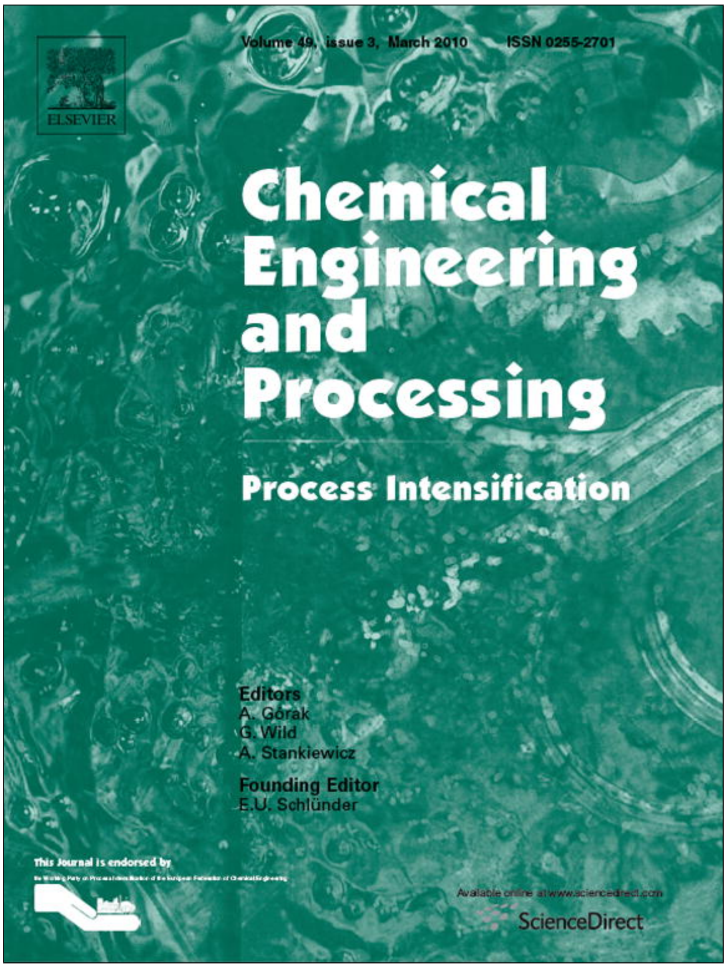

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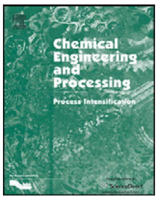

Feasibility study of a thermally coupled reactive distillation process for biodiesel production

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ABSTRACT

Biodiesel fuel represents an interesting alternative as a clean and renewable substitute of fossil fuels. A typical biodiesel production process involves the use of a catalyst, which implies high energy consumptions for the separation of the catalyst and the by-products of the reaction, including those of undesirable side reactions (such as the saponification reaction). A recently proposed process involves the use of short-chain alcohols at supercritical conditions, avoiding the use of a catalyst and the occurrence of the saponification reaction. This process requires fewer pieces of equipment than the conventional one, but its high energy requirements and the need of special materials that support the reaction conditions makes the main product, biodiesel fuel, more expensive than petroleum diesel. In this work, a modification of the supercritical process for the production of biodiesel fuel is proposed. Two alternatives are proposed. The process involves the use of either reactive distillation or thermally coupled reactive distillation. Simulations have been carried out by using the Aspen One™ process simulator to demonstrate the feasibility of such alternatives to produce biodiesel with methanol at high pressure conditions. A design method for the thermally coupled system is also proposed. Both systems have been tested and the results indicate favorable energy performance when compared to the original scheme. Furthermore, the thermally coupled system shows lower energy consumptions than the reactive distillation column.

1. Introduction

One of the major concerns on recent years is the continuous reduction on petroleum production, which in the long term could derive in an energy crisis because of the current dependency on fossil fuels. Furthermore, there is the problem of global warming, caused by high concentrations of greenhouse gases in the atmosphere. Biofuels have emerged as clean and renewable alternatives to fossil fuels. Among biofuels, bioethanol and biodiesel have been extensively studied as substitutes for gasoline and petroleum diesel, respectively. Biodiesel is produced from vegetable oils, namely, sunflower oil, safflower oil, rapeseed oil, castor oil, coconut oil and others, and also from animal fats. Biodiesel can be seen as a mixture of methyl or ethyl esters derived from fatty acids which is used as fuel in diesel engines and heating systems [1,2]. It provides several advantages with respect to petroleum diesel: (i) it is non-toxic, (ii) it is biodegradable and free of sulfur and carcinogenic compounds, and (iii) it can be used directly on the existing diesel engines [3]. On the other hand, its main disadvantages are related to its higher viscosity, lower energy content and higher nitrogen oxide emissions [4].

The conventional process for biodiesel production consists of the transesterification of triglycerides (contained in vegetable oils or animal fats used as raw materials) with a short-chain alcohol, such as methanol or ethanol, in the presence of a catalyst. The more commonly used catalysts are bases (sodium hydroxide, potassium hydroxide), acids (sulfuric acid) and enzymes. The reaction yields are usually higher than 95%, depending upon the reaction temperature and the amount of catalyst used [5]. A disadvantage of the use of a basic catalyst is the saponification reaction occurring when the raw material contains high water or free fatty acid concentrations. In the case of acid catalysts, the main disadvantage is that the reaction rate becomes very slow. In addition, the use of either kind of catalyst involves a difficult separation and high energy consumptions to obtain biodiesel and glycerin (as a by-product) with an adequate purity. In the case of the enzymes as catalyst, the main disadvantage of biodiesel production is its high cost.

Biodiesel can also be produced by using alcohols at supercritical conditions, avoiding the need of a catalyst and reducing the number of separation units. The process involves the transesterification of the triglycerides from vegetable oils or animal fats with methanol

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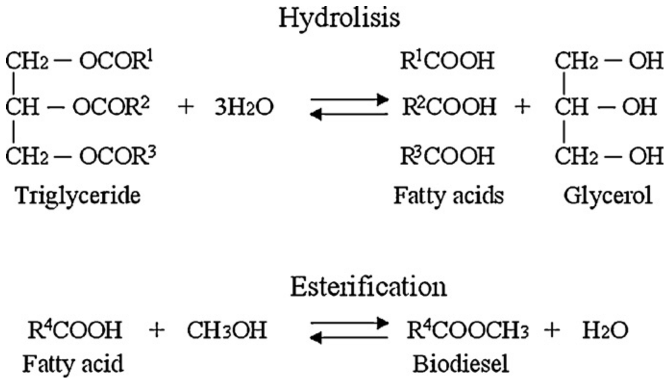

Fig. 1. Reactions involved in the two-step supercritical methanol method for biodiesel production.

at supercritical conditions, i.e. 350 °C and 20–50 MPa [6]. To reduce the severity of the reaction conditions, a two-step process has been proposed [7]. The triglycerides are first treated with water to get fatty acids and glycerol, which is immediately removed. The fatty acids then react with methanol at less severe conditions, 270 °C and 7 MPa, to get methyl esters (biodiesel) and water. Fig. 1 shows the reactions involved, where R^1, R^2, R^3 and R^4 are long hydrocarbon chains, known as fatty acid chains. As the hydrolysis reaction advances, triglycerides are first converted to di- and monoglycerides and then to fatty acids. Fig. 2 shows a simplified scheme of the two-step process. It can be observed that, although the hydrolysis reaction yields free fatty acids, their presence on the feed to the esterification reactor does not produce undesirable reactions; it has further been shown that the presence of water on the raw material does not affect the yield of methyl esters as it occurs in the catalytic process [8]. Therefore, the process is more efficient than the conventional process, since side undesirable reactions, such as the saponification reaction, are avoided. Nevertheless, due to the reaction conditions, the energy consumption of the process is higher with respect to the conventional one, which impacts directly on the final cost of biodiesel.

2. Thermally coupled reactive distillation

Process integration provides alternative schemes capable of efficiently using temperature and concentration gradients to reduce the energy requirements of a process.

In the case of conventional distillation sequences, many structures have been proposed to accomplish such a goal. One of the most important alternatives is the Petlyuk column, also known as fully thermally coupled column, which uses vapor–liquid interconnections to achieve heat transfer by direct contact of the streams, then eliminating the need for two condensers and two reboilers of conventional sequences [9]. It has been shown that the Petlyuk column provides energy savings up to 50% when compared to conventional distillation trains because it does not present the re-mixing effect [10]. This thermally coupled system is widely used on industry in a thermodynamically equivalent form known as the dividing wall column, with BASF as the leader on the use of these schemes [11].

When a chemical reaction occurs, it is common to require a separation sequence to purify the products and remaining reactants. A process intensification alternative to these operations is to carry out the reaction and the separation in just one shell, a system known as a reactive distillation column. The advantage of this kind of process is that it requires a single shell, instead of a reactor and many separation devices. When an exothermic reaction is taking place, the heat released can be used to favor the separation task, then reducing the heat requirements of the separation. There are many reports on reactive distillation processes, some of them dealing with the design of the reactive columns [12–14] with mixtures up to 4 components, and some other studying the simulation of reactive distillation columns with equilibrium and non-equilibrium stage models [15,16].

Recently, a new intensification scheme has been proposed by combining the operation of a reactive distillation column and the fully thermally coupled system; such a system is the reactive Petlyuk column [16,17]. Barroso-Muñoz et al. [17] studied the production of ethyl acetate at three different thermally coupled reactive systems, finding that the reactive Petlyuk system has lower energy requirements than the other schemes under their analysis. Hence, the reactive Petlyuk column appears to represent an interesting alternative for the esterification reaction who takes place when producing biodiesel with two-step high pressure methanol method.

In this work, a study on the feasibility of using the reactive Petlyuk column to produce biodiesel is presented. Simulation models were developed on the process simulator Aspen One™ to demonstrate that the use of these schemes can reduce energy consumptions on the process and the size of the equipment required. Because the mixture under study contains many components, no graphical design method can be used, and then a design methodology to obtain basic data for the columns is proposed.

3. Methodology

Simulations of the process were performed on the commercial simulator Aspen One™. Previous to the analysis, a fundamental decision about the appropriate physical properties model for the mixture has to be made. Following the recommendations presented by Carlson [18] and by testing different models to predict different properties of the components of the mixture as pure substances, the NRTL activity coefficient model was selected for the liquid phase and the Redlich-Kwong model was chosen for the gas phase. Unknown parameters for the NRTL equation were calculated by

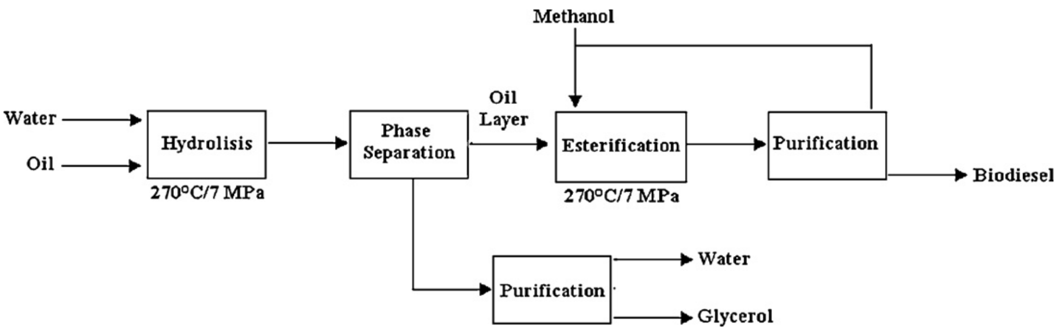

Fig. 2. Simplified diagram of the two-step supercritical methanol process.

Table 1
NRTL parameters for the binary pairs of the components in the reactive mixtures.

i	H_2O	H_2O	H_2O	H_2O	MEOH	MEOH	MEOH	GLY
j	MEOH	GLY	OLAC	MEOL	GLY	OLAC	MEOL	OLAC
a_{ij}	4.8241	−1.0937	0	0	0	0	0	0
a_{ji}	−2.63	−0.7026	0	0	0	0	0	0
b_{ij}	−1329.54	226.65	4978.86	5916.04	559.89	662.83	997.38	1804.79
b_{ji}	828.39	157.46	537.27	930.14	−221.41	−182.32	66.98	1100.31
c_{ij}	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
i	GLY	OLAC	TRI	TRI	TRI	TRI	TRI	
j	MEOL	MEOL	H_2O	GLY	OLAC	MEOH	MEOL	
a_{ij}	0	0	0	0	0	0	0	
a_{ji}	0	0	0	0	0	0	0	
b_{ij}	2684.42	−132.52	355.19	1587.78	1295.98	−415.88	756.97	
b_{ji}	2255.18	255.55	15247.84	6449.47	−709.53	1143.58	−510.58	
c_{ij}	0.3	0.3	0.3	0.3	0.3	0.3	0.3	

using the UNIFAC method. Table 1 provides the NRTL parameters obtained for the binary pairs of the components considered in the reactive mixtures (temperature units are K). Such parameters were used throughout our simulations of the reactive columns. In Table 1 (and in some of the figures) H_2O is water, MEOH is methanol, GLY is glycerol, OLAC is oleic acid, MEOL is methyl oleate and TRI is triolein. The oil was simulated as triolein, a triglyceride contained in a high concentration on many vegetable oils such as rapeseed oil, sesame seed oil, peanut oil, palm oil, and others. An advantage of using NRTL for this process is that it can predict the formation of the two phases after the hydrolysis reaction. The interaction parameters a_{ij}, b_{ij} and c_{ij} of Table 1 can then be used to calculate the activity coefficient, γ, through Eq. (1):

$$\ln\gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \qquad (1)$$

where x is the composition and

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \qquad (2)$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \qquad (3)$$

$$\alpha_{ij} = c_{ij} \qquad (4)$$

3.1. The conventional two-step reaction process

Once the physical properties method was chosen, the reactor for the hydrolysis reaction was simulated as an equilibrium reactor (Gibbs module in Aspen One). After this step, a decanter was used to separate the two phases involved: an aqueous phase which contains glycerin and water; and an oil phase which contains mainly the fatty acid and some water. Then, the stream containing the fatty acid enters to the esterification reactor, along with the methanol stream at 7 MPa and 270 °C. This reactor was also simulated as an equilibrium reactor. The resulting conversion of oleic acid is 95%. The stream leaving the reactor is introduced in a distillation column to eliminate the water contained on it. The bottoms stream is sent to a low-pressure flash drum, where the methanol is vaporized and the biodiesel fuel is obtained as the liquid stream. The diagram of the simulation is shown in Fig. 3.

3.2. A reactive distillation process

To prove first the feasibility of using a reactive distillation (RD) scheme to produce biodiesel fuel with the two-step process, a simulation was developed by using the conventional case of Section 3.1 as a starting point. Instead of entering to an esterification reactor, the stream leaving the decanter along with the methanol stream enters to a RD column. The feed mixture to the RD column therefore contains oleic acid, water, glycerol, and methanol; those components and the product (methyl oleate) constitute a five-component mixture, which makes infeasible the use of a graphic design method. Then, different schemes were proposed to achieve the reaction-separation task.

First of all, a 40-tray column was proposed, in which all the water remaining from the decanter was separated by the top of the column, the mixture of oleic acid and the water product of the esterification reaction is obtained on the side stream, and the methyl oleate is separated as the bottoms product. The reaction takes place initially at the reboiler of the column and at the 4 stages next to it. This scheme, besides its high energy requirements (almost 172,000,000 kJ/h) includes many trays in which the concentration

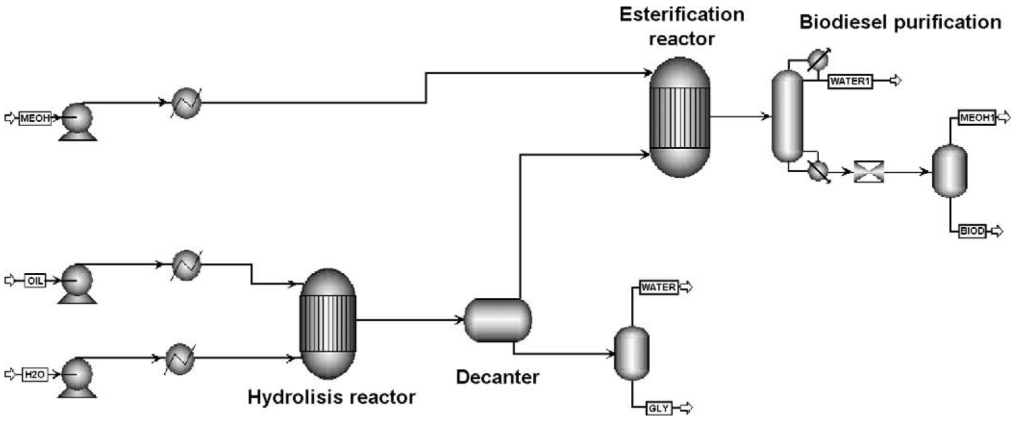

Fig. 3. Diagram of the simulation model of the biodiesel production by the supercritical methanol method.

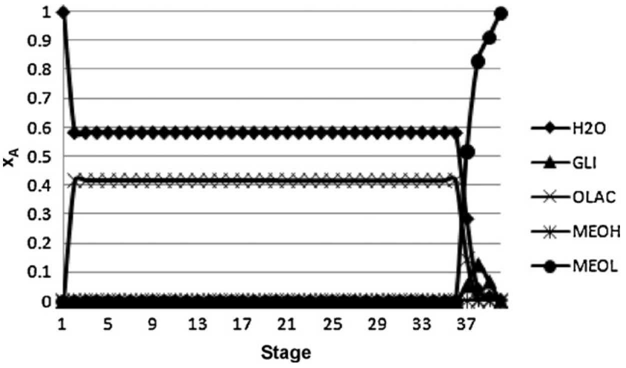

Fig. 4. Composition profile on liquid phase for the 40-tray reactive distillation column (mass%).

of all components does not change (Fig. 4). Then, schemes with a lower number of stages had to be tested.

A rearrangement for the flows was then analyzed, and the best option with respect to energy consumptions was found to be the separation of all water as the top product, part of the methanol as the side-stream product, and a mixture of methanol and methyl oleate at bottoms product. This product distribution was selected because, if the heat duty were increased to achieve high-purity biodiesel on the bottoms product, the temperature would also increase to values higher than 300 °C, temperature at which isomerization of methyl oleate to its *trans*-isomer may occur. That isomer is an undesirable product because of its bad cold flow properties [19]. Then, temperature on the reactive distillation column must be lower than 300 °C. The reactive stages were manipulated to achieve a high conversion and a low heat duty, the best arrangement was when the reboiler and the 5 stages next to it are reactive. The main product obtained consists of a mixture containing 90% mass of biodiesel, but such a product does not satisfy the standard biodiesel requirements (Table 2). Then, a low-pressure flash unit was used to eliminate the remaining impurities. The diagram for the resulting RD process is depicted in Fig. 5.

Table 2
Standard requirements for biodiesel fuel [1].

Component	Requirement	Standard
Water and sediment	0.05 max vol.%	ASTM
Free glycerol	0.020 max wt.%	ASTM/EN 14214
Total glycerol	0.25 max wt.%	ASTM/EN 14214
Monoglyceride	0.8 max wt.%	EN 14214
Diglyceride	0.2 max wt.%	EN 14214
Triglyceride	0.2 max wt%	EN 14214
Methanol	0.2 max wt%	EN 14214

3.3. A reactive Petlyuk column

Once the reactive distillation process (RD) has been successfully simulated, an equivalent scheme with a reactive Petlyuk column

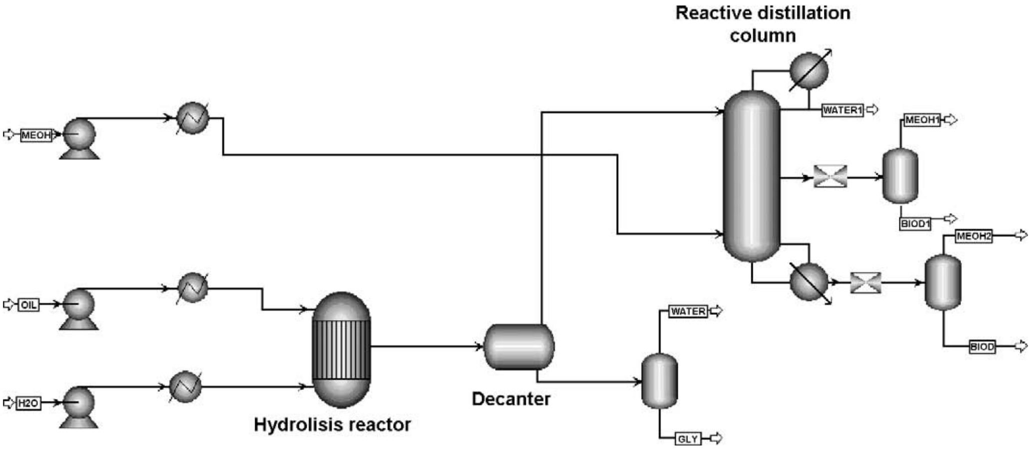

Fig. 5. Diagram of the simulation model for biodiesel production by supercritical methanol method using reactive distillation.

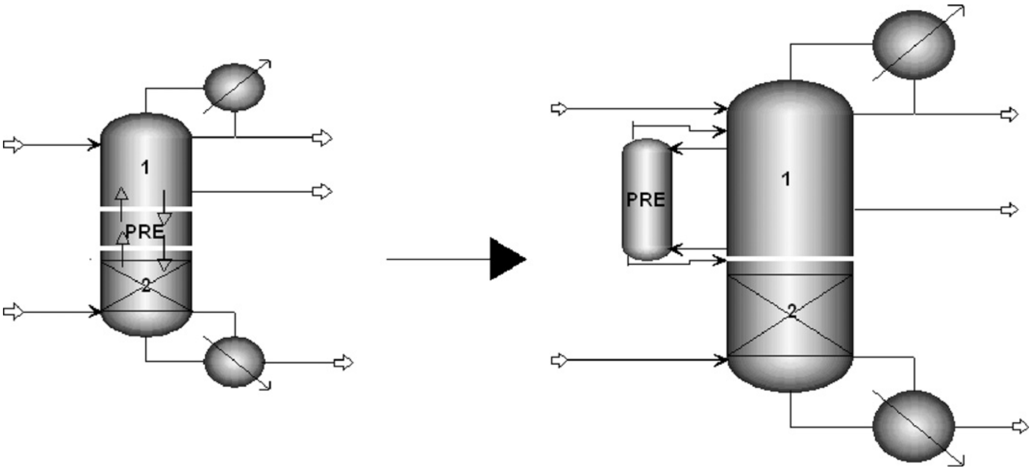

Fig. 6. Design of the reactive Petlyuk column by stage rearrangement of the reactive distillation column.

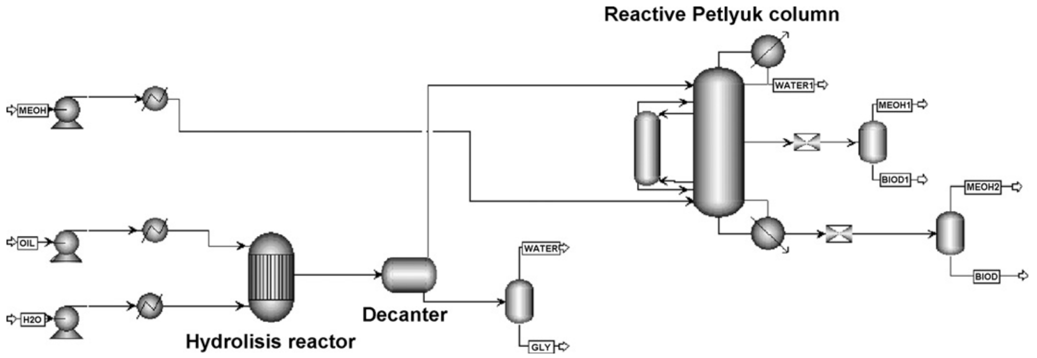

Fig. 7. Diagram of the simulation model of biodiesel production by supercritical methanol method using thermally coupled reactive distillation.

is also proposed. An initial design is required to run the simulations. That is, the number of stages in the main column, the number of stages in the prefractionator and the stages where the reaction occurs have to be determined. That information can be obtained through a rearrangement of the stages of the RD column. This approach is similar to the methodology suggested by Gómez-Castro et al. [9] for the case non-reactive dividing wall columns. Then, a section of the reactive column is removed and used to setup the prefractionator of the Petlyuk column. The scheme for the reactive Petlyuk system is shown in Fig. 6. To favor an efficient flow distribution, the prefractionator is taken from the non-reactive section of the original reactive column. In the Petlyuk system, the pressure of the prefractionator is assumed as equal to the pressure of the top of the main column. The biodiesel production process with the reactive Petlyuk column is presented in Fig. 7. Once the biodiesel purity was fixed at the bottoms of the main column of the Petlyuk configuration, an optimization of the interconnection streams has to be performed by analyzing the changes on the heat duty for different combinations of the values of the flow rates of such streams.

Table 3
Design parameters of the esterification step for the conventional process.

	Reactor
Total mole flow (kmol/h)	680.28
Conversion	99%
Heat duty (kJ/h)	12,959,745.0
Pressure (MPa)	7
	Flash drum
Vapor fraction	0.6606
Temperature (K)	423
Pressure (MPa)	0.1013
Heat duty (kJ/h)	−11,189,446
	Distillation column
Stages	10
Bottoms rate (kmol/h)	414.59
Reflux ratio	4.31
Top stage pressure (MPa)	7
Feed stage	5
Biodiesel purity (mass%)	81.87%
Heat duty (kJ/h)	45,047,117.9

4. Results and discussion

As our case-study, a 46 kmol/h stream of triolein enters the hydrolysis reactor and reacts with an excess of 2476 kmol/h of water (excess is used to shift the reaction equilibrium to the products), obtaining 138 kmol/h of oleic acid and 46 kmol/h of glycerol. In the decanter a water-rich stream is obtained, containing 2209 kmol/h of water and 99 kmol/h of glycerol. The oil phase is sent to the esterification reactor. Some design parameters of the esterification step in the conventional process are shown in Table 3. It can be seen that the separation of water consumes the higher amount of energy of this step. Table 4 provides the design parameters of the RD column and the reactive Petlyuk column (TCRD column). Two RD systems were tested, one with 15 stages (RD 1) and the other with 9 stages (RD 2). The 15-stage column shows lower energy consumptions than the 9-stage configuration; therefore, the 15-stage column was considered as the basis for the design of the reactive Petlyuk column. The stages distribution of the reactive Petlyuk system is shown in Fig. 8. In all of the configurations of Table 4 the reaction takes place in the middle stages, with high conversion of oleic acid. In terms of energy requirements, the reactive Petlyuk system shows a slightly lower heat duty than the other alternatives. To complete the analysis, the streams leaving the flash fed with the side stream are shown in Table 5, and those leaving the

Table 4
Design parameters of the reactive distillation configurations.

	RD column 1	RD column 2	Reactive Petlyuk column	
			Prefractionator	Main column
Stages	15	9	4	11
Bottoms rate (kmol/h)	255.83	255.83	141.47	255.83
Reflux ratio	2.2242	2.3697	1.6652	1.8880
Heat duty (kJ/h)	34,770,314.5	36,291,993.3	0	31,165,410.7
Methanol feed stage	15	9	–	11
Oleic acid feed stage	2	2	–	2
Side product extraction stage	10	5	–	8
Reactive stages	10–15	4–9	–	7–11
Conversion	99%	99%	–	99%
Biodiesel purity (mass%)	90%	90%	–	90%
Interlinking stages	–	–	–	3, 4–6, 7
Interlinking vapor flow (kmol/h)	–	–	–	109
Interlinking liquid flow (kmol/h)	–	–	–	100

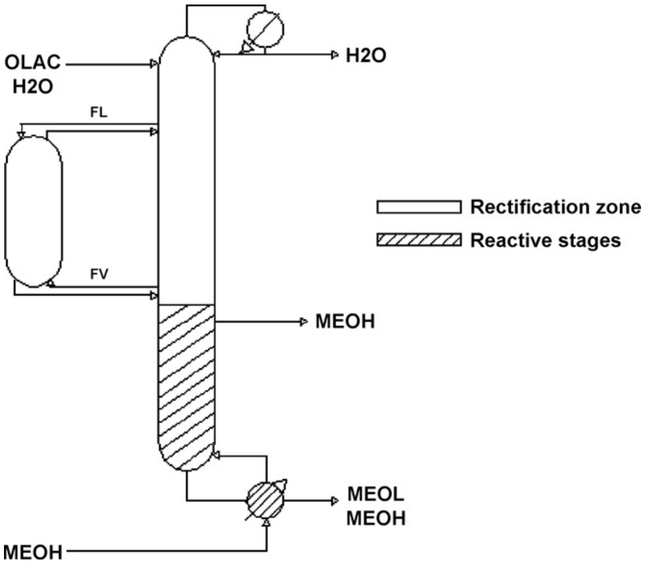

Fig. 8. Stage distribution of the reactive Petlyuk column.

Table 5
Results for the side-stream flash drum.

	RD1 process	TCRD process
T (K)	433	433
Vapor fraction	0.9335	0.9333
Vapor flow (kmol/h)	148.17	148.14
Water (kmol/h)	7.1467	4.4303
Glycerol (kmol/h)	0.0656	0.0659
Oleic acid (kmol/h)	0.0026	0.0001
Methanol (kmol/h)	140.7241	143.3971
Methyl oleate (kmol/h)	0.2357	0.2418
Heat duty (kJ/h)	1,938,004.94	1,625,417.02

flash drum connected to the bottoms stream are shown in Table 6.

A fundamental step on the design of thermally coupled systems consists of finding the optimal values for the interconnection flows in order to reduce the energy requirements of the system. Fig. 9 shows the optimization curves for the reactive Petlyuk column are shown, where FL1 is the liquid stream flowing from the main column to the prefractionator and FV2 is the vapor stream flowing in the same direction. Energy consumption is plot against FL1 for only three different values of FV2. It can be seen that the changes of the heat duty are not significant when the flow rates change, and that many local optimum values are present. The values taken for the design were FV2 = 109 kmol/h and FL1 = 100 kmol/h, which correspond to the configuration described in Table 4.

Table 7 shows a comparison of the total energy requirements for the esterification step of the configurations studied in this paper. In Table 7, total energy requirements to achieve a high-purity biodiesel fuel and a recycle methanol stream are considered. That is, the requirements of the esterification reactor, the distillation column and the flash unit in the case of conventional process; and those of the reactive column and the two flash units in the case of the reactive distillation and the thermally coupled reactive distillation processes. It can be seen that both intensification systems provide significant energy savings when compared to the conventional process, but the thermally coupled system shows the lower energy demand.

Table 6
Results for the biodiesel flash drum.

	RD1 process	TCRD process
T (K)	433	433
Vapor fraction	0.4943	0.4945
Liquid flow (kmol/h)	129.34	129.29
Water (kmol/h)	0.00008	0.0003
Glycerol (kmol/h)	0.2054	0.2051
Oleic acid (kmol/h)	0.0000	0.0000
Methanol (kmol/h)	2.4261	2.4426
Methyl oleate (kmol/h)	126.7088	126.6639
Biodiesel purity (mass%)	99.6%	99.6%
Heat duty (kJ/h)	−12,196,364	−12,147,224

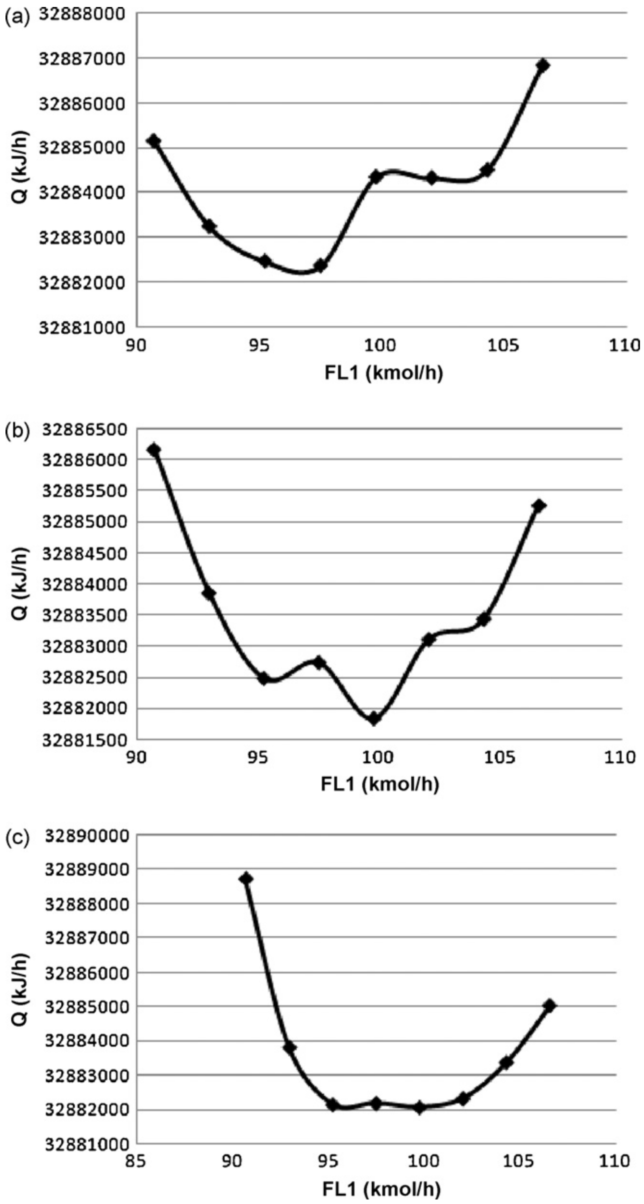

Fig. 9. Optimization of the interconnecting flows of the reactive Petlyuk column. (a) FV2 = 106 kmol/h, (b) FV2 = 109 kmol/h, and (c) FV2 = 111 kmol/h.

Finally, Figs. 10–12 show the composition (mass fraction) profiles for the reactive distillation columns; in the case of the TCRD system, the profile corresponds to the main column. Also, Fig. 13

Table 7
Total energy consumptions.

Process	Q_T (kJ/h)	Energy savings
Conventional	46,817,416.9	0%
RD1	24,511,955.4	47.64%
RD2	26,225,435.9	43.98%
TCRD	20,643,603.7	55.91%

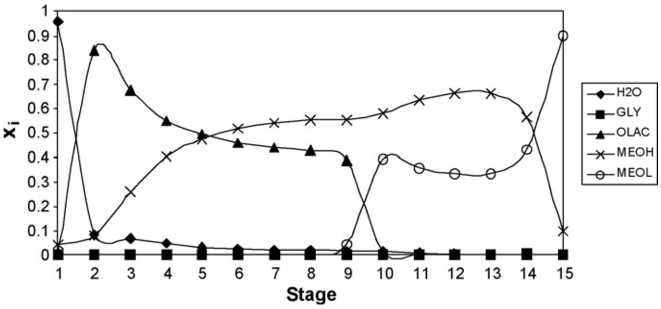

Fig. 10. Composition profiles of RD column 1 (mass fraction).

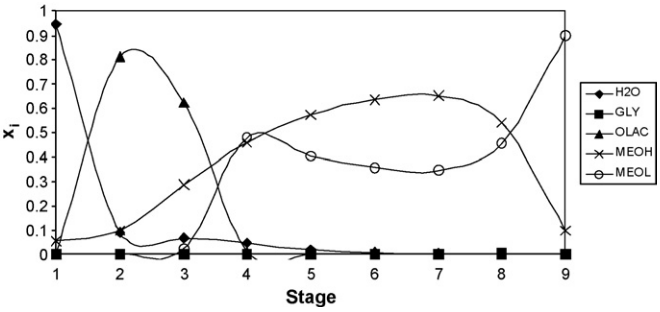

Fig. 11. Composition profiles of RD column 2 (mass fraction).

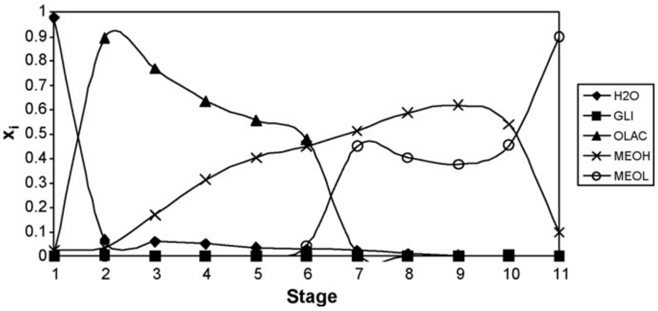

Fig. 12. Composition profiles of the TCRD column (mass fraction).

depicts the temperature profiles for the three reactive distillation systems. Notice that the temperatures of the systems do not surpass the upper limit of 300 °C, as needed for the production of high quality biodiesel fuel.

With respect to the practical issues involved in the implementation of a reactive Petlyuk column, Hernández et al. [20] describe how the reactive Petlyuk columns can be implemented as a reactive dividing wall column, and provide some key issues needed to build and operate the equipment.

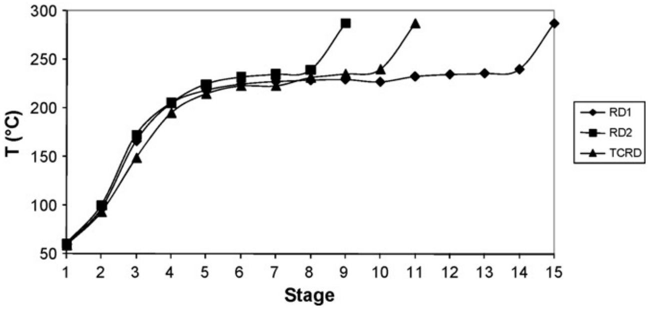

Fig. 13. Temperature profiles of the reactive distillation systems.

5. Conclusions

Biodiesel has the potential to be an alternative biofuel for transportation energy; however, it is currently hindered by its production cost and thus a higher price compared to petroleum fuel. Therefore, it is important to explore all the possibilities to reduce the production cost of the biodiesel process. Process intensification can provide a comprehensive research tool to contribute to the biodiesel production technology. Process intensification alternatives for the production of biodiesel fuel based on supercritical methanol technologies have been proposed in this work. This paper shows the feasibility of using both reactive distillation and thermally coupled reactive distillation schemes for biodiesel production at high pressure conditions. The configurations studied involve the use of reactive distillation and thermally coupled reactive distillation to carry out the esterification reaction and the purification of the product in the same shell. These alternatives have shown a significant reduction on energy consumptions when compared to a conventional process. A reactive distillation system by itself may produce high-purity biodiesel, but this alternative would imply a significant increase of the heat duty and also an increase in the product temperatures, so that isomerization could occur and the quality of the biodiesel would be reduced. Then, in the systems proposed in this work, the reaction is completed and only a partial separation of the products takes place in the reactive system, followed by a further purification at lower pressure.

5.1. Current work

The design method used allows to obtain basic designs for reactive Petlyuk systems. In our case studies, the optimization of the interconnecting flows has been done by a simple search algorithm, but because of the non-linearities of the system, the probability of obtaining local optima is high. Then, a more efficient optimization method is needed to analyze a wider optimization region for the interconnecting flows.

Furthermore, once a feasibility study has been completed, a formal optimization strategy is now needed to optimize the main design parameters of the thermally coupled reactive distillation column for biodiesel production (number of stages on the prefractionator and the main column, number and location of the reaction stages and the location of the interconnecting stages). This topic is the subject of undergoing research. We are modeling the reactive columns by using mathematical programming and are seeking the best column configurations for biodiesel production.

Finally, because of the small differences between the heat duty of the reactive distillation system and the thermally coupled reactive distillation system, further studies are required, including economic analysis and perhaps a controllability analysis of the dynamics of both schemes. Nevertheless, the processes proposed potentially represent feasible alternatives to reduce energy requirements and cost for biodiesel production.

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