MG are necessary. Therefore, a sequential strategy that includes a

FAME refining stage applied in a specific time of maximum concentration could improve FAME separation and quality. It is possible to increase the retention yield and consequently the recycle of the polar glycerol rich phase (retentate) for a new feedstock charge. Thus, a new sequential batch process including several separation-refining stages operated at high FAME content and once the maximum consumption of DG and MG is achieved was proposed.
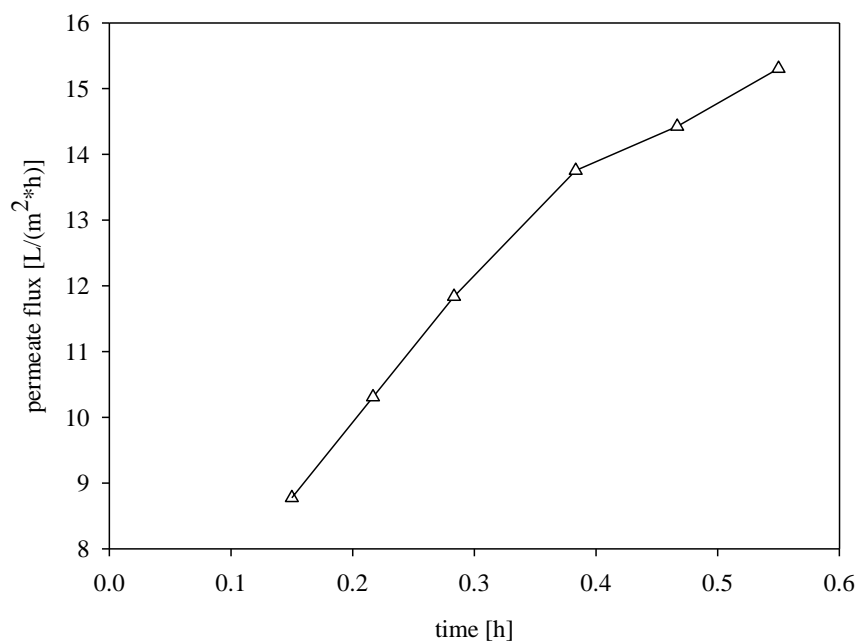

Figure 3: Permeate flux measured in the output stream during transesterification in the CBR-MS system
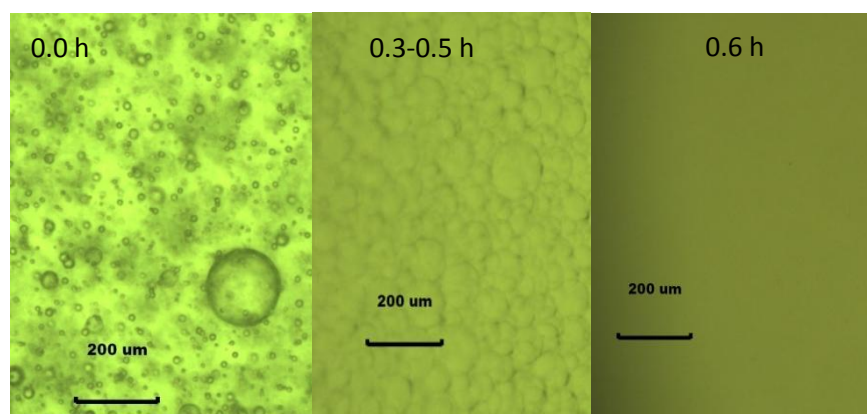

Figure 4: Emulsion dynamics during transesterification reaction A) TG-methanol (70-30 wt.%) emulsion, B) FAME-glycerol (70-30 wt.%) emulsion, and C) FAME-TG (60-40 wt.%) blend.

4.3.3. Sequential batch membrane reactor (SBMR) with refining stages strategy

The results obtained by CBR-MS strategy demonstrated that it was possible to improve the CBR product quality. However, the refining process should be operated only in the presence of a multi-component emulsion formed by non reactive-methanol, glycerides (TG, MG, DG and glycerol), and FAME, being FAME the continuous phase. For the SBMR experiment, the refining stage was applied when at least 70 % of FAME content was reached. The application of the SBMR strategy resulted in a single FAME phase as permeate, and two phases as retentate. The phases in the retentate were classified as up-polar and low-polar phase, respectively. The evolution of the FAME content in permeate and retentate flows are shown in Fig. 2C. A maximum concentration of 87 wt.% at 1.9 h was obtained for FAME in the permeate. Glycerol concentrations were always below 0.017 wt.% in permeate. In fact, the glycerol level observed in the permeate was according to B-100 biodiesel requirements [22]. This result confirmed that by using the SBMR strategy the retention of up to 99.9 % of glycerol was possible.

Fig. 2C shows the evolution for MG and DG in permeate during the SBMR operation. Low concentrations were detected for MG (< 1.4 wt.%) and DG (< 0.5 wt.%). However, the detected concentrations of MG and DG in retentate were below 0.5 wt.%, indicating that MG and DG are miscible with FAME and pass across the membrane. Similar behavior for DG was observed in a previous work by Cao et al. [7]. They attribute the DG presence to a high FAME content in the retentate and consequently in the permeate flux. Therefore, high FAME concentrations in retentate favor DG solubility in non-polar biodiesel-rich phase, explaining its presence in permeate flux. Cao et al. [7] concluded that a decrease in hydraulic retention time (HRT) and decreasing the concentration of catalyst used in the transesterification could favor the retention of DG and other impurities in retentate, but this would cause a drastic reduction in the reaction yield if the methanol to oil molar ratio used is low. According to Cao et al. [7], high methanol to oil molar ratios are necessary for both shifting the reaction equilibrium to the product side and for solubilize MG and DG in the methanol-rich or glycerol-rich polar phase. Nevertheless, higher amounts of alcohol increases the reactor size and a distillation stage is needed for recovering methanol [9]. Gomes et al. [28], using ethanol as acyl acceptor, found that the alcohol/oil molar ratio affects the membrane refining processes where an excess of alcohol results in smaller

droplets diameter of dispersed glycerol in FAEE (fatty alkyl ethyl ester), allowing its permeation through the membrane, and decreasing FAEE refining efficiency.
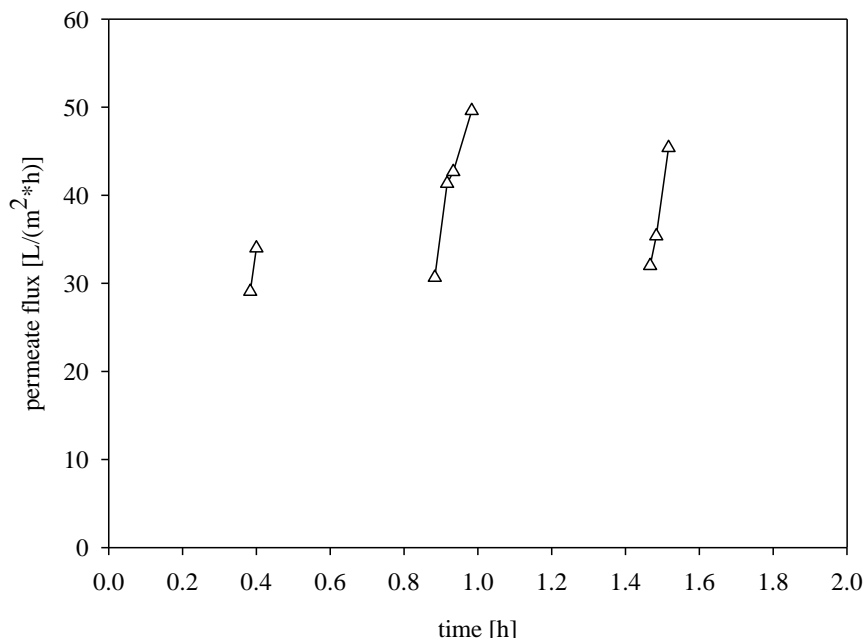

Figure 5: Permeate flux measured in the output stream during transesterification in the SBMR system.

Fig. 5 shows the permeate flux for the SBMR process at 6 psi, where the flux increased during filtration. A minimum flux of 28 L h^{-1} m^{-2} and a maximum of 50 L h^{-1} m^{-2} were measured during the operation. The low viscosity of the obtained permeate achieved after TG transesterification could decrease the effect of surface fouling in the membrane. Similar results were found by Wang et al. [19], who used a membrane of 100 nm at a temperature of 60 °C and a pressure of 7.2 psi. They obtained a permeate flux of 100 L h^{-1} m^{-2} discarding significant effects of fouling and concluded that pressure and temperature are factors influencing the permeate flux. Gomes et al. [15] observed a continuous decrease in the permeate flux using ceramic membranes of different sizes when refining a synthetic emulsion of FAEE, glycerol and ethanol. In our work, the application of a selective short time of membrane operation coupled to a continuous retentate recycling allowed us to maintain and increase the permeate flux.

An important difference between the flux measured for CBR-MS and SBMR was observed (Figs. 3 and 5). Higher permeate fluxes were measured for SBMR, because membrane

refining stages were separating the FAME rich-phase at times where its viscosity was theoretically at a minimum, while FAME conversion yield reached a maximum value. On the opposite, when using the CBR-MS system, a single stage under a constant trans-membrane pressure gradient promoted the transfer of the more viscous fraction at the beginning of the transesterification reaction. These results suggest that the SBMR strategy could diminish fouling and the cleaning stages of the membrane.

4.3.4 Performance comparison between CBR and CBR-MS and SBMR strategies

The results of the CBR showed that even using a vegetable oil with a low FFA content, the FAME produced at a low methanol to oil molar ratio presented impurities that must be removed. In addition, the reversible nature of transesterification interferes gradually in the conversion of TG, MG, and DG when a low methanol to oil ratio is used. These are important aspects because the removal of free and bonded glycerin (MG, DG and TG) are considered the most difficult stage in the refining cycle and determines the quality of the final product [8]. In this sense, the phases separation achieved by CBR-MS and SBMR strategies allowed the removal of unwanted components in the non-polar biodiesel-rich phase. Fig. 6 shows the content of DG, MG, FAME and glycerol in product obtained by the different refining strategies. FAME content in CBR-MS was 11% higher compared to CBR (Fig 6A and 6B). The CBR-MS showed lower MG and DG contents compared to the traditional CBR. This confirms that applying a membrane filtration step FAME refining was possible. However, the results obtained showed the pass of MG and DG through the membrane, favored at the beginning of the reaction. Fig. 6C shows the results for SBMR. Over 80 wt.% FAME free of glycerol, with a low content of intermediary products (0.79 wt.% MG and 1.1 wt.% DG), was measured in the FAME-rich non-polar permeate phase at the end of SBMR operation. The application of the SBMR improved in a 34% the FAME content in the final product compared to the CBR and in a 13% compared to CBR-MS. Moreover, the MG content was reduced a 79% in comparison to the CBR and in a 20% compared to the CBR-MS. Finally, the DG content was reduced a 78% in comparison to the CBR and a 50% in comparison to CBR-MS using SBMR strategy.

Yields of 0.48, 0.59 and 0.66 (kg FAME/kg vegetable oil) were achieved in CBR, CBR-MS and SBMR, respectively (Table 1). The increase in FAME conversion yield for SBMR compared to CBR-MS is probably due to the effect of emulsions dinamics during the reaction. As FAME and TG are miscible (Fig 4C), the application of a membrane filtration during transesterification favors the pass of TG at the beginning, decreasing the amount of TG available to perform a complete reaction. The Table 2 shows a comparison between the mass balance of the different operational strategies based in kilogram of TG used.

According to the retentate composition, a low-polar phase with a higher content of glycerol was obtained in CBR-MS (39 wt.%) and SBMR (42 wt.%) compared to the polar phase obtained by CBR after centrifugation (22 wt.%) (Figs. 6A, 6B and 6C). Fig. 6C shows a permeate characterization for each refining stage (non-polar phases 1, 2 and 3) and retentate phases obtained (up-polar and low-polar) at the end of the SBMR experiments. According to Gomes et al., [28], the retention of un-reacted alcohol and soaps formed in retentate could increase the interface tension between biodiesel and glycerol. This condition also promotes a decrease of the solubility between the phases, allowing a glycerol drops size increment. Thus, the retention of MG and DG via polar hydroxyl groups could be increased. These particular conditions can explain the best results obtained for glycerol, MG and DG retention observed in CBR-MS and SBMR in comparison to CBR.

Table 2: Mass balance comparison between the different operational strategies

	Input (kg)	Output (kg)	
Strategy	Total raw material (kg)	FAME (kg)	Crude glycerol* (kg)
CBR	1.00	0.73	0.27
CBR-MS	1.00	0.75	0.25
SBMR	1.00	0.76	0.24

(*): Crude glycerol= Glycerol +TG+ FAME+MG+DG

The results obtained in the SBMR strategy show that a separation of immiscible phases coupled to the application of refining stages when a high FAME yield was reached is possible and appropriate. In fact, this operational strategy promoted a higher methanol use efficiency, a decrease in the presence of intermediary products and glycerol, simultaneously

avoiding the need of a settling (to separate glycerol) and washing (to remove impurities from biodiesel) stages. This last point is crucial to diminish the time of the process and operational costs. Thinking in a full-scale industrial application, glycerol should be purged after each transesterification cycle shifting the reaction to the product side.
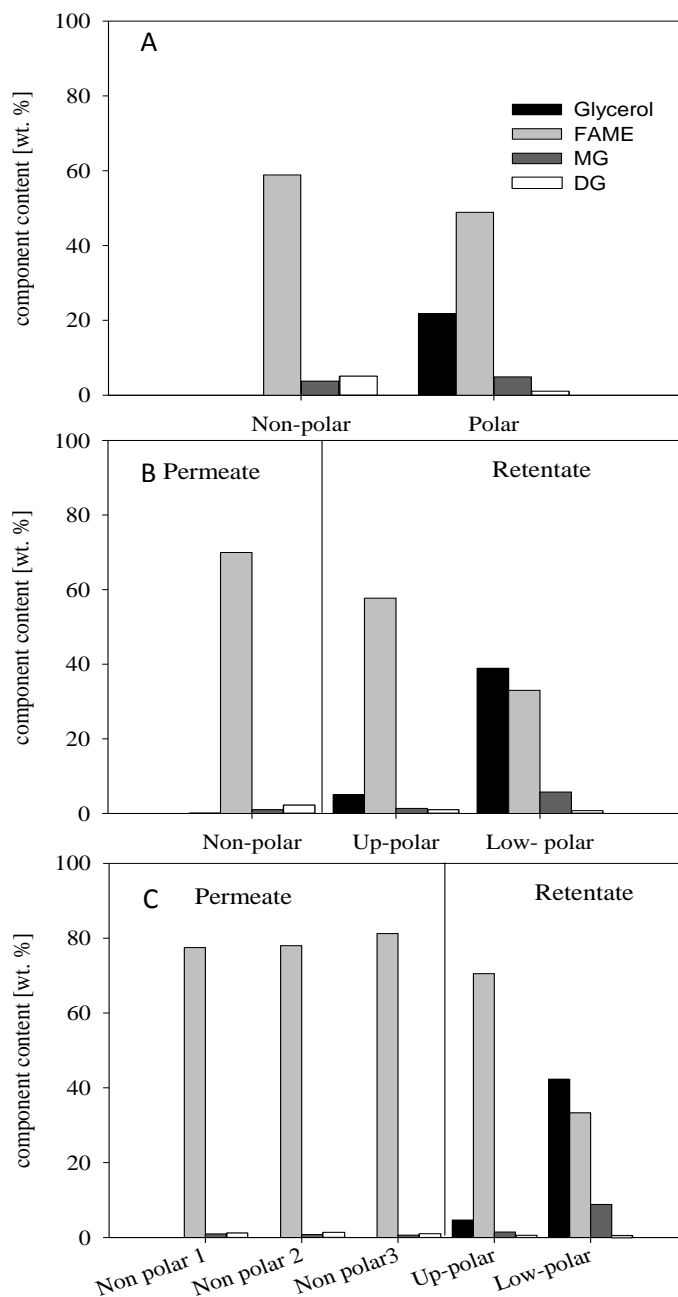

Figure 6: Glycerol, FAME, MG and DG content for the different phases obtained as final product for the (A) CBR, (B) CBR-MS, and (C) SBMR strategy.

4.4. Conclusions

A new semi-continuous strategy to produce and refine FAME at low methanol to oil molar ratio using a ceramic membrane filtration process was proposed. The sequential batch coupled with membrane rector (SBMR) strategy was based on the operation of the latter operated only when a 70% FAME conversion yield was reached. This allowed an operation with a high permeate flux, due to the low viscosity of FAME compared to vegetable oil.

The use of a stoichiometric methanol to oil molar ratio in the transesterification increases the accumulation of mono and diglycerides in a conventional batch reactor (CBR). However, this conventional batch reactor coupled to a membrane system (CBR-MS) favors the permeation of these compounds, especially at the beginning of process.

On the contrary, the SBMR removed 99% of glycerol and decreased in a 79 and 78% the presence of mono and diglycerides in FAME, respectively, compared to CBR. In this sense, the emulsion dinamics during transesterification is a crucial aspect to be considered in the implementation of a FAME separation-refining process, as the ceramic membrane is not able to remove MG and DG, but using the adequate operational strategy, the removal of these compounds was established to be possible.

Finally, a potential application of the SBMR strategy in biodiesel production could avoid the use of a sedimentation stage, simultaneously promoting a high permeate flux of FAME.

4.5. Acknowledgments

4.6. References

1. I.M. Atadashi, M.K. Aroua, A. Abdul Aziz, Biodiesel separation and purification: A review, Renewable Energy 36 (2010) 437- 443.

2. B. Freedman, R. Butterfield, E. Pryde, Transesterification kinetics of soybean oil, J. Am. Oil Chem. Soc. 63 (1986) 1375-1380.

3. V.B. Veljkovic, S.H. Lakicevic, O.S. Stamenkovic, Z.B. Todorovic, M.L. Lazic, Biodiesel production from tobacco (Nicotiana tabacum L.) seed oil with a high content of free fatty acids, Fuel 85 (2006) 2671-2675.

4.   H.J. Berchmans, S. Hirata, Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids, Bioresource Technology 99 (2008) 1716-1721.

5.   Y. Liu and L. Wang, Biodiesel production from rapeseed deodorizer distillate in a packed column reactor, Chemical Engineering and Processing 48 (2009) 1152-1156.

6.   K.G. Georgogianni, A.K. Katsoulidis, P.J. Pomonis, G. Manos, M.G. Kontominas, Transesterification of rapeseed oil for the production of biodiesel using homogeneous and heterogeneous catalysis, Fuel Processing Technology 90 (2009) 1016-1022.

7.   P. Cao, M.A. Dubé, A.Y. Tremblay, Methanol recycling in the production of biodiesel in a membrane reactor, Fuel 87 (2008) 825-833.

8.   L.H. Cheng, Y.F Cheng., S.Y Yen., J. Chen, Ultrafiltration of triglyceride from biodiesel using the phase diagram of oil–FAME–MeOH, Journal of Membrane Science 330 (2009) 156-165.

9.   Z. Qiu, L. Zhao, L. Weatherley, Process intensification technologies in continuous biodiesel production, Chemical Engineering and Processing 49 (2010) 323-330.

10. L. Azócar , G.Ciudad , H. J. Heipieper, R. Muñoz, R. Navia, Improving fatty acid methyl ester production yield in a lipase-catalyzed process using waste frying oils as feedstock. J Biosci. Bioeng. 109 (2010) 609-614.

11. Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from transesterified vegetable oils. JAOCS 61 (1984)1638-1643.

12. Ma F, Hanna MA. Biodiesel production: a review. Bioresour Technol 70 (1999)1-15.

13. Karaosmanoglu F, Cigizoglu KB, Tuter M, Ertekin S. Investigation of the refining step of biodiesel production. Energy Fuels 10 (1996) 890-895.

14. Demirbas A. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. Energy Convers Manage 44 (2003) 2093-2109.

15. M.C.S. Gomes, N.C. Pereira, S.T. Davantel de Barros, Separation of biodiesel and glycerol using ceramic membranes, J. Membr. Sci. 352 (2010) 271-276.

16. R. Subramanian, M. Nakajima, Membrane degumming of crude soybean and rapeseed oils, JAOCS 74 (1997) 971-975.

17. A.R. Majid, S.B. Badlishah, A.Fakhr'ul-Razi, C.M. Yaakob, Processing of crude palm oil with ceramic microfiltration membrane, Journal of Food Lipids 7 (2000) 113-126.

18. M.A. Dube´, A.Y. Tremblay, J. Liu, Biodiesel production using a membrane reactor, Bioresource Technology 98 (2007) 639-647.

19. Y. Wang, X. Wang, Y. Liu, S. Ou , Y. Tan, S.Tang, Refining of biodiesel by ceramic membrane separation, Fuel Processing Technology 90 (2009) 422-427.

20. ASTM-D 974. Standard test method for acid and base number by color-indication titration. ASTM International; 2000.

21. S. Zarinabadi, R. Kharrat, A.V. Yazdi,. Estimate Solubility of Canola oil (Oleic Acid) in Supercritical Carbon dioxide - Experimental and Modeling. Journal of American Science 6 (2010) 606-611.

22. ASTM-D 6584, Test method for determination of free and total glycerine in B-100 biodiesel methyl esters by gas chromatography, ASTM USA, 2000.

23. L.C.Meher, D.V.Sagar, S.N.Naik; Renewable and Sustainable Energy Reviews 10 (2006) 248 - 268

24. X. Liu, H. He, Y. Wang, S. Zhu, X. Piao, Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst, Fuel 87 (2008) 216-221.

25. EN 14214 Biodiesel standard. Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods European Standard Organization, 2003.

26. H. Noureddini, D. Zhu, Kinetics of transesterification of soybean oil, Journal of American Oil Chemists Society 74 (1997) 1457-1463.

27. S. Judd, The MBR book, first ed., Elsevier, Oxford, 2006.

28. M.C.S. Gomes, P.A. Arroyo, N.C. Pereira, Biodiesel production from degummed soybean oil and glycerol removal using ceramic membrane, J. Membr. Sci. 378 (2011) 453-461.

UNIVERSIDAD DE LA FRONTERA

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Title of the thesis

STUDY OF BIODIESEL PRODUCTION BY MEANS OF A CONTINUOUS SEPARATION SYSTEM BY CERAMIC MEMBRANES.

Chapter V

Title

General discussions

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General discussion

The works about membrane reactors applied to biodiesel production reported the presence of methanol, catalyst, glycerol and FAME in the permeate (Dubé et al. 2007; Cao et al. 2008). That mean not only products are separated from the reaction medium, but also transesterification reactants. Therefore give no reports clearly the effects of modifying the balance during a stage of transesterification/refining simultaneously. Thus, usefulness of the process of membrane has been represented by performance (conversion) as well as refining. Several authors report that no additional devises are necessary to separate glycerol (settler), reducing the operation time (Cheng et al., 2009; Dube et al., 2007; Wang et al., 2009). However, effective separation of phases (polar/non-polar) as well as saving of methanol is not reported.

The literature review shows the lack of strategies to study the dynamics of the emulsion in membrane reactors. Especially, while transesterification of reactants and product extraction is occurring at the same time. This requires experimentation with synthetic blends and narrows the results to an ideality. In this context, in the chapter III of this thesis was proposed an approach to understanding glycerides retention and FAME refining by studying the miscibility between the phases of non-reactive mixtures using phase equilibrium diagrams. The chapter III analysis provides useful information for decision making in operation of refining processes proposed in chapter IV.

The experimentation reported in Chapter III on phase diagram of FAME/TG/Methanol system demonstrated that to achieve immiscibility between TG and FAME is require a concentration in the mixture less than 73 wt.% in FAME and 10 wt. % in methanol. This result makes a critic point for get an efficient separation of FAME/TG during a transesterification reaction. Indeed was used as a criterion to propose a strategy sequential operation. Thus, a product reaction consisting in 70 wt.% of FAME, a 16 wt. % of unreacted TG and a 14 wt. % of unreacted methanol (as end of reaction) can be easily separated by forming two phase. Similar results were found by Chen et al., (2008) for FAME-TG-Methanol system at 20°C where an increase of miscibility of FAME /TG/Methanol system with increasing the amount of FAME was reported.

Usually high methanol/oil ratios have been used in membrane reactors (Cheng et al., 2010; Hamma et al., 2007; Zhang 2003; Dubé et al. 2007; Cao et al. 2008). Thus, excess methanol not only is used for ensure complete conversion of TG but also to maintain the dispersed phase droplets in retentate side and as well as a continuous phase. However, due to methanol excess used in transesterification, the solubilization of glycerides (TG, MG, DG and glycerol) in the non-polar FAME-rich phase remains a problem in the FAME membrane refining (Cheng et al., 2010; Hamma et al., 2007; Zhang 2003). In fact, the course of current thesis has shown that a membrane process is not suitable at the start of a transesterification because unreactive TG and FAME are miscible and form a single permeable phase. Therefore, methanol plays a key role as a surfactant between TG and transesterification products. Thereby, an excess of methanol can not only facilitate permeation of TG but also FAME and intermediates of the reaction. Additionally, considering the constant extraction of methanol from the reaction medium (as permeate), excess available methanol as reactant is required, not represent cost savings in the process. The chapter III and IV of this thesis

demonstrates that the excess methanol is not the only way to achieve a refinement of intermediate compounds of the transesterification.

The previous results exposed in chapter III showed that TG and FAME are miscible in any of the proportions tested. Therefore, FAME and TG completely permeated through the membrane. This showed the importance of the emulsion formation for apply the membrane separation, since when there is no emulsion formation, the membrane step can not to separate the mixture components. Considering the degree of separation of MG, DG and glycerol achieved by SBMS, this thesis demonstrated that the emulsion dynamics during reaction is a crucial aspect to be considered in the implementation of a FAME production/refining process.

In the literature reviewed, there is consensus on control parameters that govern the process. However, operational parameters for TG retention have not been reported in detail in literature. The results exposed in chapter III demonstrated that TG retention by a membrane not will be a problem if TG concentration exceeds 10 wt.% in comparison to methanol and glycerol. In fact, results reported in chapter III, showed that TG concentrations greater than 10% preferably in a polar-phase generate an emulsion. However, if TG less than to 10% in a glycerol-rich environment generate a single phase. This can permeate through the membrane, but experimentation (chapter IV) showed that glycerol-rich phase does not pass through the membrane because has a higher viscosity to the biodiesel and fluxes are significantly lower than those of biodiesel.

The permeate behavior during a transesterification/refining cycle is influenced by variables: temperature, pressure and recirculation flow. The results reported in chapter III demonstrated that most significant variable in permeate flux behavior was the temperature, followed by the recirculation flow and finally, the pressure. At higher temperatures   and recirculation flows results in higher permeate fluxes. On the other hand, higher permeate fluxes are obtained at pressures under 18 psi. However, the diagrams reported in Chapter III show some degree of solubility between immiscible phases (FAME-, and glycerol-rich), thus the permeate flow measurement as an indicator of the performance of the process without permeate composition analysis, it may be misinterpretation. In fact, some authors have associated oil and glycerol through the membrane to pressures   higher than 29 psi (Gomes et al. 2010; Wang et al. 2000)

The results obtained by the solubility diagrams (Chapter III) were useful to analyze the permeation of glycerides using different trading strategies (Chapter IV). Thus, a conventional biodiesel batch reactor (CBR), a batch reactor membrane system (CBR-MS) and a sequential batch membrane reactor (SBMR) were implemented and studied. At the beginning of the stoichiometric transesterification, methanol droplets are dispersed in the vegetable oil phase. However, during the reaction progress the emulsion changes to glycerol droplets dispersed in a continuous FAME phase. As FAME and TG are miscible and form one single and permeable phase. As expected the permeation of TG, DG, MG and glycerol was tested by a method tansesterification/refining at the same time (CBR-MS strategy). Permeation is particularly high during the first minutes of the transcesterification and then decrease over time. Thus, an innovative semi-continuous reactor strategy (SBMR) was developed to decrease the presence of intermediary products based three consecutive cycles of transesterification/refining. The goal was achieved as the results showed the concentration of FAME achievement be maintained over time by 80 wt.% FAME. A minimum flux of 28 L h^{-1} m^{-2} and a maximum of 50 L h^{-1} m^{-2} were measured during SBMR operation. Considering

that the reaction medium consists of all the species involved in the transesterification reaction, the fluxes obtained by SBMR, correlated well with the fluxes obtained for refining of FAME/glycerol mixtures (80/20 wt.%). These results suggest that the SBMR strategy could diminish fouling and the cleaning stages of the membrane.

The application of the SBMR improved in a 34% the FAME, removed 99% of glycerol, and decreased in a 79 and 78% the presence of mono and diglycerides in FAME, respectively, compared to conventional batch reactor. On the other hand the yield of the transesterification was not substantially exceeded, however the results of separation of glycerol and glycerides refining give real possibilities to SBMR method in the production of biodiesel.

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Chapter VI

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General conclusions

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General conclusions

The literature review reports the importance of this thesis work and clarifies its role not only to propose solutions to a biodiesel production process, but also to generate a proposal for mitigation of global energy needs. In recent years, research technology applied to the production of biodiesel has mainly addressed advances in mass and energy transfer. However, the reaction reversibility is still one of the non-solved gaps of these proposed technologies. Recently, the latter has been addressed through the use of membranes. Difficulties regarding the use of membrane in biodiesel production and refining are related to the retention of glycerides and maintaining a biphasic condition of the reaction medium which facilitates the continuous refining of fatty acid methyl esters (FAME). These problems are not yet solved since the separation mechanism is not entirely clear, and so the control variables of this process based on reaction/refining. Therefore the research now focuses in these aspects. However, recent reports of membrane reactors applied to biodiesel are characterized by the use of methanol excess, aspect that is critical because methanol excess increases downstream stages and process costs are not reduced.

As the ceramic membrane is not able to remove glycerides during transesterification reaction, the emulsion dynamics during reaction is a crucial aspect to be considered in the implementation of a FAME production/refining process. An approach to understanding glycerides retention and FAME refining is accomplished by studying the miscibility between the phases of non-reactive mixtures by phase equilibrium diagrams. Although the interpretation of the results is based on the ideality of non-reactive mixtures, this analysis provides an understanding of the composition evolution of the phases during transesterification. The equilibrium phase analysis provides useful results for decision making in the future operation of refining processes. In fact, miscibility analysis discussed in the second chapter of this thesis work was useful to generate operational criteria that were used in transesterification/ refining system proposed in the next chapter.

 Using theory and experimentation in a membrane refining process, a new semi-continuous strategy (SBMR) to produce/refine FAME at low methanol to oil molar ratio was proposed. The strategy was based on sequential transesterification/refining cycles, wherein the refining step operated only when a 70% FAME conversion yield was reached. This allowed an operation with a high permeate flux, because glycerol, triglycerides, and intermediates in dispersed phase form an emulsion which facilitates the permeation of FAME, which is in higher concentration. The proposed membrane reactor removed 99% of glycerol and decreased in a 79 and 78% the presence of mono- and di-glycerides in FAME rich phase, respectively, compared to a conventional batch reactor.

This thesis work provides useful information for the improvement of biodiesel production process using membrane reactors under an operational condition not studied until now. The results offer a potential application for SBMR strategy in biodiesel refining that could avoid the use of a sedimentation stage, simultaneously promoting a high permeate flux of FAME.