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Supporting Information
available online

Production of Methyl Oleate in Reactive-Separation Systems

The esterification of oleic acid and methanol using sulfuric acid as a homogeneous catalyst is studied in reactive-separation systems. The conversion of the free fatty acid was investigated in two different experiments with the molar ratio of methanol/oleic acid, amount of catalyst, temperature, and reaction time as variables. The conversion of the free fatty acid was found to depend strongly on the molar ratio of methanol/oleic acid. The reaction time had a direct effect on the conversion of the free fatty acid, and this conversion decreased with higher temperature. These results were valuable for a preliminary study on biodiesel production, using an acid homogeneous catalyst in a reactive dividing-wall distillation column.

Keywords: Biodiesel production, Esterification reaction, Methyl oleate, Reactive distillation

Received: July 23, 2015; *revised:* September 05, 2015; *accepted:* September 30, 2015

DOI: 10.1002/ceat.201500423

1 Introduction

Distillation is considered one of the most important separation techniques for multicomponent mixtures [1]. However, its main disadvantage is associated with the large amount of energy required in the reboiler to purify the mixture [2, 3]. Several approaches have been applied in order to save energy, e.g., the use of thermal links in distillation columns can provide significant energy savings [4]. The classical direct and indirect distillation sequences, i.e., two conventional distillation columns for each sequence, for the separation of a ternary mixture (ABC) can be converted to thermally coupled distillation sequences by thermal couplings.

The thermal links imply the elimination of a reboiler or a condenser by using vapor or liquid recycle streams, respectively. The resulting distillation sequences are called thermally coupled distillation sequences that can save around 30 % of energy consumption when compared with conventional distillation sequences [5] for the separation of some ternary mixtures. These energy savings have been explained in terms of the composition profiles of the distillation columns. For instance, in the composition profile of the intermediate component (B), in the first distillation column of the conventional direct distillation column, its composition increases from the feed stage to the bottom of the distillation column, reaching a maximum and diminishing as the bottom is reached [2]. This maximum in the composition profile of the intermediate component is called remixing, and causes more energy consumption in the second distillation column to repurify the intermediate component. The remixing effect is avoided in the case of the thermally coupled distillation sequence with a side rectifier.

It is important to note that the vapor side stream of the first distillation column is extracted from the stage where the composition profile of the intermediate component reaches the maximum. The side stream replaces the reboiler of the second distillation column and is introduced to the bottom of the second distillation column. Several thermally coupled distillation sequences have been proposed for multicomponent mixtures, but surely the most important is the fully thermally coupled distillation sequence or Petlyuk distillation column. The Petlyuk distillation column has been implemented in industrial practice using the dividing-wall distillation column as displayed in Fig. 1 [6, 7].

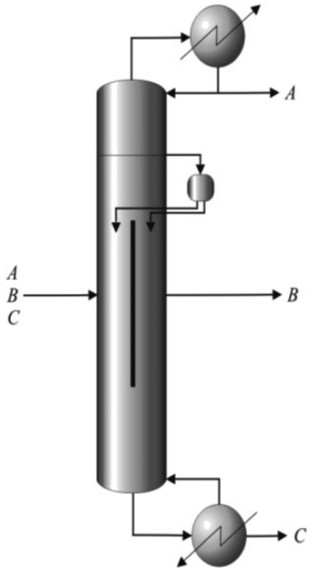

Figure 1. Dividing-wall distillation column.

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The dividing-wall distillation column is thermodynamically equivalent to the Petlyuk distillation column when no heat transfer occurs through the middle wall. Several applications have been reported for the dividing-wall distillation column, such as separation of hydrocarbon mixtures [8], production of fatty esters [9, 10], and purification of bioethanol [11] among others. Of the aforementioned applications, reactive distillation has gained importance with reports on its implementation in both pilot- and industrial-scale plants [12, 13]. The simultaneous reaction and separation in a dividing-wall distillation column enabled savings in energy consumption and higher conversions for equilibrium reactions since the products are removed as they are formed. This technology can be used to produce biodiesel. When esterification reactions are carried out in dividing-wall distillation columns, additional benefits can be obtained, e.g., the reduction in the energy required in the reboiler can be translated into lower pollutant emissions since less fossil fuel is burned. Also, the reduction of the energy consumption causes less traffic of vapor in the distillation column and the flow of cooling water in the condenser is reduced [13].

Regarding the efficiency of the dividing-wall distillation column, it is important to highlight that in a single distillation column, the biodiesel is obtained as bottoms product, the excess of methanol is recovered as distillate product that can be recycled, and the water can be removed in the side stream [14]. Also, the conversion can be increased by using an adsorption system coupled to a reactor, since the removal of water displaces the equilibrium to the products [15].

The production of biodiesel can be considered as series of equilibrium reactions between fatty organic acids and methanol using a homogeneous catalyst like sulfuric acid (Eq. (1)). Diminishing oil reserves coupled with high dependency on fossil fuels in the transport sector has led to an increase of studies on alternative sources of energy. However, the high production cost of biodiesel with around 50 US cents/L compared with the cost of petroleum-based diesel with around 35 US cents/L [16] has delayed its widespread use [17, 18]. Previous studies [19] reveal that the raw materials constitute around 80 % of the total annual cost. Studies on new sources of free fatty acids (FFAs) are therefore important. Low-cost raw materials with high FFA contents are not suitable for use with a basic catalyst due to saponification problems in the transesterification reaction [19, 20]. The application of KOH in the transesterification of an edible-grade canola oil and methanol was studied in a batch reactor and the results indicated that the reaction can be conducted by using enzymes and microalgae lipids, waste oils, bioethanol, and biobutanol [21].

$$\begin{aligned}&\mathrm{CH_3(CH_2)_7CH = CH(CH_2)_7COOH}\\&+\mathrm{CH_3OH} \overset{\mathrm{H_2SO_4}}{\rightleftarrows} \mathrm{CH_3(CH_2)_7CH}\\&=\mathrm{CH(CH_2)_7COOCH_3 + H_2O}\end{aligned} \tag{1}$$

In order to use low-cost raw materials, FFA esterification may be achieved with sulfuric acid as a catalyst, but the reaction is 4000 times lower than when using a basic catalyst [19]. Consequently, in this work, the esterification of oleic acid (O. A.) with methanol taking H_2SO_4 as catalyst is studied first in a batch reactive-separation system. As a second part of the study, the information was applied for scaling up the process to an experimental reactive dividing-wall distillation column, where a preliminary experimental study was carried out in order to corroborate the production of methyl oleate.

2 Experimental

The reagents used were oleic acid (technical grade, Aldrich), anhydrous methanol (J. T. Baker), and sulfuric acid (Jalmek). A reactive system coupled to a distillation column was implemented (Fig. 2). The experimental system consisted of a 1000-mL round bottom flask with three necks. A thermocouple

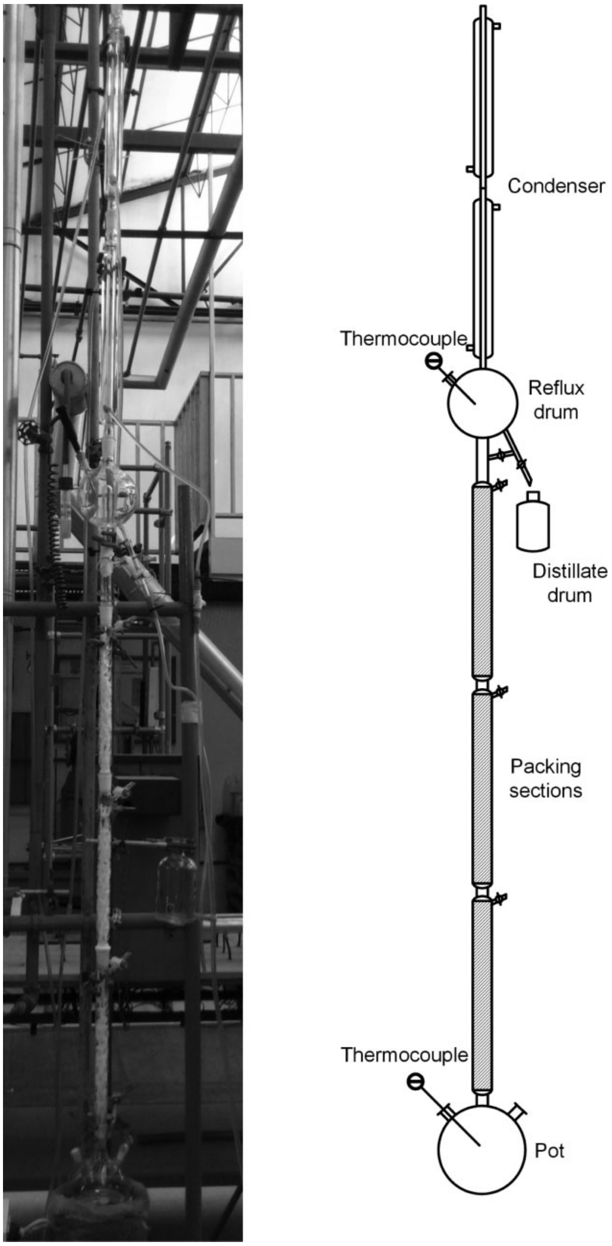

Figure 2. Experimental system for the production of methyl oleate.

was connected to the first neck and the column was inserted into the second one. The column had a diameter of 3 cm and a packed height of 80 cm of Teflon^{TM} strips.

The reaction was carried out in the reboiler and the byproducts and the excess methanol were recovered in the top product of the distillation column. The experiments were conducted under an ambient pressure of 604 mmHg and replicated twice.

The first part of the study considered a 2^3 factorial design; the studied variables were molar ratio of methanol/O.A. (3:1–9:1), amount of sulfuric acid as catalyst (1–3 wt %), and maximum reaction temperature (130–150 °C). The second class of experiments was carried out in a flask under total reflux without the packing section. In this second part of the study, the molar ratios of methanol/O.A. used were 2.5, 5.0, and 10, the reaction times were 1.5, 2.0, 2.5, 3.0, and 3.5 h, and the amount of catalyst was fixed at 1 wt %.

To complement the study, the experimental dividing-wall distillation column shown in Fig. 3 was used to explore the production of methyl oleate. It consists of three packed sections using modified Teflon^{TM} Raschig rings. The total height of the distillation column was 2.5 m and the internal diameter 0.17 m. Briefly, the liquid leaving the first packed section (numbered from top to bottom) is collected in a side tank where it is divided, and the two liquid streams are introduced to the top of the middle packed section. This middle packed section is divided by a wall and is considered the most important part of a dividing-wall distillation column. More details of the design of the dividing-wall distillation column can be found in Hernández et al. [22]. The third packed section is located in the top of the reboiler where the oleic acid, methanol, and sulfuric acid are introduced to the dividing-wall distillation column. In the operational fashion, the steam vapor is supplied to the reboiler of the dividing-wall distillation column under total reflux until a constant temperature profile is measured using six thermocouples. After that, the valve of the distillate is opened and the excess of methanol is recovered as distillate product and the methyl oleate remains in the reboiler. It is important to highlight that the experimental dividing-wall distillation column was designed to operate under ambient pressure. Consequently, supercritical processes cannot be conducted [23].

The products of the reaction were analyzed and quantified by gas chromatography (Perkin Elmer Clarus 500) using a capillary DB-23 column (60 m long, 0.25 mm inner diameter, 0.2 μm film) and a standard of 19 fatty acid methyl esters (FAMEs) provided by SUPELCO®.

3 Results

Fig. S1 in the Supporting Information presents a chromatogram of the standard where several peaks that correspond to the FAMEs are observed. Since oleic acid and methanol were used for the experimental tests, the methyl oleate is highlighted in the standard.

A typical gas chromatogram for an experimental run in the glass system is illustrated in Fig. S2, and the peak for methyl oleate is indicated.

Figure 3. Experimental dividing-wall distillation column.

The results, obtained in the 2^3 factorial design for the first case study, were processed in Minitab™ 15. It was found that the effect of the catalyst was not statistically significant when using a confidence level of 95 %, and that increased temperature reduced the conversion of FFAs as indicated in Figs. 4 and 5. This can be explained by side reactions that can occur when FFAs

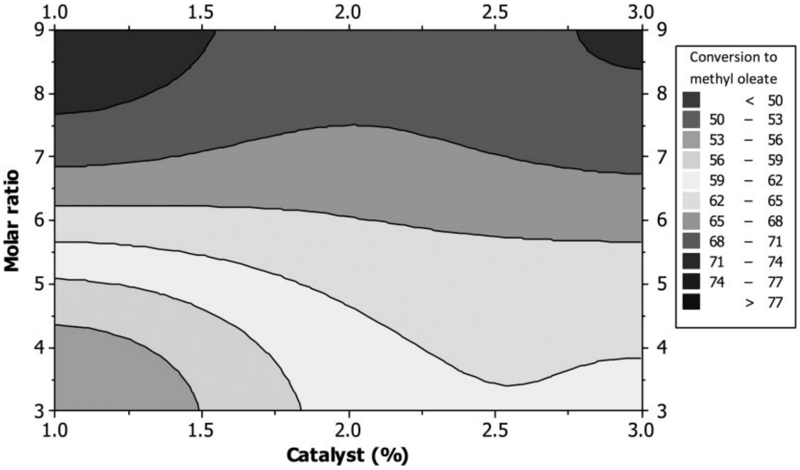

Figure 4. Contour plot for the conversion of FFA to methyl oleate considering the molar ratio of methanol/O.A. and catalyst.

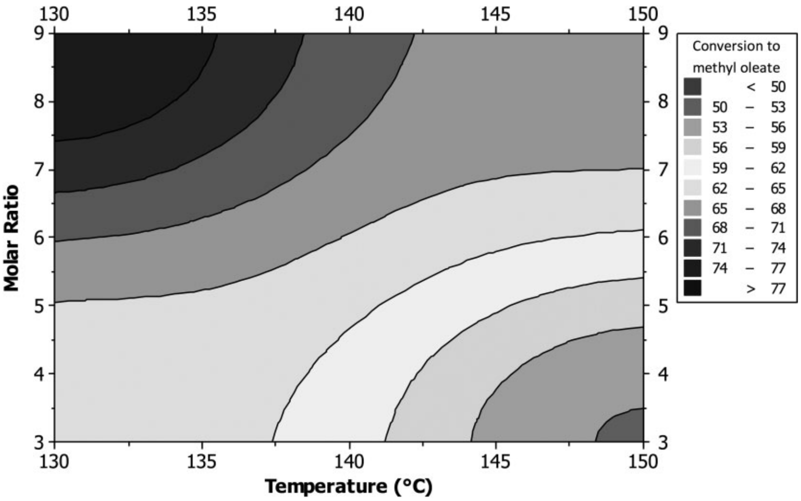

Figure 5. Contour plot for the conversion of FFA to methyl oleate considering the molar ratio of methanol/O.A. and temperature reaction.

are heated at high temperatures where methanol is vaporized [24].

Obviously, increasing the ratio of methanol/O.A. had a positive effect on the conversion. The optimal values of the variables were: a molar ratio of methanol/O.A. of 9, maximum temperature of 130 °C, and 1 wt % of catalyst. For this case, a conversion of 79.64 % of FFAs was obtained (Fig. 6).

The results for the second case study were analyzed with Design-Expert 7.0. In this case, according to Fig. 7, the conversion increases with higher molar ratio of methanol/O.A. and longer reaction time, the optimal values being 9 and 120 min, respectively. The maximum conversion for the second class of experiment was 79.2 %.

When the dividing-wall distillation column was used to carry out the esterification reaction, a molar ratio of 1:9 of oleic acid to methanol was applied and 2 % of sulfuric acid served as catalyst. The time required to achieve the steady state was 1.25 h, after that the distillate was obtained during 1.5 h. The final content in the reboiler was analyzed and a conversion of 56 % of methyl oleate was achieved (Fig. S3). This preliminary result indicates that methyl oleate can be obtained in the experimental dividing-wall distillation column, but more tests are required to find the optimal operational conditions.

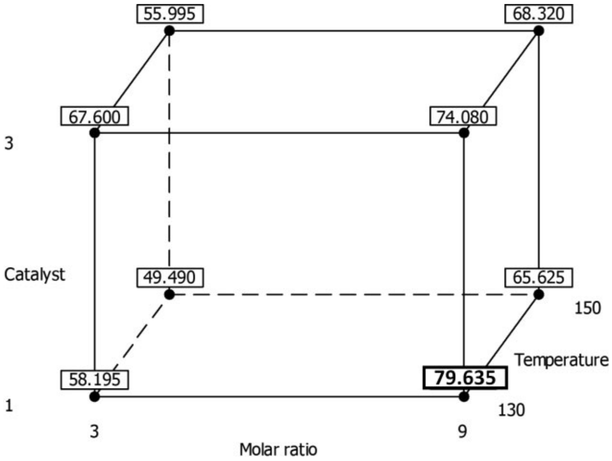

Figure 6. Cube plot for conversion to methyl oleate (percent).

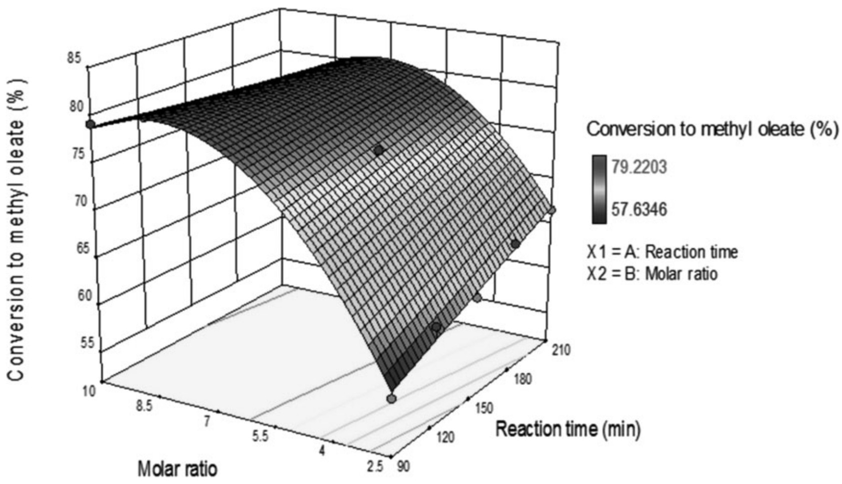

Figure 7. Response surface for the conversion of FFA to methyl oleate vs. molar ratio of methanol/O.A. and reaction time for 1 wt % of catalyst.

4 Conclusions

A laboratory-scale system to study the esterification reaction of oleic acid and methanol using sulfuric acid as homogeneous catalyst was implemented. According to experimental tests, the best conditions for the production of FAMEs using a single equilibrium stage are: molar ratios of methanol/O.A. higher than 8, reaction time shorter than 120 min, a temperature of 130 °C, and 1 wt % of catalyst. Finally, preliminary experimental studies were carried out in a dividing-wall distillation column to produce FAMEs. The experimental runs indicate that methyl oleate was obtained, but more tests are required to optimize the reactive-separation system.

Acknowledgment

The authors acknowledge the English grammar revision by DAIP (Universidad de Guanajuato).

The authors have declared no conflict of interest.

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