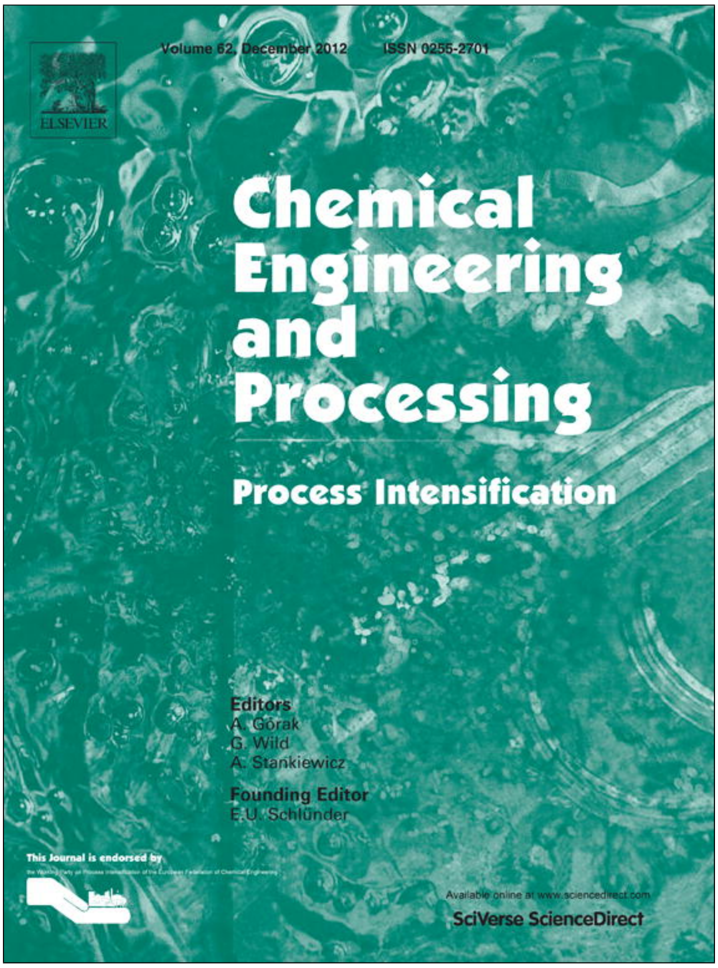

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Short communication

Thermally coupled distillation sequences: Steady state simulation of the esterification of fatty organic acids

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ABSTRACT

Thermally coupled distillation columns have been used for the separation of multicomponent mixtures achieving energy savings in contrast to the well known conventional distillation sequences. In this work, the reaction between fatty organic acids (a mixture similar to *Jatropha curcas* L. seed oil) and methanol to produce esters in reactive thermally coupled distillation options is studied. The results showed that it is possible to obtain esters as bottoms products with high purity suitable for use as biodiesel. Some additional benefits were found, for instance, recovering of the excess of methanol and removing of the water produced, achieving the total consumption of the acid. Also, energy savings of around 30% were achieved in the case of thermally coupled reactive distillation systems in contrast to the classical two feeds reactive distillation column.

1. Introduction

Distillation is considered as a mature technology and it is used for the separation of many mixtures; however, some improvements are being made in order to reduce the energy and cooling water demands, since it is well known its high energy requirements. Nowadays, the problematic associated to the energy requirements is more severe because of the reductions in fossil fuels and policies in green house gases emissions. As a result, important developments have been carried out in biofuels, for instance, bioethanol, biodiesel, bioturbosine and others [1–3]. In the case of the biodiesel production, reactive distillation and reactive absorption have been considered in order to achieve higher conversions and lower requirements of energy and cooling water [4,5].

In the field of distillation, one option that has been studied in both, academia and industry is the thermally coupled distillation sequences (TCDS) that can present energy savings in contrast to conventional distillation sequences for the separation of some mixtures [6–8]. Regarding thermally coupled distillation sequences, maybe the most important is the fully thermally coupled distillation sequence named Petlyuk distillation column. The Petlyuk distillation column has been implemented in industrial practice using a single shell divided by a wall [9,10]. This option is known as dividing wall distillation column (DWDC) that can achieve important reductions in both energy and capital costs. Also, distillation columns thermally coupled to side rectifiers or side strippers have been used in the petroleum industry to obtain several cuts with reductions in energy demands in the reboilers.

Biodiesel as an alternative fuel for diesel engines is becoming increasingly important due to diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum-fuelled engines. Biodiesel, which is made from renewable sources, consists of the simple alkyl esters of fatty acids. As a future prospective fuel, biodiesel has to compete economically with petroleum diesel fuel. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as inedible oils, animal fats, waste food oil and byproducts of the refining vegetables oils. The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial and determinant aspect for delivering a competitive biodiesel to the commercials filling stations. Fortunately, inedible vegetable oils, mostly produced by seed-bearing trees and shrubs can provide an alternative. With no competing food uses, this characteristic turns attention to *Jatropha curcas* L., which grows in tropical and subtropical climates across the developing world [11]. The interest in using *J.* curcas L. seed oil as a feedstock for the production of biodiesel is rapidly growing. The properties of the crop and its oil have persuaded investors, policy makers and clean development mechanism project developers to consider *J. curcas* L. as a substitute for fossil fuels to reduce greenhouse gas emissions. Additionally, biodiesel production from *J. curcas* L. seed oil is one of the

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options being considered for partially substituting diesel fuel for transportation [12].

Taking into account the reduction in fossil fuels and the necessary increment in the production of biofuels, using clean technologies and low cost of operation, TCDS options can be considered as good options in order to carry out the production of biodiesel using reactive distillation. These options can conduct to reductions in energy requirements and intensification of the operation since reaction and separation are conducted in the same equipment. The importance of these options is that reactions are carried in the distillation column and the fatty methyl esters are obtained as bottoms products and the excess of methanol typically used can be recovered in the same distillation column. This route considers the use of acid homogeneous catalysts like sulfuric acid, but also solid catalyst like metal oxides can be used in packed distillation columns [13,14]. It is important to mention that the use of acid catalysts in reactive distillation for the production of biodiesel avoids the formation of glycerol and other byproducts, but other important problems must be taken into account according to the next section of the paper.

2. Production of biodiesel using the acid route

Zhang et al. [15] have reported that biodiesel can be produced using waste cooking oil in order to reduce costs considering the use of sulfuric acid as catalyst. The proposed process is less complex than the alkali-catalyzed process but important problems are present like neutralization of the acid and elimination of the salt. Also, it is important the recovery of the methanol that is used in excess.

In the same context, Kiss [16,17] has reported the problems of corrosion, salt precipitation and environmental penalties associated to the use of sulfuric acid as catalyst. He considers the use of packed reactive systems using acid solid catalysts, but regarding this topic Helwani et al. [18] reported that heterogeneous catalysts can be deactivated with a water content as low as 0.5 wt%, and the production of esters in completely inhibited at 5 wt% of water content. Also, potential problems regarding mass transfer can be presented.

Lam et al. [19] have reported that the main advantages of the use of homogeneous catalysts are the insensitivity to the content of the free fatty acids and water content in the feed, and it is the preferred method with low grade oil. However, problems associated to corrosion and elimination of the acid must be considered in the flowsheet.

It is important to mention that the use of reactive distillation can have some benefits like increment in the conversion due to elimination of the products as they are formed, integration of energy *in situ* and avoiding the formation of some azeotropes and recovery of the excess of methanol in the same reactive distillation column, but the problems of corrosion and neutralization of the acid must be taken into account.

3. Production of biodiesel using reactive distillation and acid homogeneous catalyst

As depicted in Figs. 1–3, the TCDS options have three stream products, distillate, side-product and bottoms product and according to the reactions of Eqs. (1)–(5), we expect three main products, assuming that the fatty organic acid is consumed totally, the fatty methyl ester can be obtained as bottoms products and the excess of methanol is recovered in the distillate, and finally, the water is removed in the side product. The assumption of total conversion of fatty organic acids is valid, since in reactive distillation the products are removed as they are formed. It is important to mention that the reactions contained in Eqs. (1)–(5) are common esterification reactions of fatty organic acids with methanol [20]. For steady state studies, the reactions are considered in equilibrium, but for dynamic simulations kinetic models and residence times are required.

$$\text{Methanol} + \text{dodecanoic acid} \leftrightarrow \text{methyl dodecanoate} + \text{water} \tag{1}$$

$$\text{Methanol} + \text{linoleic acid} \leftrightarrow \text{methyl linoleate} + \text{water} \tag{2}$$

$$\text{Methanol} + \text{oleic acid} \leftrightarrow \text{methyl oleate} + \text{water} \tag{3}$$

$$\text{Methanol} + \text{stearic acid} \leftrightarrow \text{methyl stearate} + \text{water} \tag{4}$$

$$\text{Methanol} + \text{palmitic acid} \leftrightarrow \text{methyl palmitate} + \text{water} \tag{5}$$

Biodiesel is a mixture of fatty methyl esters, for that reason, after removing the water, sulfuric acid and the methanol excess, the remaining mixture of fatty organic esters can be considered as biodiesel.

4. Case study

Three reactive distillation sequences were considered: a two feed distillation column (Fig. 1), a TCDS involving a side rectifier (TCDS-SR, Fig. 2) and the Petlyuk distillation column (Fig. 3). The methanol (120 lb mol/h) is supplied as saturated vapor in the bottoms part of the column and the fatty organic acid (100 lb mol/h) is introduced near the top of the column. It is important to mention that Kiss et al. [21] have reported that the use of reactive distillation can reduce the excess of methanol to only around 20%, reducing the energy requirements.

The introduction of the feed streams in this form implies that the column acts like a reactive absorption and because of the methanol is introduced in vapor phase, the energy required in the reboiler is reduced. According to these flows, it is expected a flow of ester of 100 lb mol/h since the acid is consumed totally. Also, the reaction generates the same amount of water that needs to be removed in order to favor the production of the ester.

Reactions indicated in Eqs. (1)–(5) were considered at equilibrium and carried out between the stages of the two feeds. The liquid–liquid–vapor equilibrium was calculated using the NRTL model because of the complexity of the mixture. The complex reactive distillation sequences have 30 stages and the comparison is made in terms of total energy required in the reboilers [22–24]. Also, the operational pressure in each reactive distillation column is 1.5 bar.

First, the simulation study using AspenONE Aspen Plus includes the esterification of a single fatty organic acid with methanol, and finally a mixture of fatty organic acids (oleic, linoleic and palmitic) with a molar composition similar to the *J. curcas* L. seed oil is analyzed. The optimized designs obtained in AspeONE Aspen Plus were compared in terms of total energy requirements, since the complex distillation sequences have 30 stages according to the work of Bildea and Kiss [24]. It is important to highlight that the main contribution of this study in contrast to other studies [25,26] is the use of several fatty organic acids and a ternary mixture with a similar composition to the *J. curcas* L. seed oil. Additionally, the energy optimization is carried out using a formal optimization method implemented in AspenONE Aspen Plus.

5. Results

Regarding the complex reactive distillation column with two feeds indicated in Fig. 1, it is important to mention that the design is adjusted using a design specification between the mole composition of the ester and the heat duty required in the reboiler. The

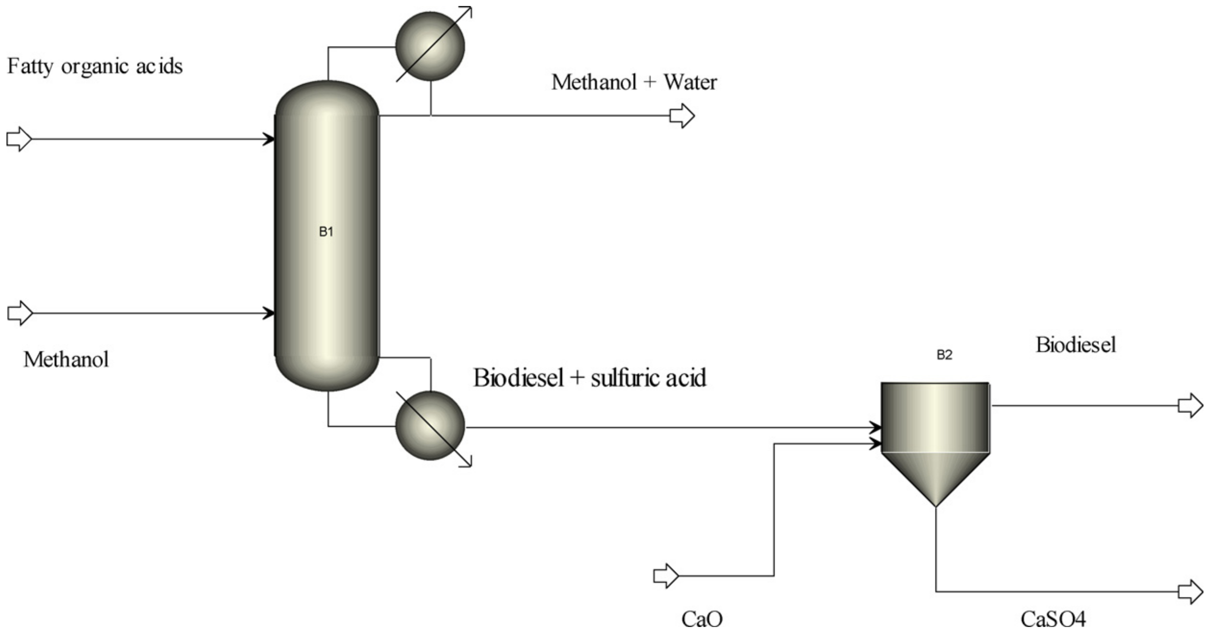

Fig. 1. Two feeds complex reactive distillation column.

composition imposed to the bottoms product was 0.999 mole fraction in order to ensure a very low content of water since the main objective is the use of this product as biodiesel.

The procedure used for adjusting the composition of the bottoms product of the TCDS options is more complicated, and an optimization task is formulated in AspenONE Aspen Plus using the tool of sequential quadratic programming (SQP) included in the simulator. The minimum energy requirement is determined by a complete search in the interconnecting flows, one vapor stream for the TCDS-SR and vapor and liquid streams for the Petlyuk distillation column. In both complex reactive distillation sequences a constraint in the mole composition was included in the optimization problem to ensure a mole fraction of at least 0.999 in the ester.

In the case of the TCDS-SR, Fig. 4 shows the search for the minimum energy requirement using the SQP method implemented in Aspen Plus. Note that the optimization task conducts to a minimum energy requirement of 1552.1 kW when oleic acid is used. The same optimization method implemented in the process simulator is used for the detecting the minimum heat duty supplied to the reboiler of the Petlyuk distillation column.

Table 1 presents the minimum energy required for the three complex reactive distillation sequences and the five fatty organic acids. According to Table 1, the minimum energy required was achieved in the TCDS-SR for all mixtures, presenting reductions in the energy of around 28%. This result is in agreement with that reported for the separation of ternary mixtures without chemical reaction, and we can say that the energy savings are obtained for

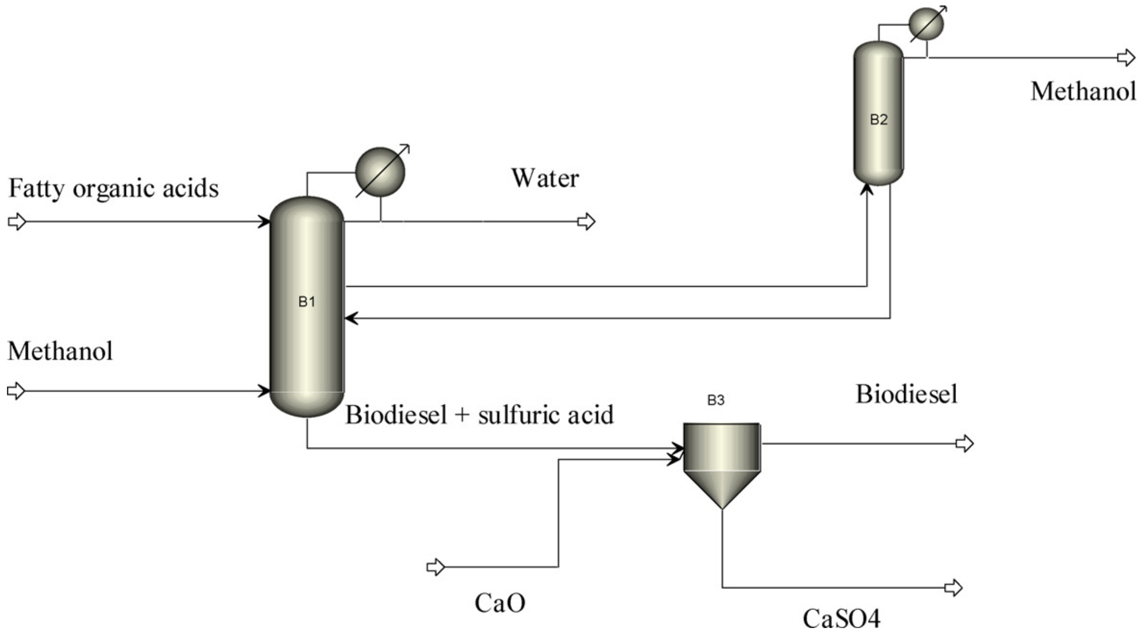

Fig. 2. Reactive thermally coupled distillation sequence with side rectifier (TCDS-SR).

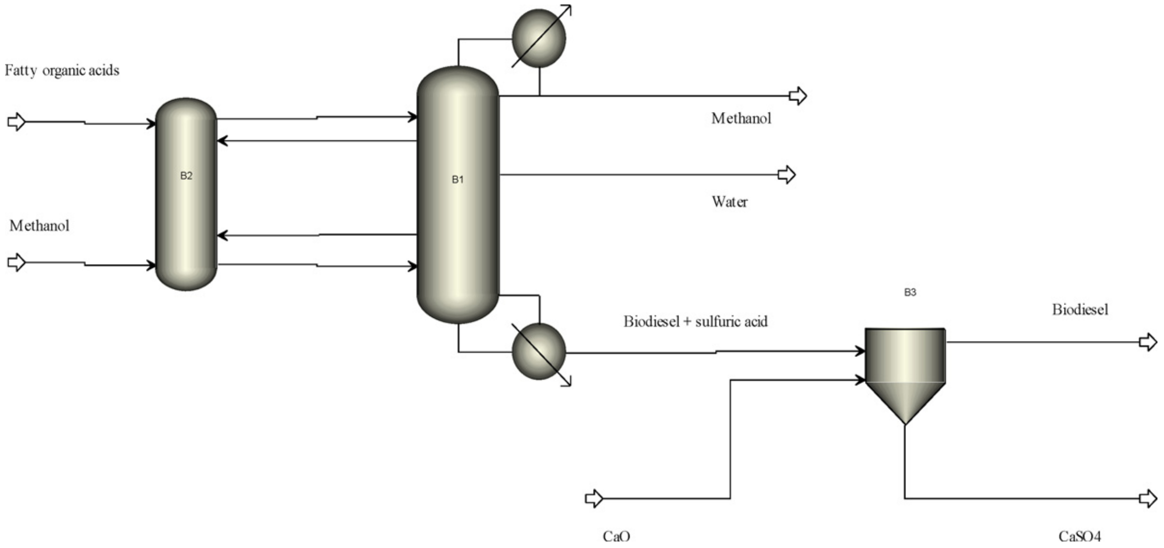

Fig. 3. Reactive Petlyuk distillation column.

Table 1
Energy requirements (kW) of the complex reactive distillation sequences.

Distillation sequence	Oleic acid	Linoleic acid	Dodecanoic acid	Stearic acid	Palmitic acid
Two feed column	2161.2	2142.9	2114.0	2059.3	2161.2
TCDS-SR	1552.1	1559.6	1511.0	1504.8	1552.1
Petlyuk	1826.7	1781.2	1730.3	1736.5	1826.7

both reactive and nonreactive distillation. With regarding the Petlyuk distillation column, this complex distillation sequence only presented energy savings of around the half of those obtained in the TCDS-SR. It is important to mention that both thermally coupled distillation sequences presented lower energy requirements than those of the complex distillation column with two feeds (Fig. 1). However, it is important to compare the complex reactive distillation sequences in terms of total energy requirements, the comparison of the composition profiles can give important information about of the needing of an additional distillation column to recover the excess of methanol. For instance, in Fig. 5, the composition profiles for the ester in the three reactive complex distillation sequences are presented, and it is important to highlight, that according to this figure, the distillation sequences can produce the ester with mole purity of around 0.999. When the composition profiles for the methanol are analyzed (Fig. 6), it is possible to see that in the TCDS-SR option, the side column produces a distillate with a high composition of methanol (around 0.95 mole fraction); as result, in this complex reactive distillation column the recovery of methanol is achieve in the same unit, and the other two distillation sequences produce distillate streams of composition around 0.26 mole fraction of methanol, requiring additional distillation columns to recover the excess of methanol used in the reaction. Finally, in the case of the composition profiles for the water (Fig. 7), two important aspects are observed. First, the reactive TCDS-SR presents a distillate stream in the first distillation column where the water is removed. Second, the Petlyuk distillation column presents a maximum in the composition of the water around stage 5 where the side stream is extracted with the highest composition in water. In terms of the analysis of the composition profiles, it is important to mention that the reactive TCDS-SR gives three products: biodiesel, water and methanol. As a result, the TCDS-SR is the best option to

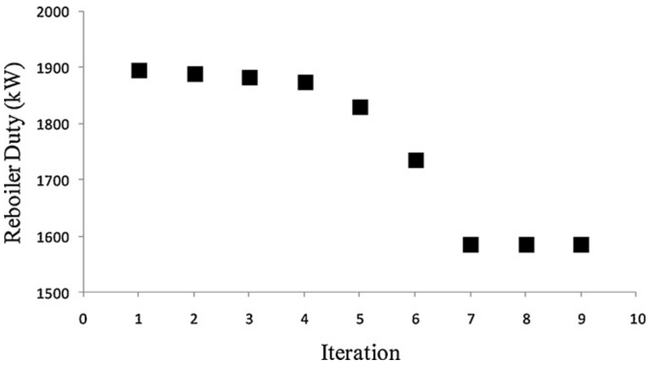

Fig. 4. Search for the minimum energy requirement of the reactive TCDS-SR, for the case of oleic acid.

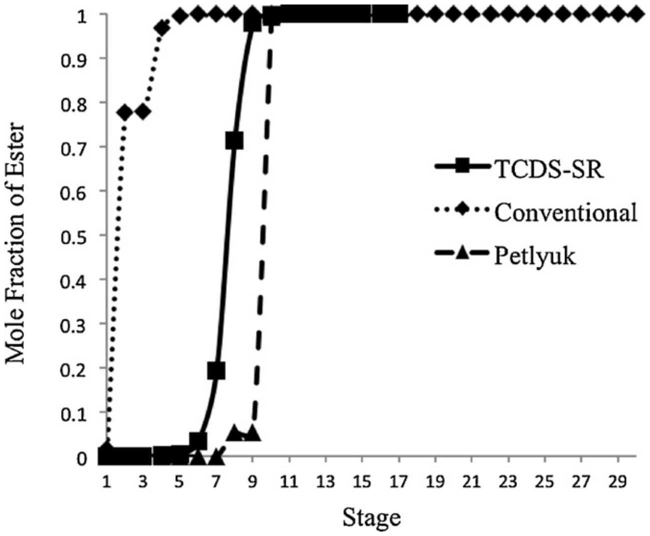

Fig. 5. Composition profiles for the ester in the three complex reactive distillation sequences.

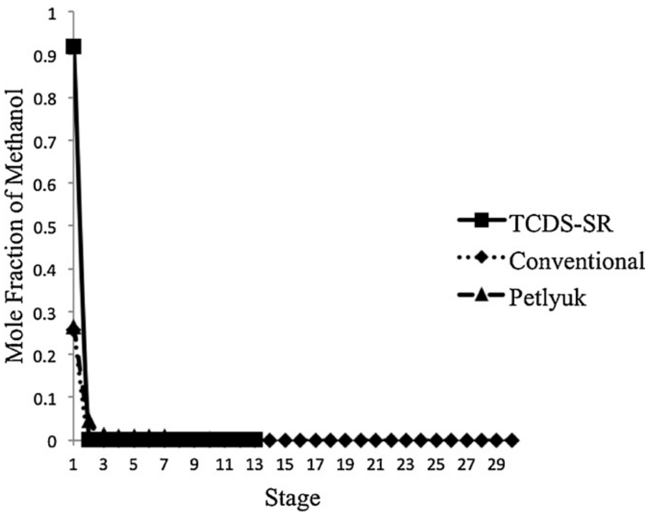

Fig. 6. Composition profiles for the methanol in the three complex reactive distillation sequences.

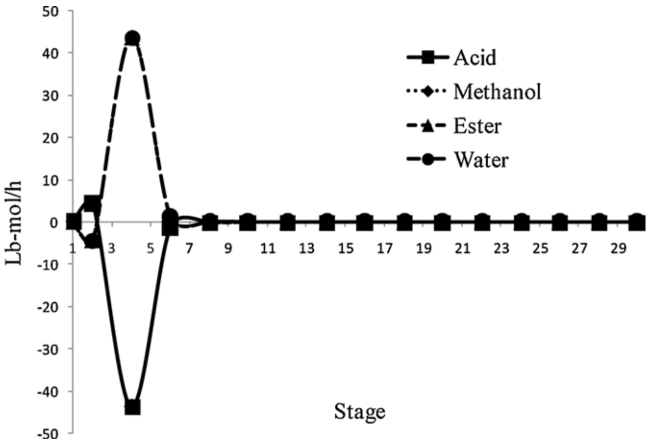

Fig. 8. Reaction profiles of two feeds complex reactive distillation column (reactive zone, from stage 2 to 30).

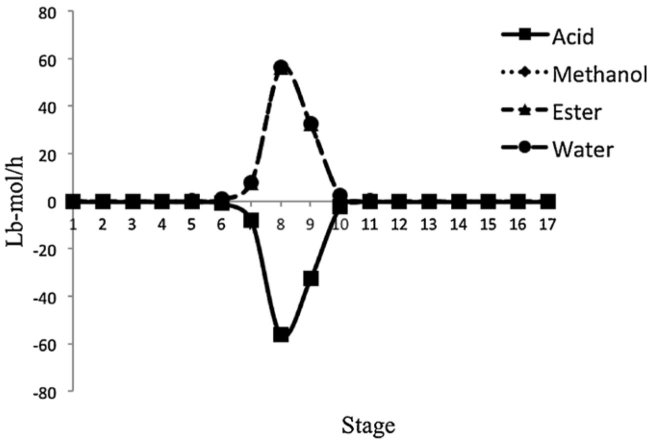

Fig. 9. Reaction profiles of the reactive TCDS-SR (reactive zone, from stage 2 to 17).

carry out the esterification reaction. In accordance with previous works dealing with the biodiesel production using acid homogeneous catalysts [15,19], it is necessary to use a neutralization unit (Figs. 1–3) and the separation of the salt ($CaSO_4$). Because of the use of sulfuric acid, the reactive distillation columns must be constructed using stainless steel due to corrosion problems. Also, in terms of comparison with those works, the use of complex reactive distillation columns achieves higher conversions since the products are removed as they are formed and the excess of methanol is recovered in the same reactive distillation column.

Figs. 8–10 present the reaction profiles of the complex distillation sequences. In the cases of schemes of Figs. 1 and 3, the reaction is carried out around the feed of the fatty organic acid, but in the case of the reactive TCDS-SR (Fig. 2), most of the reaction is carried out in the middle section of the column around the extraction of the vapor feed to the second distillation column, where the methanol is recovered. The difference in the reaction profiles is due to the recovery of methanol in the second distillation column. The previous works [15,19] indicate that it is necessary a high ratio of methanol to fatty organic acids, but the use of reactive distillation requires only 20% of excess of methanol in order to consume all the acid, and the excess of methanol is easily recovered and recycled in the same reactive distillation column.

According to the previous results, it is possible to obtain a high composition in the ester obtained as bottoms product when only one acid reacts with methanol. In particular, the reactive TCDS-SR

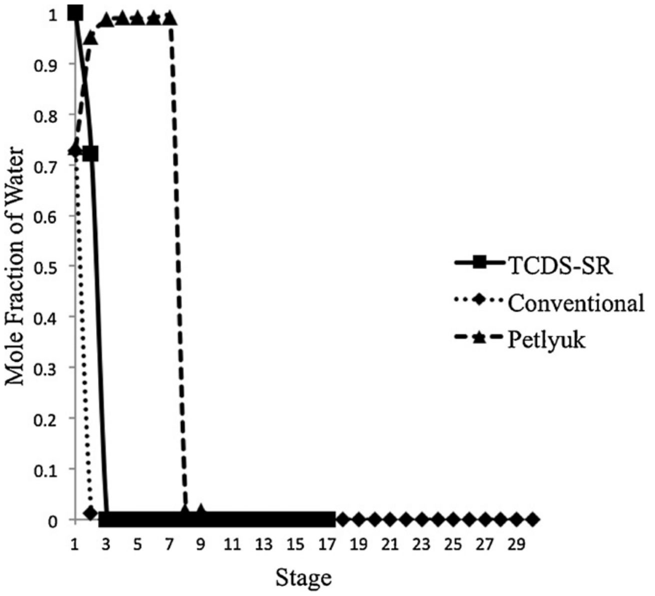

Fig. 7. Composition profiles for the water in the three complex reactive distillation sequences.

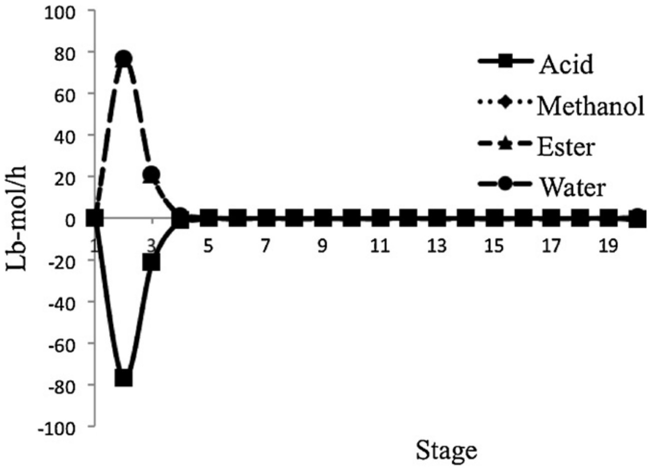

Fig. 10. Reaction profiles of the Petlyuk distillation column (reactive zone, from stage 2 to 20).

Table 2
Mole fraction composition of the biodiesel using *Jatropha curcas L.* seed oil as feed.

Distillation sequence	Methanol	Oleic ester	Linoleic ester	Palmitic ester	Water
Two feed column	0.0016	0.4507	0.3506	0.1969	5.63E−10
TCDS-SR	0.0013	0.4508	0.3506	0.1970	2.32E−10
Petlyuk	0.0013	0.4508	0.3505	0.1968	4.62E−10

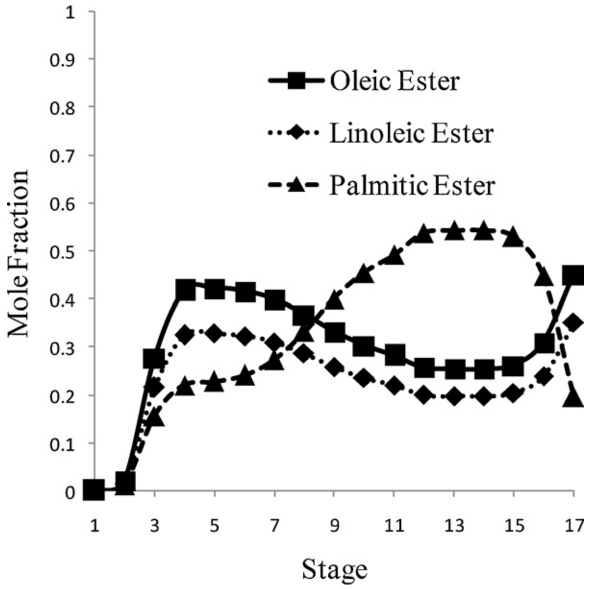

Fig. 11. Composition profiles for the esterification of *Jatropha curcas L.* seed oil using the reactive TCDS-SR.

resulted the best option in terms of energy and separation of the products of the reaction and recovery of the excess of methanol. Taking into account this result, the reactive TCDS-SR option was simulated for the esterification of one mixture of fatty organic acids. The main components of the *J. curcas* L. seed oils are oleic, linoleic and palmitic acids with molar compositions of 0.45, 0.35 and 0.2 respectively, according to the work of Gui et al. [27]. The composition profiles of the esters in the first column of the reactive TCDS-SR option are shown in Fig. 11. It can be seen that the bottoms product is a ternary mixture of esters with a combined mole fraction of 0.999 at 1.5 bar and 359.2 °C. When the same mixture is analyzed using the other two complex reactive distillation sequences, the composition of the biodiesel is very similar to that obtained in the reactive TCDS-SR according to Table 2. However, the compositions of the biodiesel obtained in the three reactive complex distillation are similar, it is important to highlight that the energy requirements are 2238.7, 1586.6 and 1790.4 kW for the two feed complex reactive column, reactive TCDS-SR and Petlyuk column, respectively. Again, savings in the energy requirements of the reactive thermally coupled distillation sequences between 20 and 30% are obtained in comparison to the two feed complex reactive distillation column. As a result, the TCDS-SR can be considered the best option to produce a ternary mixture of esters from *J. curcas* L. seed oil that can be used as biodiesel. Finally, it is important to comment that a complete flowsheet for the biodiesel production must include the separation of the salts generated in the neutralization process. These simulation results can be useful in order to reduce time and costs during the experimental stage.

6. Conclusions

Esterification reactions of fatty organic acids and a mixture of fatty organic acids with composition similar to *J. curcas* L. seed oil with methanol were carried out in a complex reactive distillation sequence and two thermally coupled distillation sequences, obtaining that it is possible to produce esters with a very high composition as bottoms products that can be used as biodiesel after neutralization of the sulfuric acid used as catalyst. This route of production of biodiesel takes into account process intensification principles; for instance, reductions in energy requirements and reaction and separation in the same unit. Also, the excess of methanol used in the reaction can be recovered in the same reactive complex distillation column.

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