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Simulation study of the production of biodiesel using feedstock mixtures of fatty acids in complex reactive distillation columns

E. Cossio-Vargas, S. Hernandez*, J.G. Segovia-Hernandez, M.I. Cano-Rodriguez

Universidad de Guanajuato, Campus Guanajuato, DCNyE, Noria Alta s/n, Guanajuato 36050, Gto., Mexico

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ABSTRACT

Biodiesel can be produced from a number of natural, renewable sources, but vegetable oils are the main feedstocks. The current manufacturing biodiesel processes, however, have several disadvantages: expensive separation of products from the reaction mixture, and high costs due to relatively complex processes involving one to two reactors and several separation units. Therefore, to solve these problems, in recent years several researchers have developed a sustainable biodiesel production process based on reactive distillation. In this paper the production of biodiesel using feedstock mixtures of fatty acids is explored using reactive distillation sequences with thermal coupling. The results indicate that the complex reactive distillation sequences can produce a mixture of esters as bottoms product that can be used as biodiesel. In particular, the thermally coupled distillation sequence involving a side rectifier can handle the reaction and complete separation in accordance with process intensification principles.

1. Introduction

Biodiesel, a mixture of fatty methyl/ethyl esters derived from plant/animal triglycerides through transesterification with an alcohol, is a fuel that is under a great deal of consideration [1–4]. It has been assessed that biodiesel yields 93% more energy than that invested in its production, and relative to fossil fuels, greenhouse gases are reduced 41% by biodiesel production and combustion while less air pollutants are released per net energy gain. Although these benefits are very attractive, the current biodiesel final cost is prohibitively high without governmental subsidies. Much of the actual technological complexity, involving multiple steps on triglycerides pretreatment and biodiesel separation/purification, originates from contaminants in the feedstock (e.g., water and free fatty acids) or impurities in the final product (e.g., glycerol, methanol, and soaps). Therefore, to solve these problems, some authors have developed a sustainable biodiesel production process based on reactive distillation using acid catalysts [3,5]. Reactive distillation integrates reaction and separation in one unit. This intensifies mass transfer and allows *in situ* energy integration while simplifying the process flowsheet and operation. However, combining the two operations is possible only if the reactions show reasonable conversion and selectivity data at pressures and temperatures that are compatible with the distillation conditions. The reduction in the number of processing units and the direct heat integration between reaction and separation can reduce capital investment as well as utility costs. Increased overall conversion, as well as improved selectivity in competing reactions, can be achieved in reactive distillation by the continuous removal of products from the reaction zone of equilibrium limited reactions.

The design of new processes in chemical engineering takes into account policies of process intensification, which can be stated as any chemical engineering development that leads to a substantially smaller, cleaner, and more energy-efficient technology [6]. Distillation continues being the most used separation technique in chemical industry, and it is well known that requires large amounts of energy in order to achieve a given separation and the use of the energy is accompanied by a very low second law thermodynamic efficiency [7–10]. Considering these facts, several improvements have been made to distillation directed to reductions in both energy and capital costs that can be related to reductions in greenhouse gas emissions and usage of cooling water. Since process intensification takes into account reduction in energy consumption, miniaturization, integration of several operations into one equipment, safe operation and others, maybe the reactive distillation is the most representative operation in process intensification because the reaction and separation are carried in the same unit leading to energy savings due to internal integration and higher conversions in equilibrium reactions since products are removed as they are formed. Another important development in distillation is

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* Corresponding author. Tel./fax: +52 4737320006.
E-mail address: hernasa@ugto.mx (S. Hernandez).

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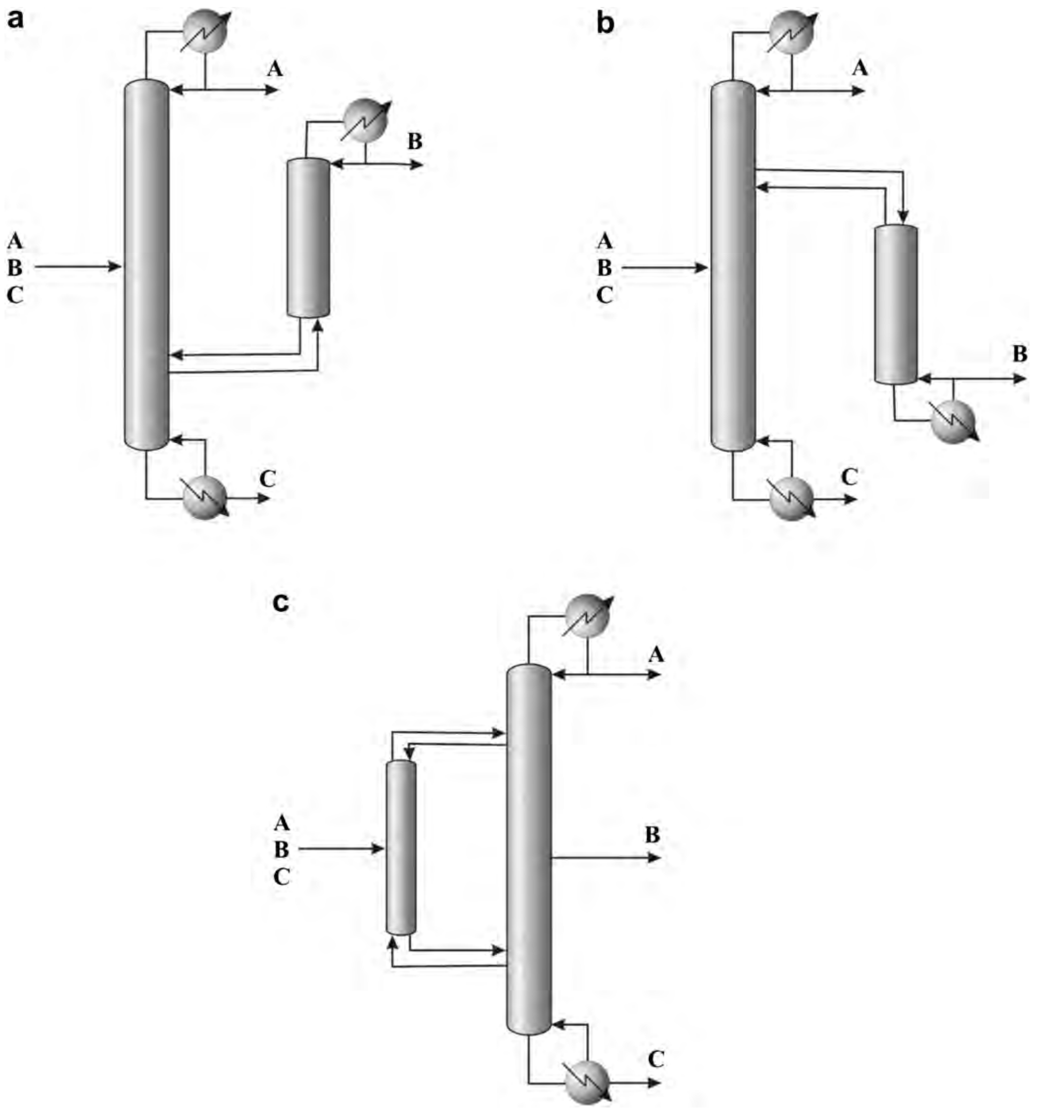

Fig. 1. Thermally coupled distillation sequences for the separation of ternary mixtures: (a) side rectifier, (b) side stripper and (c) fully thermally coupled.

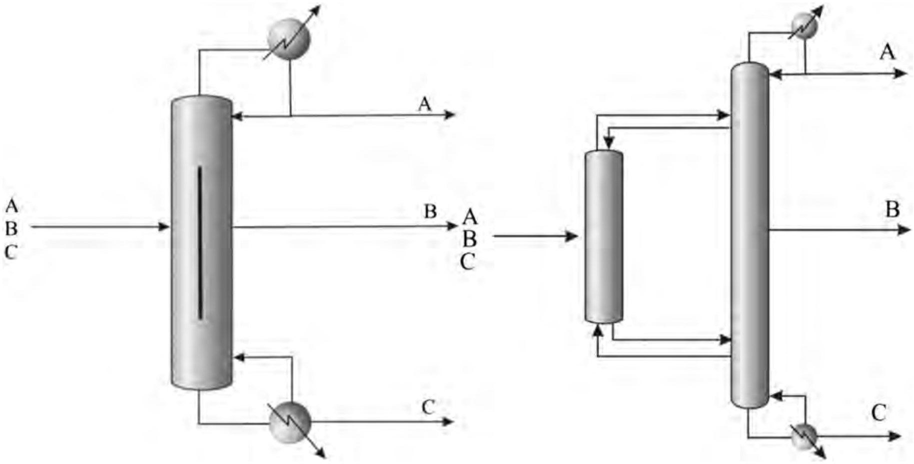

Fig. 2. Dividing wall distillation column and Petlyuk column.

Table 1
Characteristics of the feeds to the complex reactive distillation sequences.

Feed	Characteristics
Fatty organic acids	Mole flow of oleic acid (AC1) = 100 lb-mol/h Mole flow of linoleic acid (AC2) = 100 lb-mol/h Mole flow of n-dodecanoic acid (AC3) = 100 lb-mol/h Saturated liquid at 1.5 bar Temperature = 690.1 K
Methanol	Mole flow of methanol (ME) = 360 lb-mol/h Saturated vapor at 1.5 bar Temperature = 348 K

the thermally coupled distillation columns that can be implemented using a dividing wall distillation column that presents both reductions in energy consumption and capital costs. There are many thermally coupled distillation sequences, for instance, for the separation of a ternary mixture, Fig. 1 depicts the most common: the thermally coupled distillation sequences using side columns and the fully thermally coupled distillation column (Petlyuk distillation column). Many studies have shown that the thermally coupled distillation sequences can achieve energy savings between 30 and 50% in comparison to the well-known conventional distillation sequences for the separation of ternary mixtures [11–13]. The dividing wall distillation column has been implemented in industrial practice using a single shell divided by a wall (Fig. 2), and it has been found that the operation and control can be achieved in a similar manner to those of conventional distillation columns [14].

Considering the use of acid catalysts, the biodiesel can be obtained carrying out esterification reactions in a distillation column conducting to higher conversions since the products are removed as they are formed. Conceptually Equation (1) can represent the

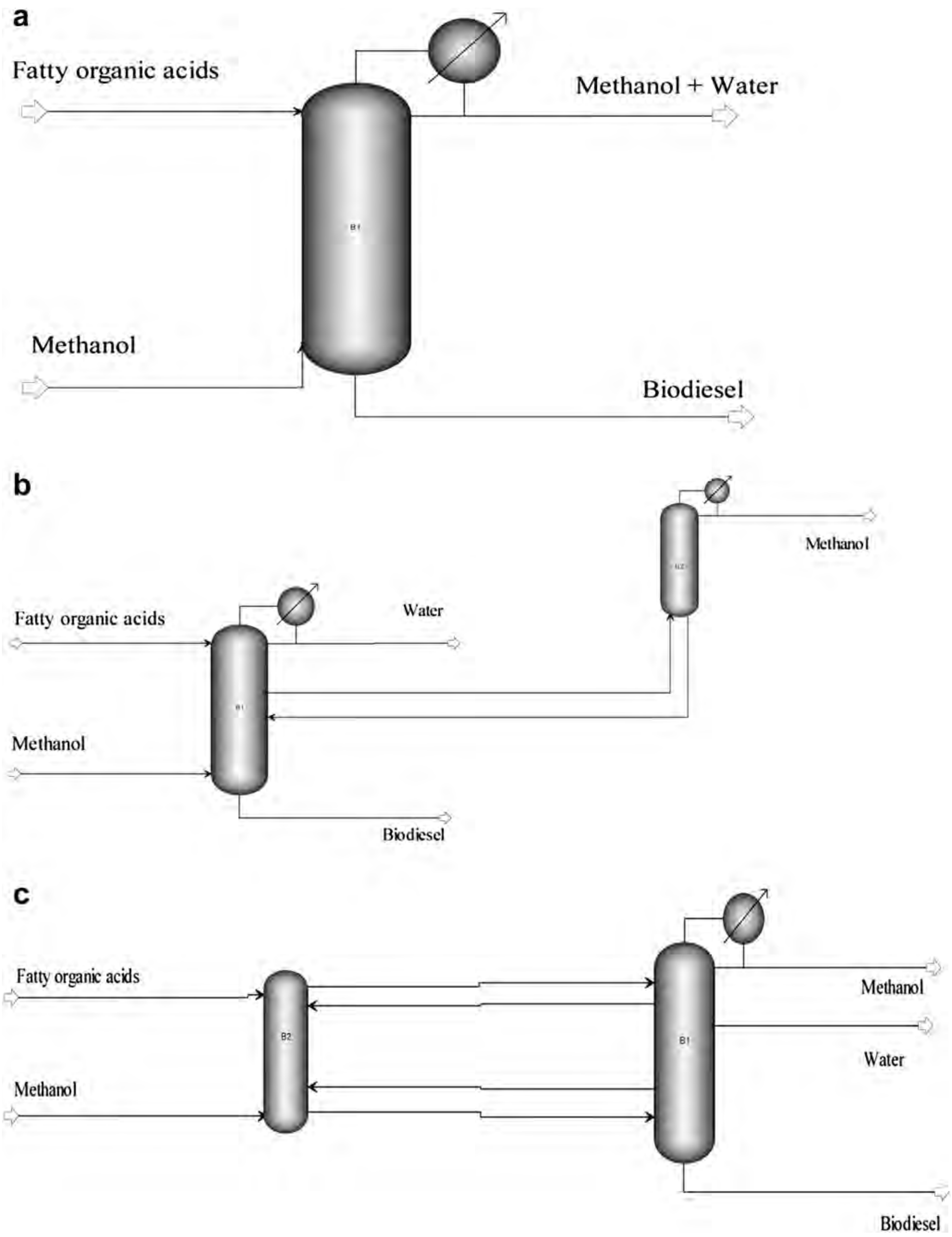

Fig. 3. Complex reactive distillation sequences implemented in AspenONE Aspen Plus: (a) Complex reactive distillation column, (b) Reactive thermally coupled distillation with a side rectifier and (c) Reactive Petlyuk column.

Table 2
Important design variables for the complex reactive distillation sequences.

Distillation sequence	Design variables
Complex reactive distillation column (Fig. 3a)	Total number of stages 30 Operational pressure 1.5 bar Temperature of the biodiesel stream 419.4 K
Reactive thermally coupled distillation with a side rectifier (Fig. 3b)	Number of stages in the main column 17 Number of stages in the side rectifier 13 Operational pressure 1.5 bar Interconnecting vapor flow = 120 lb-mol/h Temperature of the biodiesel stream 415.0 K
Reactive Petlyuk column (Fig. 3c)	Number of stages in the prefractionator 20 Number of stages in the second column 10 Operational pressure 1.5 bar Interconnecting vapor flow = 95 lb-mol/h Interconnecting liquid flow = 270 lb-mol/h Temperature of the biodiesel stream 413.0 K

production of biodiesel. The reaction can be catalyzed with homogeneous catalyst like sulfuric acid or *p*-toluenesulfonic acid, but solid catalyst can be used in packed distillation columns. Solid catalyst like modified solids of CaO and ZrO_2 have been proposed for the production of biodiesel [15,16] with some advantages like reductions in the total annual costs, since no separations of catalyst from biodiesel, by-products and excess of reactants are required.

$$\text{Fatty organic acids} + \text{Methanol} \Leftrightarrow \text{Ester} + \text{Water} \qquad (1)$$

According to Equation (1), it is necessary stoichiometric amounts of organic acids and methanol, but in practice it is difficult to maintain the ratio because fluctuations in the raw materials can occur; for that reason, usually the methanol is used in excess. It is important to mention that the excess of methanol favors the production of esters, but more energy and an additional distillation column maybe required to recover the methanol that can be recycled to the reactive section.

Regarding thermodynamic aspects, the reactive mixture can present homogeneous and heterogeneous azeotropes. As a result, appropriated thermodynamic models like NRTL, UNIFAC and UNIQUAC are needed to represent the correct thermodynamic behavior when the reactive system is analyzed using process simulators.

In most of the papers published, the esterification reaction is carried out using a single fatty acid. Few authors, as Tapasvi et al. [17] have analyzed the production of biodiesel by reactive distillation using as raw material mixtures of fatty acids. In light of these ideas, in this paper the esterification of mixtures of organic acids like oleic, linoleic and dodecanoic with methanol using sulfuric acid as catalyst is studied considering reactive complex distillation. The study is carried out using the commercial simulator AspenONE Aspen Plus.

2. Case study

Using the process simulator AspenONE Aspen Plus we have studied the esterification of the mixture of fatty organic acids and methanol indicated in Table 1. The three reactive distillation sequences shown in Fig. 3 have been implemented in the simulator, using the radfrac model that includes total and component mass balances, energy balance, summation constraints and NRTL model for the equilibrium liquid–vapor in each equilibrium stage.

Because the optimal design of the complex distillation sequences is a very complex task, we have considered the previous designs of Hernandez et al. [18] for the esterification of dodecanoic acid and methanol. This is important, because the main objective of this work is the study of the esterification of mixtures of fatty organic acids giving a mixture of esters that can be used as biodiesel. This is important since most of the works for production of biodiesel using reactive distillation considers only the reaction between the methanol and dodecanoic acid [19–21].

Table 2 presents the design characteristics of the complex distillation sequences used for the simulation study; as it can be seen in Table 2, the three complex reactive distillation sequences have a total number of stages of 30, because we are interested in studying the esterification of mixtures of fatty organic acids.

At this point it is important to mention that AspenONE Aspen plus has been used in many works considering reactive distillation [5,8,9]. For that reason, it is suitable for the study of complex reactive distillation columns. As mentioned previously, the stages of the distillation columns are modeled using the MESH equations (material balances, energy balance, summation constraints, energy balance). The MESH equations in the reactive distillation columns are solved using the bubble point method [22] with a tolerance error of 0.001. In the case of the thermally coupled distillation

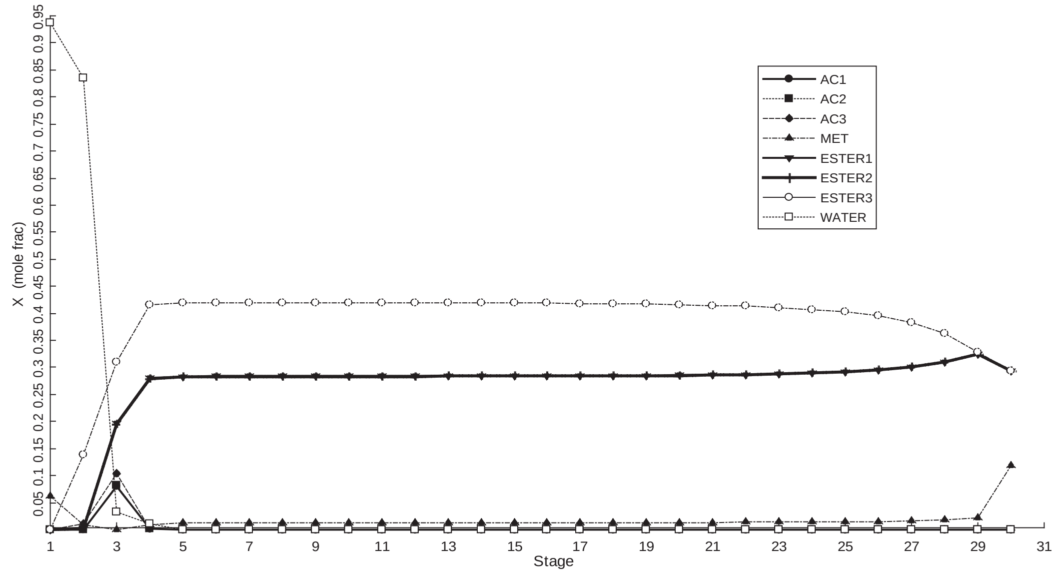

Fig. 4. Composition profiles for the liquid phase of the complex reactive distillation column of Fig. 3a.

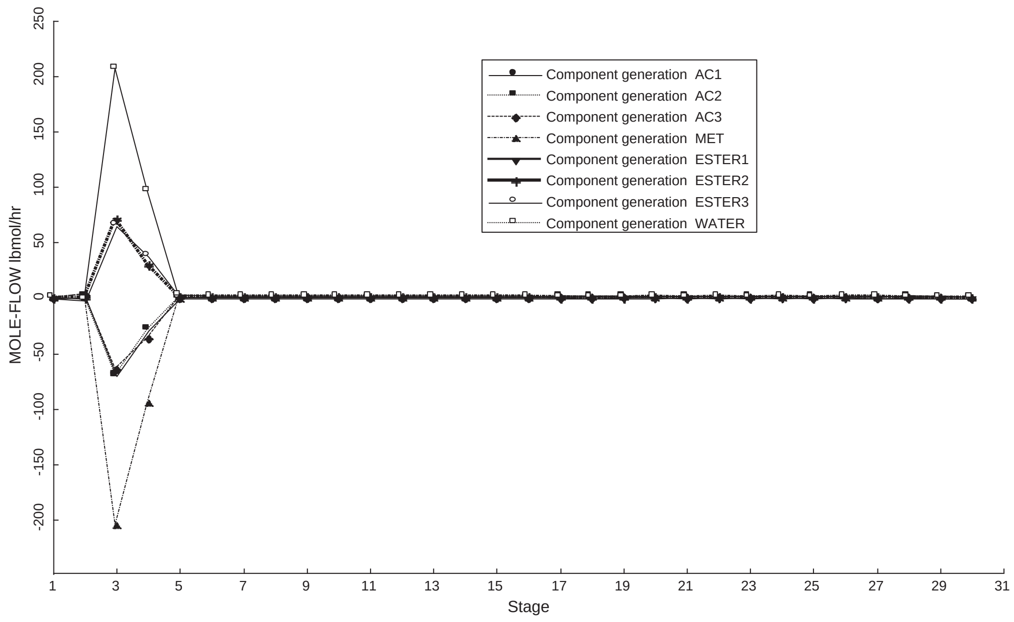

Fig. 5. Reaction profiles for the complex reactive distillation column of Fig. 3a.

sequences, the recycle streams are converged via the Wegstein method with the same tolerance error.

3. Methodology

As indicated previously, the complex distillation sequences indicated in Fig. 3 were implemented in AspenONE Aspen Plus using the radfrac model. Regarding the work of Kiss [4], the mixture of organic acids were fed into one stage close to the top of the distillation column as saturated liquid (690.1 K at 1.5 bar), meanwhile the methanol was introduced in the bottoms part of the distillation column as saturated vapor (348 K at 1.5 bar). The last fact implies reduction in the energy required in the reboiler and the distillation column acts like a reactive absorption. The equilibrium reactions were considered in all the stages of the first distillation columns where the reactants are introduced. The esterification reactions are shown in Equations (2)–(4).

$$\begin{aligned}&\text{Oleic acid}(\text{AC1})\\&\quad+\text{methanol}(\text{ME})\Leftrightarrow\text{methyl oleate}(\text{ESTER1})+\text{water}\end{aligned}\tag{2}$$

$$\begin{aligned}&\text{Linoleic acid}(\text{AC2})\\&\quad+\text{methanol}(\text{ME})\Leftrightarrow\text{methyl linoleate}(\text{ESTER2})+\text{water}\end{aligned}\tag{3}$$

$$\begin{aligned}&N-\text{dodecanoic acid}(\text{AC3})\\&\quad+\text{methanol}(\text{ME})\Leftrightarrow\text{methyl dodecanoate}(\text{ESTER3})+\text{water}\end{aligned}\tag{4}$$

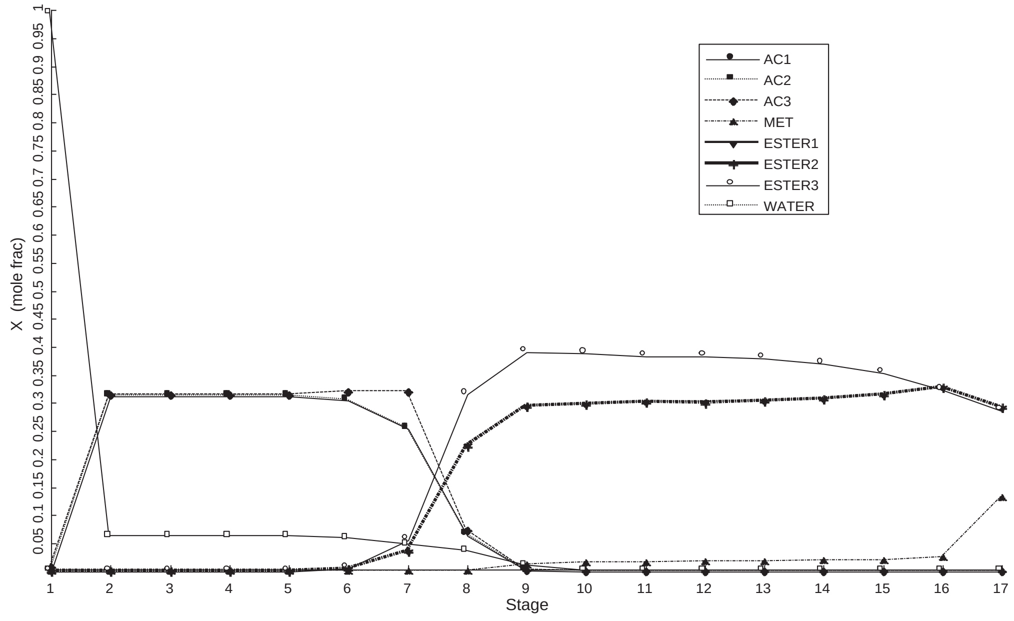

Fig. 6. Composition profiles for the liquid phase of the main distillation column of Fig. 3b.

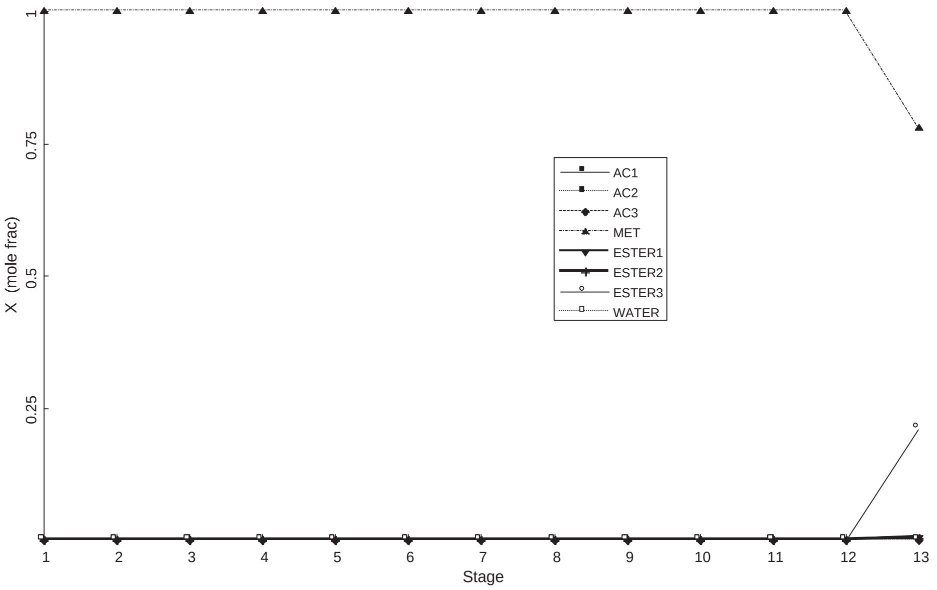

Fig. 7. Composition profiles for the liquid phase of the side rectifier of Fig. 3b.

In the three complex distillation sequences, a mixture of the three esters is obtained as bottoms product and it can be considered as biodiesel.

The complex reactive distillation depicted in Fig. 3a includes the esterification reactions in all stages. The distillate product of this distillation column is a mixture of methanol and water. As a result, an additional distillation column is required to recover and recycle the methanol.

The reactive thermally coupled distillation sequence with a side rectifier (Fig. 3b) considers reactions in all the stages of the first distillation column and the side rectifier is used to recover the methanol.

Considering the reactive Petlyuk distillation column (Fig. 3c), the reactions are included in all the stages of the prefractionator column, and the methanol is recovered in the top product of the main distillation column.

4. Results

The composition profiles for the liquid phase in the reactive distillation column of Fig. 3a are displayed in Fig. 4. According to this Figure, the top product is almost a binary mixture of methanol and water. The bottoms product contains the three esters in a combined mole fraction of around 0.9 and 0.1 mole fraction of methanol. Usually, the bottoms product is introduced into a single flash in order to achieve a combined mole fraction of esters greater than 0.99. This is possible since the large difference between the bubble point of methanol and esters (around 210 °C). Fig. 5 presents the reaction profiles, and it can be seen that most of the reaction takes place around stage 3 where the fatty organic acids are introduced to the reactive complex distillation column.

When the composition profiles for the reactive thermally coupled distillation with a side rectifier are analyzed, it is observed

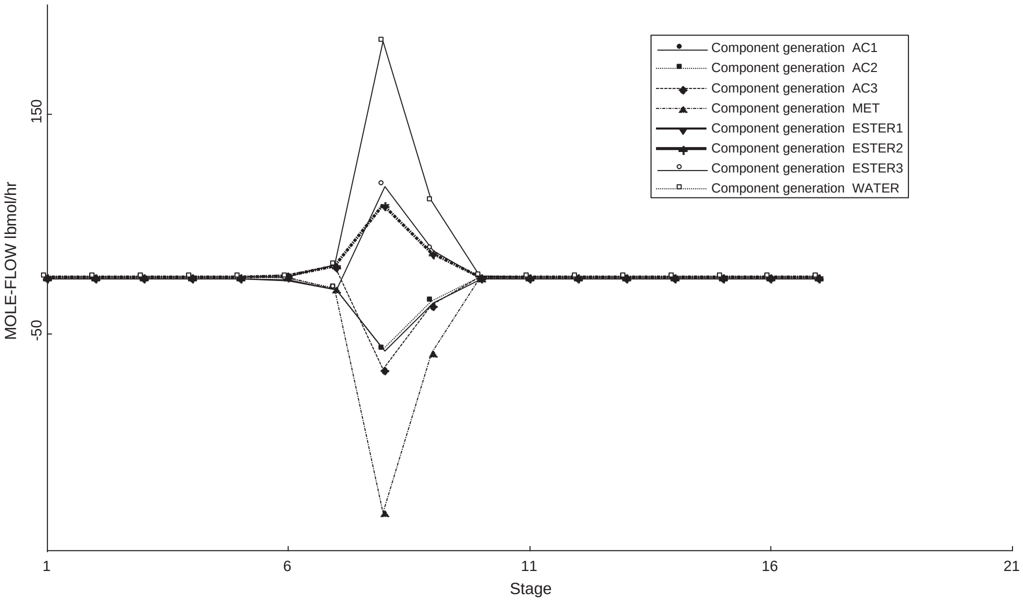

Fig. 8. Reaction profiles for the main distillation column of Fig. 3b.

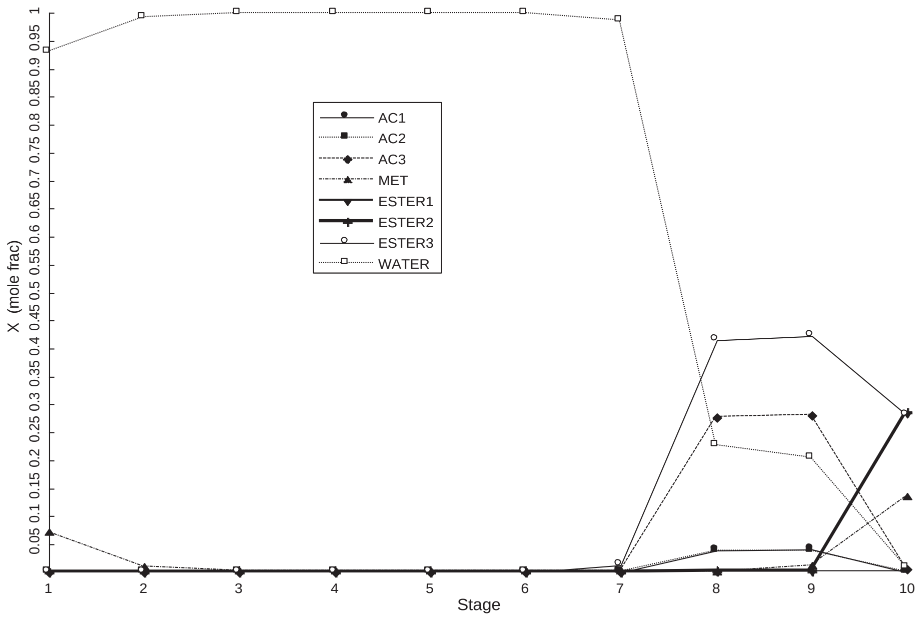

Fig. 9. Composition profiles for the liquid phase of the main distillation column of Fig. 3c.

that this reactive distillation sequence can separate three products almost pure. For instance, Fig. 6 presents the composition profile of the main distillation column, where pure water is obtained in the top product and the bottoms products is composed of the three esters and a small amount of methanol. Also, an additional flash is required to achieve a higher composition in the biodiesel stream.

The composition of the biodiesel is similar to that obtained in the complex reactive distillation sequence of Fig. 3a. In the side rectifier of Fig. 3b, the composition profiles shown in Fig. 7 indicate that the methanol is recovered in the top product of the rectifier. It is important to highlight that this complex distillation sequence can combine the reaction and complete separation. Note that in Fig. 8, most of the reactions occur between stages 6 and 10.

In the case of the reactive Petlyuk distillation column, similar results to those presented in the complex reactive distillation of Fig. 3a are obtained. According to Fig. 9, the composition of biodiesel is similar to those obtained in the other two distillation sequences, but the composition of the top product is a mixture of methanol and water that needs an additional distillation column to recover and reuse the methanol. The side product is almost pure water. In this case, the reactions take place in the top of the prefractionator column.

From an energetic point of view, it is important to mention that the three reactive distillation sequences do not have reboiler because the methanol in vapor phase is injected directly in the bottoms part of the columns. It is important to mention that distillation requires a heat load in the reboiler to achieve the separation, but in this case, the energy is supplied when the methanol stream is vaporized and the mixture of fatty organic acids is heated until its bubble point. The energy supplied in the vapor stream is used for the reaction and separation in each stage and the remaining is rejected in the condenser.

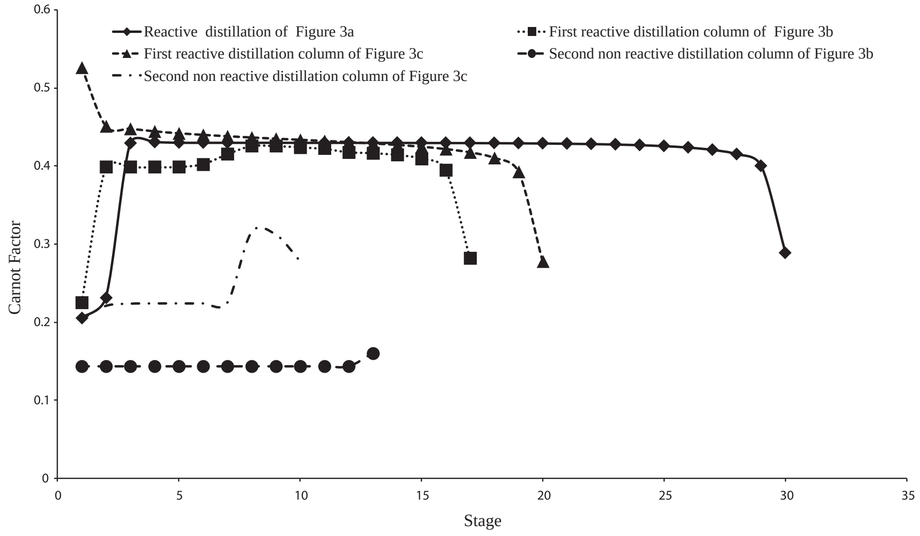

Fig. 10. Carnot's factor of the columns of the three complex reactive distillation sequences of Fig. 3.

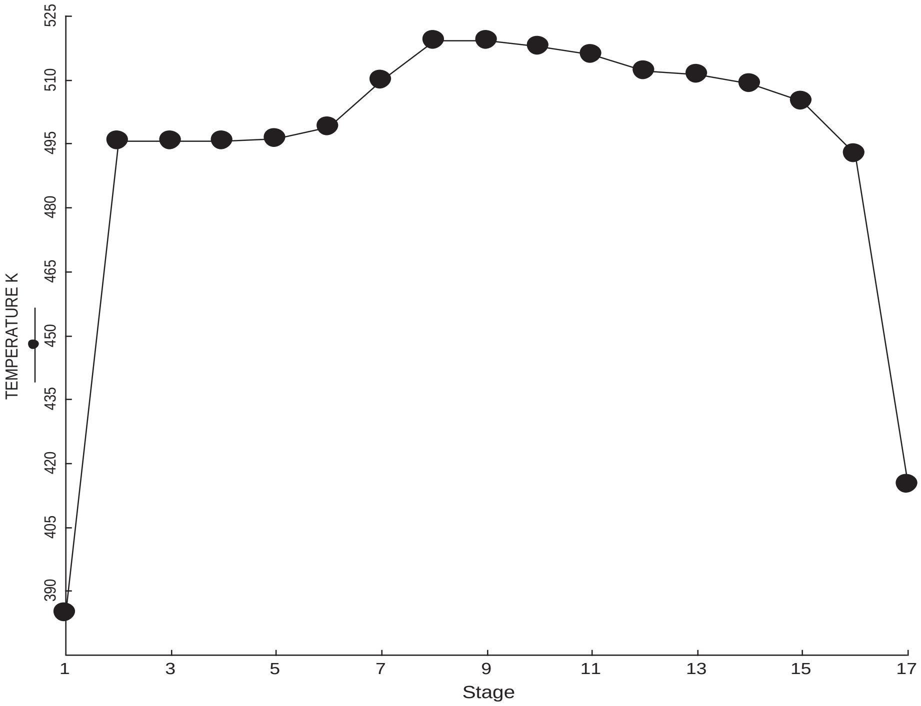

Fig. 11. Temperature profile of the first reactive distillation column of Fig. 3b.

To our knowledge designs of thermally coupled reactive distillation columns without the presence of reboiler for the esterification of mixture of fatty acids have not been reported. As a result, arrangements should be compared in terms of heat that must be removed in the condensers using cooling water. The heat duties eliminated in the condensers are 6651, 6506 and 6753 kW of the distillation sequences of Fig. 3a–c respectively. It is important to note, that the reactive thermally coupled distillation sequence with a side rectifier removes the lowest heat duty in the condenser in comparison to the others; as a result, this complex distillation sequence will require the minimum amount of cooling water. Additionally, the other two reactive distillation sequences will need an additional distillation column to recover the excess of methanol. In this sense, the best option for biodiesel production is the reactive thermally coupled distillation with a side rectifier.

Finally, it was mentioned that reactive distillation represents the best example of process intensification because the reaction and separation are conducted in the same unit giving *in situ* heat integration and higher conversions because of removing of the products. This idea can be supported considering the results Carnot's factor presented in Fig. 10. This factor can be obtained from the temperature profile (Fig. 11) for the first reactive distillation column of Fig. 3b, where temperatures in the middle section are increased due to the reactions. From this temperature profile, the Carnot's factors for the stages are calculated using Equation (5), where CF is Carnot's factor, T_{ref} is a reference temperature and T is the stage temperature.

$$\mathrm{CF} = 1 - \left[T_{\mathrm{ref}}/T\right] \tag{5}$$

As mentioned previously, in the cases of reactive complex distillation sequences of Fig. 3b and c, only the reactions take place in the first distillation column and the second distillation columns only perform a separation. For that reason, note that Carnot's factors for the reactive distillation columns are considerably higher (around 0.5) that those of the distillation columns that only carry out separations (around 0.2). This implies that thermodynamic efficiencies for reactive distillation columns can be higher than those of non-reactive distillation columns.

5. Conclusions

The esterification of a ternary mixture of fatty organic acids with methanol catalyzed by sulfuric acid was studied. A complex reactive distillation column and two thermally coupled distillation columns were simulated considering the reaction inside the column, and the results indicate that the three reactive distillation columns can produce a ternary mixture of esters as bottoms product that can be used as biodiesel. It is important to mention that the reactive thermally coupled distillation with a side rectifier can handle the reaction and the complete separation. These results are an incentive for the implementation of a process with low operating cost that makes biodiesel production economically viable. Also, the process could be improved considering new solid catalysts in packed distillation columns.

Acknowledgments

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