Simulation study on biodiesel production by reactive distillation with methanol at high pressure and temperature: Impact on costs and pollutant emissions

Fernando Israel Gomez-Castro [a,b], Vicente Rico-Ramirez [a,*], Juan Gabriel Segovia-Hernandez [b], Salvador Hernandez-Castro [b], Mahmoud M. El-Halwagi [c]

[a] *Instituto Tecnologico de Celaya, Departamento de Ingenieria Quimica, Av. Tecnologico y Garcia Cubas S/N, Celaya, Guanajuato 38010, Mexico*
[b] *Universidad de Guanajuato, Campus Guanajuato, Division de Ciencias Naturales y Exactas, Departamento de Ingenieria Quimica, Noria Alta S/N, Guanajuato, Guanajuato 36050, Mexico*
[c] *The Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, United States*

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ABSTRACT

Recently, a two-step biodiesel production process which uses short-chain alcohols at supercritical conditions has been proposed. In addition, literature reports suggest that the COSMO-SAC thermodynamic model is a suitable alternative for the prediction of VLE for supercritical methanol/methyl esters mixtures. Thus, in this work a simulation study of the two-step supercritical method for the production of biodiesel is performed by using the COSMO-SAC model. Further, alternative system configurations for biodiesel production based on reactive distillation are proposed and their total emissions are compared to those corresponding to the conventional catalytic method. The study demonstrates the benefits of using reactive distillation for the esterification step and discusses the environmental impact of the supercritical production process. It has been found that the intensified alternatives reduce the emissions considerably and, through the reuse of the excess methanol, the emissions level of the supercritical process can be compared to those of the catalytic method.

1. Introduction

1.1. Biodiesel production

Extensive research efforts are being conducted to reduce the dependence of power and energy generation processes on fossil fuels. Biodiesel is an alternative fuel used as a substitute of petro diesel; it consists of a mixture of mono alkyl esters of long chain fatty acids produced from vegetable oils or animal fats (Al-Zuhair, 2007). It has several advantages over petroleum diesel: (i) it is renewable, (ii) it possesses a closed carbon cycle, (iii) it produces lower greenhouse gases emissions and (iv) it is biodegradable and non-toxic (Van Gerpen, 2005; Vicente, Martinez, & Aracil, 2004).

Biodiesel is usually produced by using a basic catalyst such as sodium hydroxide or potassium hydroxide; that reaction provides a relatively high reaction rate and low catalyst costs. However, alkaline catalysts are very sensitive to the presence of water and free fatty acids in the feedstock, which may cause saponification of the methyl esters. Further, the formation of soaps consumes catalyst and may cause the formation of emulsions, making more complex the purification of biodiesel. Acid and enzymatic catalysts may also be used to produce biodiesel, but the transesterification reaction catalyzed by acids occurs at a very slow reaction rate, and problems of corrosion are associated with the use of liquid acids (Lotero et al., 2005). In the case of process catalyzed by enzymes, the catalyst is expensive (Marchetti, Miguel, & Errazu, 2007) and the activity of immobilized enzymes might be inhibited by methanol and glycerol, which are present in the reaction (Ranganathan, Narasimhan, & Muthukumar, 2008). Thus, alternatives for biodiesel production have been proposed, including the use of heterogeneous catalysts in reactive distillation systems (De Lima da Silva, Garcia Santander, Batistella, Maciel Filho, & Wolf Maciel, 2010; Kiss, 2010, 2011; Kiss, Omota, Dimian, & Rothenberg, 2006; Marchetti, Miguel, & Errazu, 2008) and dividing wall reactive distillation systems (Kiss, Segovia-Hernández, Bildea, Miranda-Galindo, & Hernández, 2012), production in a reactive distillation system with two alcohols (Dimian, Bildea, Omota, & Kiss, 2009), production by reactive absorption (Kiss, 2009; Kiss & Bildea, 2011), or the use of special reactor technologies as membrane reactors, micro-channel reactors, microwave reactors, among others (Kiss & Bildea, 2012; Qiu, Zhao, & Weatherley, 2010). In the case of solid acid catalysts, such as vanadyl phosphate and sulfated zirconia, Semwal, Arora, Badoni, and Tuli (2011) reported that they present low reaction rates and unfavorable side reactions, but acid–base catalysts have some potential because they promote simultaneous esterification and transesterification. Among the recent

* Corresponding author. Tel.: +52 461 611 7575x156; fax: +52 461 611 7744.
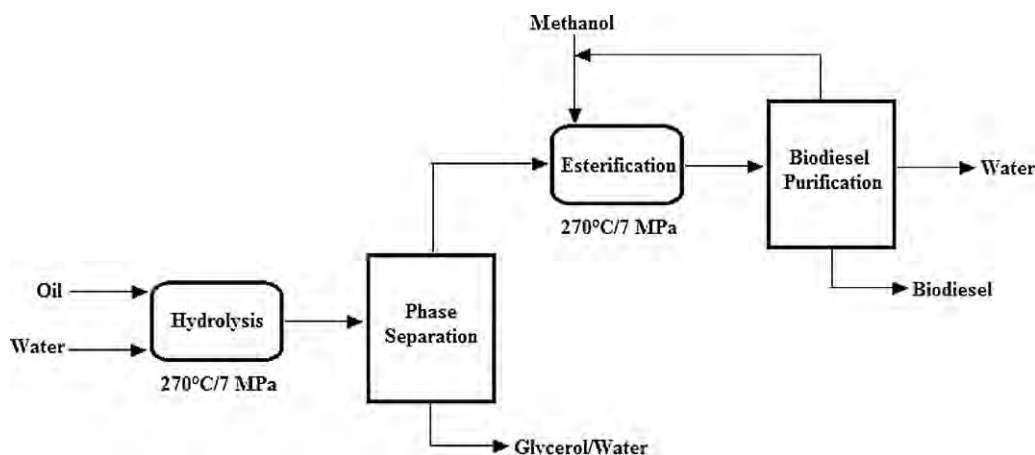*E-mail address:* vicente@iqcelaya.itc.mx (V. Rico-Ramirez).

Fig. 1. Simplified representation of the Saka–Dadan process.

alternatives, one of the special interests consists of the use of alcohols at supercritical conditions, or near to the critical point. The most common supercritical process consists on the trans-esterification of the triglycerides contained on vegetable oils and the simultaneous esterification of the resulting free fatty acids at 8.4–35 MPa and 320–350 °C, depending on the feedstock (Demirbas, 2009; Hawash, Kamal, Zaher, Kenawi, & El-Diwani, 2009; He, Wang, & Zhu, 2007; Kusdiana & Saka, 2001). Nevertheless, such conditions may cause the methyl esters to decompose into their *trans* isomer, causing bad cold flow properties of the fuel (Imahara, Minami, Hari, & Saka, 2008). An alternative supercritical process has been proposed by Saka (2005), in which two reaction steps are considered. First, free fatty acids are obtained from triglycerides by a hydrolysis reaction. Then, in a second reaction step, free fatty acids react with supercritical methanol to form methyl esters. That reaction takes place at extreme pressure and temperature conditions, 7 MPa (70 bar) and 270 °C (Saka, 2007; Saka, Kusdiana, & Minami, 2006), but it avoids the decomposition of methyl esters and keeps the benefits of the supercritical processes: (i) high reaction rates and yields, (ii) no undesirable reactions when treating feedstock with high compositions of free fatty acids and, since no catalysts are used, and (iii) simpler purification steps. The two-step method is commonly known as the Saka–Dadan process (see Fig. 1). Another important advantage of such processes for biodiesel production is that, since fatty acid composition on the feedstock does not affect the yield on the reaction, low price feedstock (such as used oils and fats) can be used to produce biodiesel, reducing up to 60–80% the total cost of biodiesel production (Glisic, Lukic, & Skala, 2009).

1.2. Previous studies on supercritical processes

Some studies have been conducted to compare the performance of the supercritical methods to that of the conventional catalytic method. Glisic and Skala (2009) compared the energy demand for the supercritical transesterification of triolein and the catalytic transesterification of the same triglyceride, claiming that the difference between the energy requirements of both processes is small. Kiwjaroun, Tubtimdee, and Piumsomboon (2009) analyze the environmental impact of the one-step supercritical process, concluding that the supercritical process causes higher impact on the environment than the conventional catalytic process, due mainly to its high requirements of methanol to obtain high yields in the trans-esterification reaction. On the contrary, from the economic point of view, West, Posarac, and Ellis (2008) report that the one-step supercritical process is superior to the catalytic processes. Furthermore, Marchetti and Errazu (2008) presented a study on the economics

of the supercritical process and established that, although the process has potential, making it economically profitable requires lower temperature and pressure conditions to reduce the pumping and heating requirements as well as the fixed cost of the reactors.

As an approach to reduce the energy requirements of the Saka–Dadan process, Gomez-Castro, Rico-Ramirez, Segovia-Hernandez, and Hernandez (2010, 2011) proposed the use of reactive distillation and reactive thermally coupled distillation, showing that these kinds of intensified systems may reduce energy requirements and costs in the process. Nevertheless, the NRTL-RK thermodynamic model used in that work for the prediction of VLE seems to be not accurate enough for the temperature and pressure conditions of the process. Thus, a better model should be considered to achieve more reliable results.

Glisic, Montoya, Orlovic, and Skala (2007) claim that the Redlich–Kwong–Aspen equation of state fits experimental data for the VLE for triglyceride/methanol mixtures under conditions of high pressure and temperature. Shimoyama, Abeta, and Iwai (2008) show that the combined use of the COSMO-SAC model with the Wong–Sandler mixing rule and the Redlich–Kwong–Soave equation has the ability to predict the VLE for different mixtures of alcohol/fatty acid methyl ester at high pressures. The COSMO-SAC (Segment Activity Coefficient) is a prediction method which describes the electric fields on the molecular surface of polarizable species. Calculations for the activity coefficients in a mixture consider the activity coefficients of charge segments at the molecular surface. The complete model can be found in the AspenPlus® user's manual.

1.3. Our simulation study

In this work, the conventional two-step process for biodiesel production at high pressure and temperature is analyzed through the use of the COSMO-SAC thermodynamic method which, according to the literature, is more reliable for the study of methanol systems at high pressure and temperature than the model considered in previous works (Gomez-Castro et al., 2011). Also, the feasibility of the use of reactive distillation systems (instead of the original reactor-separation sequence) is studied. We analyzed both the impact of reactive distillation on the production costs and its effect on emissions of different kinds of green house gases. A comparison between the results for the conventional catalytic process with a basic catalyst and both the conventional and the intensified two-step processes at high pressure and temperature is performed. In previous works (Gomez-Castro et al., 2011), the calculations of the environmental impact were limited to the emissions of carbon dioxide. In the present work, a more complete
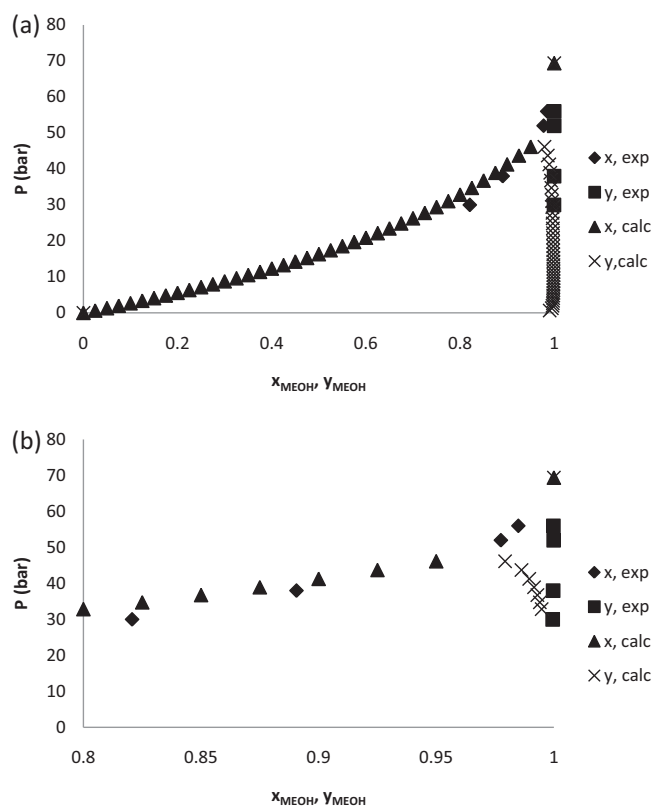
Fig. 2. Comparison of estimated and experimental data for methanol/triolein system at 503 K: (a) complete profile and (b) high composition zone.

Fig. 3. Comparison of estimated and experimental data for methanol/methyl oleate system at 548 K: (a) complete profile and (b) high composition zone.

analysis of environmental impact is presented for the conventional supercritical process as well as for the intensified (those including reactive distillation) processes. The environmental impact is analyzed for different scenarios, considering the emissions due to the fuel needed to satisfy the energy requirements of the processes as well as the emissions due to the electricity generation and those corresponding to the production of the methanol used as reactant.

2. Vapor–liquid equilibrium calculations

As a step previous to the simulations, the results for the VLE calculations obtained by the thermodynamic models considered in this work were tested against experimental data. In particular, the equilibrium compositions for binary pairs obtained by using Aspen Plus were compared with experimental data available in the literature.

Fig. 2 shows a comparison between the results of the Redlich–Kwong–Aspen (RKA) equation of state and the experimental data provided by Glisic et al. (2007) for the triolein/methanol mixture at 503 K; such value is the highest temperature for which experimental data is available. It can be seen that the predictions of the RKA equation of state properly fit the data. Therefore, this model is assumed as appropriate to simulate the hydrolysis stage of the process.

With respect to the esterification reaction step, the three main components involved are methyl ester, methanol and water. The equilibrium calculations and the experimental data for the methyl oleate–methanol system are shown in Fig. 3. Experimental data have been taken from the work of Fang et al. (2008). In this case, VLE calculations were performed by using the COSMO-SAC model, which is available on Aspen Plus and uses the information provided by Mullins et al. (2006) for the parameters required by the model. The COSMO-SAC model accurately predicts the vapor phase
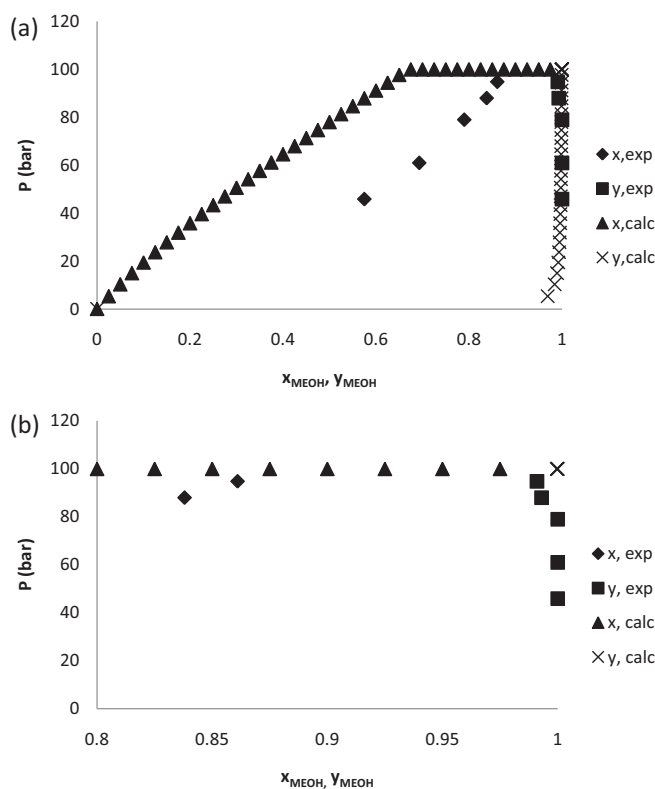
compositions for methanol, but not those of the liquid phase. Similarly, Fig. 4 shows the VLE data for the methanol/water system at 423 K. Experimental values were taken from Horstmann, Mougin, Lecomte, Fischer, and Gmehling (2002) at the highest temperature reported. Unfortunately, no experimental data was found for the binary system methyl oleate/water. In general, the equilibrium data predicted by the COSMO-SAC model are very close to the experimental data (the liquid phase compositions in the methanol/methyl oleate system are exceptions). Therefore, the model is considered as acceptable for comparison purposes. The predicted residual curve map for the ternary system methanol/water/methyl oleate is shown in Fig. 5 at 70 bar. The separation appears to be feasible, but large amounts of energy are required to reach high purities. Particularly, the most difficult separation corresponds to the binary pair methanol–water.
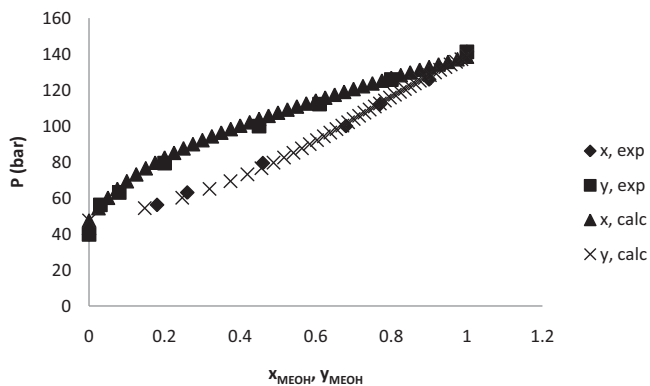

Fig. 4. Comparison of estimated and experimental data for methanol/water system at 423 K.
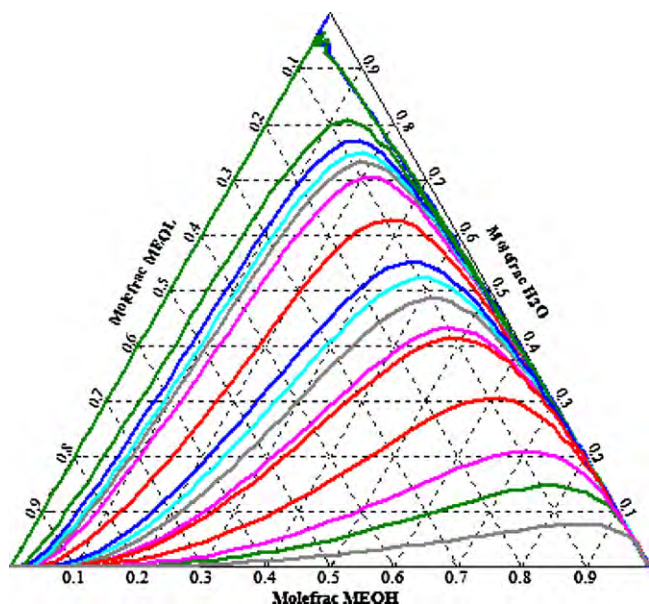
Fig. 5. Calculated residual curves for the system methanol/water/methyl oleate at 70 bar.

3. Pollutant emissions analysis

Calculations of pollutant emissions generated by the two-step supercritical method for biodiesel production and the related processes have been performed by using the database provided by the free software GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model) (Wang, 1999). The following contributions to the pollutant emissions have been considered:

1. Emissions due to the fuel burnt to generate the steam that provides the thermal energy required by the process.
2. Emissions due to the production of the fuel used to generate steam.
3. Emissions due to the generation of electricity required by the process.
4. Emissions due to the production of the methanol used as the main reactant on the process.

The use of natural gas as fuel is assumed to generate the steam and to produce methanol. Electricity is considered as obtained from a distribution network in the United States. The equations required for the calculation of emissions are obtained using as a basis the data found in GREET (Wang, 1999) for a basic catalyst process, and

applied for the high temperature processes. The total emissions of a pollutant X_T are then are calculated as:

$$1 \times 10^6 X_T = X_{QP} + X_E + X_{MEOH} \tag{1}$$

where X_{QP} are the emissions caused by the production and burnt of natural gas, X_E are the emissions due to the electricity production and X_{MEOH} are the emissions caused by the methanol production. Each term of Eq. (1) is calculated as follows:

$$X_{QP} = \dot{Q}_{NG}[(\%_{LB}X_{NG,LB}) + (\%_{SB}X_{NG,SB}) + X_{P,NG}] \tag{2}$$

$$X_E = \dot{E}[X_{E,FP} + X_{E,FB}] \tag{3}$$

$$X_{MEOH} = \dot{M}[f_L X_{NG,M} + X_{EN,M}] \tag{4}$$

$\dot{Q}_{NG}$ is the energy (per pound of biodiesel product) to be delivered by the natural gas to provide the steam for the biodiesel production process. Since steam is required at two different temperatures, two boiler sizes have been considered for the generation of steam; a large industrial boiler and a small industrial boiler. In Eq. (2), $\%_{LB}$ and $\%_{SB}$ are the percent of use for the large boiler and the small boiler, respectively. We assume both values to be 50%, i.e., each boiler delivers exactly half of the energy requirements of the process. $X_{NG,LB}$ and $X_{NG,SB}$ are the emissions due to the burning of natural gas in a large boiler and in a small boiler, respectively. $X_{P,NG}$ are the emissions due to the production of the natural gas. $\dot{E}$ represents the electricity required by the process per pound of biodiesel. $X_{E,FP}$ are the emissions due to the production of fuel for the generation of electricity and $X_{E,FB}$ are the emissions due to the burning of that fuel in the power plant. $\dot{M}$ is the energy content of the methanol required by the biodiesel production. $X_{NG,M}$ are the emissions due to the production of the natural gas used for producing the methanol. $X_{EN,M}$ are the emissions caused by burning fuel to generate the energy required by the methanol production process. Finally, f_L is a factor which indicates the energy losses in the production of the natural gas from which the methanol is obtained; this value is assumed as 1, i.e., no losses are considered. The contributions to the total emissions for a given pollutant are shown in Fig. 6. Standard values for emissions corresponding to the different contributions have been taken from the database of the GREET software (Wang, 1999). Pollutants under analysis are: volatile organic compounds (VOC), carbon monoxide (CO), nitrogen oxides (NO$_x$), particulate matter of less than 10 μm (PM10), particulate matter of less than 2.5 μm (PM2.5), sulfur oxides (SO$_x$), methane (CH$_4$), nitrous oxide (N$_2$O) and carbon dioxide (CO$_2$).

4. Case study

The Saka–Dadan process is assumed as our base case. Simulations have been performed in the Aspen Plus process simulator. The
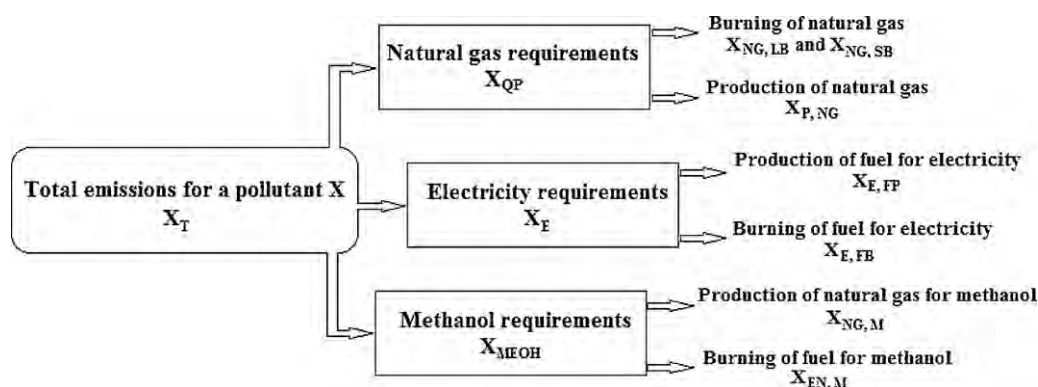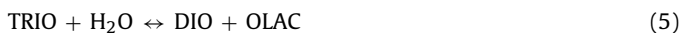

Fig. 6. Contributions to the total emissions of a given pollutant.

oil used as feedstock is assumed as pure triolein, since that component is contained in a high proportion in many vegetable oils (Demirbas, 2008). The feedstock is first pressurized from atmospheric conditions to 70 bar and then heated to 270 °C. Then, triolein is hydrolyzed with water at these sub-critical conditions (for water, $T_c = 374$ °C, $P_c = 221$ bar), following three reaction steps:

$$TRIO + H_2O \leftrightarrow DIO + OLAC \qquad (5)$$

$$DIO + H_2O \leftrightarrow MONO + OLAC \qquad (6)$$

$$MONO + H_2O \leftrightarrow GLY + OLAC \qquad (7)$$

where OLAC stands for oleic acid and TRIO, DIO and MONO correspond to triolein, diolein and monolein, respectively. The global hydrolysis reaction can then be stated as:(8)$TRIO + 3H_2O \leftrightarrow GLY + 3OLAC$

Once the oleic acid is obtained, it reacts with methanol at the same conditions of the hydrolysis reaction, which are close to the critical point for methanol ($T_c = 239$ °C, $P_c = 80.9$ bar), obtaining methyl esters (esterification step). The reaction is:

$$OLAC + MEOH \leftrightarrow MEOL + H_2O \qquad (9)$$
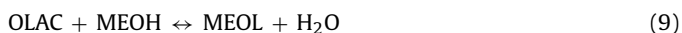
In Eq. (9) MEOH is methanol and MEOL is methyl oleate. It is important to make clear that, on the esterification step, only methanol is at supercritical (or near to the critical point) conditions.

5. Simulation approach

5.1. Hydrolysis step

The hydrolysis step is common to all of the processes we considered; thus, it will be presented in a single section. The three components considered in the feedstock (fed at 1 bar and 298.15 K) are the triolein (45.89 kmol/h), water (2476.45 kmol/h) and methanol (412.77 kmol/h). The three streams are pressurized up to 70 bar and then heated up to 270 °C. The water and the triolein enter to the hydrolysis reactor, which is simulated as a tubular reactor. Water and triolein react in a 1/1 volumetric ratio to shift the equilibrium to the products (Minami & Saka, 2006). The reaction occurs at 70 bar and 270 °C, and a first order kinetic model is considered for the hydrolysis reaction:

$$\frac{dC_{OLAC}}{dt} = k_H C_{TRIO} \qquad (10)$$

where the value of k_H has been taken as 2.60×10^{-3} s^{-1} at 270 °C (Minami & Saka, 2006). Activation energy for the hydrolysis reaction has been calculated as 63,553.05 J/mol. Since water is fed in excess to promote the reaction to the side of products, its effect on the reaction rate is taken into account in the rate constant. Furthermore, the inverse reaction effect has been assumed as negligible. The Redlich–Kwong–Aspen equation of state is used to simulate the hydrolysis reactor. Once the hydrolysis takes place, the stream leaving the reactor enters a decanter, where the oil phase is separated from the aqueous phase. The decanter is simulated using the UNIFAC model to predict the formation of two liquid phases. The aqueous phase leaving the decanter contains water and glycerol, which requires a purification step. The oil phase then goes to the esterification step.

5.2. Esterification step in the conventional process

The stream containing the oleic acid enters the esterification section and reacts with methanol. The alcohol feed rate is required to accomplish a 0.9/1 volumetric ratio of methanol/fatty acid to obtain high yields (Minami & Saka, 2006). A first-order kinetic model has been used to simulate the esterification reaction (Gomez-Castro et al., 2011):

$$\frac{dC_{MEOL}}{dt} = k_E C_{OLAC} \qquad (11)$$

The reaction rate constant for esterification, k_E, is 2.90×10^{-3} s^{-1} at 270 °C (Saka, 2007), and a value of 75,372.23 J/mol has been calculated for the activation energy. The vapor–liquid equilibrium for the esterification step is calculated using the COSMO-SAC model. Two alternatives have been considered for the simulation of the esterification step on the conventional supercritical process. In the first one, the reaction takes place in a single shell until a conversion higher than 99% is reached, then the biodiesel is purified and the unreacted methanol separated from water for its possible reuse (see Fig. 7, configuration SR). Purification of biodiesel takes place in a flash drum at atmospheric pressure, while separation of methanol is performed in a distillation column. The second alternative involves two reactors with an intermediate separation step; that configuration is designed to increase the concentration of oleic acid and, as a consequence, the reaction rate on the second reactor, where a global conversion higher than 99% is expected to be achieved. Following the reaction step, purification of biodiesel and recovery
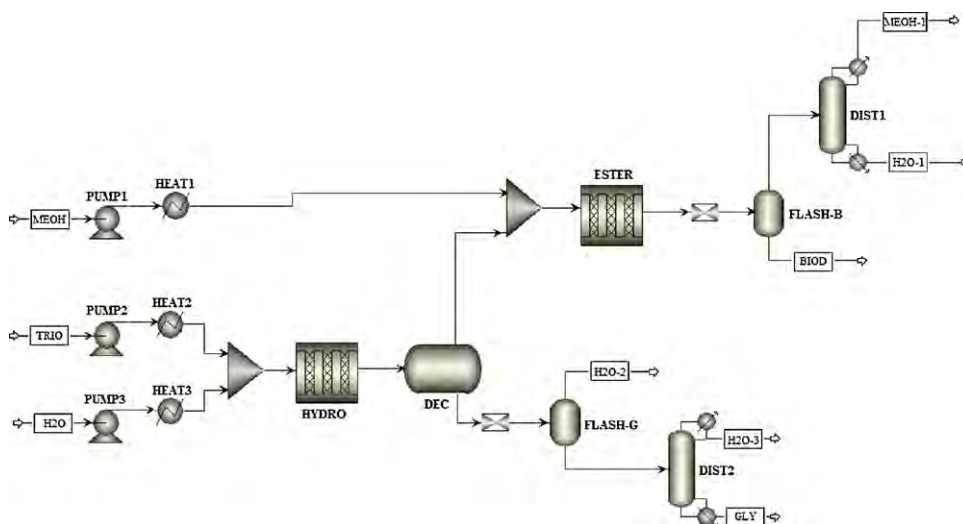

Fig. 7. Process flowsheet for biodiesel production with supercritical methanol using a single esterification reactor.
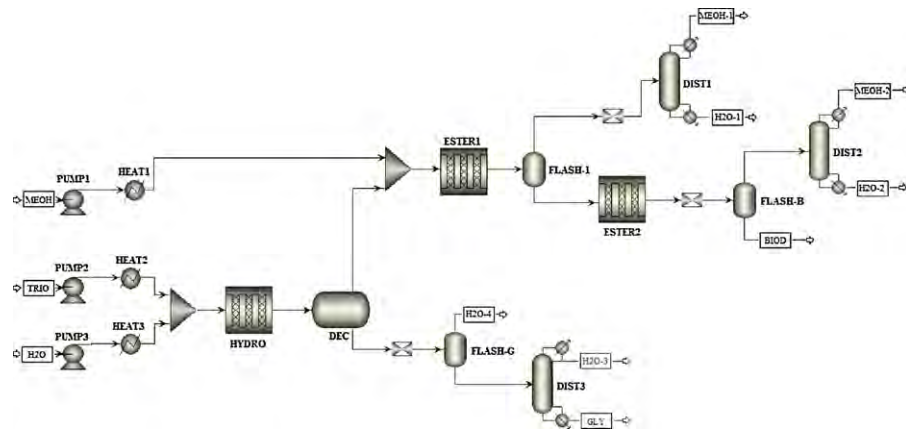
Fig. 8. Process flowsheet for biodiesel production with supercritical methanol using two esterification reactors.

of methanol occurs. Fig. 8 shows a flowsheet of this process, identified as flowsheet TR. The stream leaving the first reactor enters a flash drum, where the excess of water and methanol is vaporized and then purified. The liquid stream leaving the flash drum enters the second esterification reactor; the conditions on the flash drum are established to allow this stream containing enough methanol to keep the volumetric ratio close to 0.9/1 relative to the remaining oleic acid.

The distillation columns designs were obtained through Aspen Plus simulation; such designs were further analyzed in terms of its number of stages and feed stream to reach the lowest possible energy requirements.

5.3. Esterification step with reactive distillation

The use of a reactive distillation column is proposed to reduce energy requirements and equipment costs on the esterification step. Such a column performs simultaneously reaction (9) and the separation of the excess methanol and water from biodiesel. Nevertheless, given the reaction conditions, reaching a high purity product involves an energy intensive operation. Thus, an important design parameter is the purity for the bottoms product (methyl oleate). Its maximum value has to be specified so that the need for excessive energy requirements (which may have a negative impact on the operation costs of the process) is avoided. In this work, mass purities of 80% and 90% for the methyl oleate have been tested. Once the reaction takes place, the bottoms stream is further

purified in a flash drum to reach the purity for biodiesel established by international standards (Vicente et al., 2004); the methanol and water leave the flash as the vapor product and enter a distillation column, where methanol is recovered. On the other hand, the top product of the reactive distillation column contains water and methanol; this stream enters a distillation column where methanol is obtained as top product. The completed process is presented in Fig. 9. The reactive distillation (RD) configurations tested in this paper are identified as RD80 and RD90 depending on the mass purity of methyl oleate considered.

5.4. Purification of glycerol

The aqueous phase leaving the decanter consists mainly of water and glycerol, which must be further purified. Purification levels will depend on the use of glycerol. In this work, high purity for glycerol (99.5 mol%) is specified in order to determinate the impact of glycerol purification on the total annual costs for the whole process. Since there is a large amount of water in the stream, a flash drum is first used to vaporize the excess of water. Then, the liquid stream leaving the flash is fed to a distillation column, where the high-purity glycerol is obtained as the bottoms product.

5.5. Costs estimation

Estimation of the processing costs considers both the investment required for the equipment and the variable costs of utilities
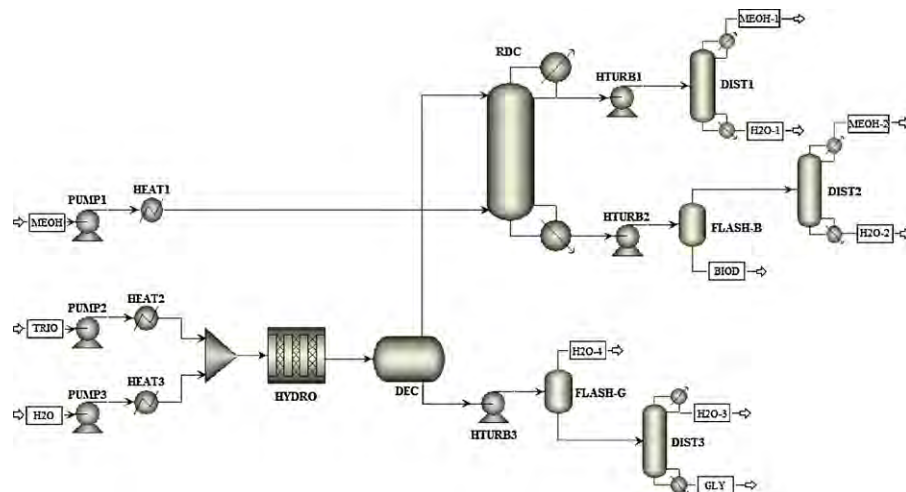

Fig. 9. Process flowsheet for biodiesel production with supercritical methanol using a reactive distillation column.

Table 1
Energy requirements for pumps and heat exchangers.

Equipment	PUMP1	PUMP2	PUMP3	HEAT1	HEAT2	HEAT3
Electricity (kW)	79.76	336.23	174.47	–	–	–
Heat duty (MJ/h)	–	–	–	20,014.2	18962.6	56173.9

(water, steam and electricity). Costs for equipment have been estimated by the Guthrie method (Turton, Bailey, Whiting, & Shaeiwitz, 2009) and updated by using the Chemical Engineering Cost Index corresponding to May 2010, with a value of 558.2. The values used for the unitary cost of the utilities are given in Appendix A (Turton et al., 2009). Total annual cost (TAC) is thus given by:

$$\text{TAC} = \frac{C_F}{t} + C_V \tag{12}$$

where C_F represents the fixed costs (equipment), C_V stands for the variable costs (utilities) and t is the expected payback period (time for the return of an investment) which, for calculation purposes, has been assumed as 5 years.

6. Results

6.1. Simulation of the hydrolysis step

As mentioned in the previous section, hydrolysis step is the same for all of the alternative configurations proposed; thus, the results are presented here. Table 1 provides the energy requirements for the pumps and heat exchangers, including those corresponding to the pressurization and heating of methanol. A large amount of electricity is required on the triolein pump, since it is the fluid with highest viscosity involved in the process. The estimated parameters for the hydrolysis reactor are shown in Table 2. In the decanter, about 99.9% of the oleic acid from the feed stream is recovered to the oil stream, while a 98.2% of the water and a 99.5% of the glycerol goes to the aqueous stream. The oil stream is fed to the esterification step; the aqueous stream goes to the glycerol purification step.

6.2. Simulation of the esterification step: conventional process

Results for both of the alternatives considered for the conventional esterification step are discussed here. Table 2 provides the design parameters of the esterification reactors for both cases (one-reactor and two-reactor systems). The parameters information for the flash drums used in both processes is presented in Table 3. Results for the distillation columns are shown in Table 4. The unit named FLASH-B is the flash drum where pure biodiesel is obtained under atmospheric pressure; FLASH-1 is used to reduce the concentration of water on the stream leaving the first esterification reactor (ESTER1) in the two-reactor approach. The distillation units are used to recover methanol. High purity methanol is achieved in both processes. It is clear that energy requirements due to distillation are considerably higher when using a single reactor, because

the whole separation of the binary mixture methanol–water takes place in just one conventional column.

6.3. Simulation of the esterification step involving reactive distillation

The design of the reactive distillation column for an esterification reaction is not an easy task; mainly due to the number of components involved in the reaction-separation operations and the complexity of the thermodynamic model under consideration. Thus, the design of the reactive distillation systems has been performed by a parametric analysis.

First, the goal of the design is obtaining a purity of methyl oleate of 90% mass at the bottoms of the column, with the unreacted methanol and the water produced leaving at the top. An initial design including 13 stages was tested; the four stages at the bottom section (excluding the reboiler) were assumed as reactive stages. This design was then modified to find a structure which allows reducing the heat duty of the column. The effect of the location of the oleic acid feed stream on the energy requirements is presented in Fig. 10(a). Similarly, Fig. 10(b) shows the effect of the location of the methanol feed stream. Location of the feed streams is limited by both the phase equilibrium and the kinetics of the reaction; thus, only a few points are feasible to reach the conversion and purities established as design specifications. Interestingly,
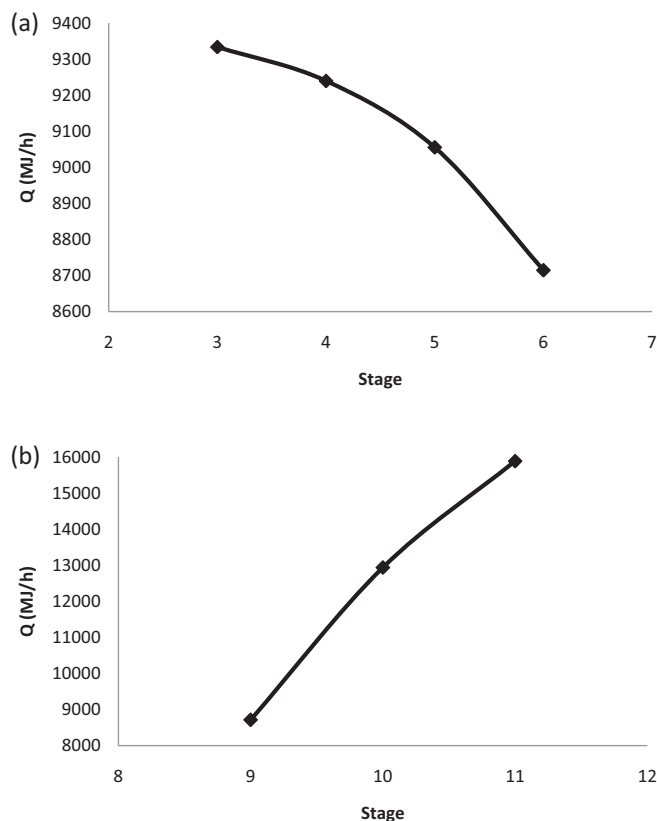
Fig. 10. Variation in energy requirements in the reactive distillation column with respect to the location of the feed streams: (a) oleic acid feed stream and (b) methanol feed stream.

Table 2
Design parameters of the conventional reactors.

	Hydrolysis	Esterification		
		SR	TR	
		ESTER	ESTER1	ESTER2
Length (m)	28.96	27.43	17.37	15.24
Diameter (m)	3.05	2.44	2.13	1.52
Residence time (h)	0.6326	0.4451	0.2255	0.2804
Heat duty (MJ/h)	11,374.1	10,774.2	10,045.7	2266.8
Conversion	99.83%	99.03%	90.48%	92.58%
Global conversion	99.83%	99.03%	90.48%	99.29%

Table 3
Design parameters of the flash drums.

| | SR | TR | | RD90 | RD80 | ALL |
	FLASH-B	FLASH-1	FLASH-B	FLASH-B	FLASH-B	FLASH-G
Temperature (°C)	158	260	165	160	160	105
Pressure (bar)	1.00	69.08	1.00	1.00	1.00	1.00
Vapor fraction	0.7641	0.5307	0.4983	0.5332	0.7263	0.8883
Heat duty (MJ/h)	−14,254.1	−1729.7	−11,715.5	−9815.4	−7614.6	47,313.2

Table 4
Results for the distillation columns in the esterification section of the conventional process and the glycerol purification step.

| | SR | TR | | ALL |
	DIST1	DIST1	DIST2	DIST3
Number of stages	13	17	17	16
Feed stage	10	12	12	5
Diameter (m)	2.03	1.54	1.02	0.88
Height (m)	3.72	4.46	4.46	4.28
Pressure on top (bar)	1.00	1.00	1.00	1.00
Condenser	Partial-vapor	Partial-vapor	Partial-vapor	Partial-vapor
Purity of methanol	99.5%	99.5%	99.5%	99.5%
Purity of water	98.5%	98.5%	98.5%	98.5%
Reflux ratio	2.2753	1.7499	1.6083	0.0086
Reboiler duty (MJ/h)	13,071.6	3591.6	2282.2	11059.5

the optimal location of the feed streams is at the top of the reactive zone. This may be due to the high reaction rate, which causes the reaction to take place immediately once the methanol is fed and has contact with the oleic acid, with some additional conversion on the lower stages. Furthermore, there are three stages between the two feed streams. Decreasing the number of these intermediate stages causes the drying of some of the stages of the column.

The effect of the number of reactive stages on the thermal duty is shown in Fig. 11(a). A large number of reactive stages increases the energy requirements of the system, while a number of reactive stages lower than 4 also causes drying of the column. It seems that the minimum number of reactive stages required to achieve the conversion that results in the desired purity is precisely 4. In a similar way, Fig. 11(b) shows the effect of the number of non-reactive stages on the energy requirements. A local optimum exists at a number of non-reactive stages equal to 4. For a higher number of stages, energy requirements increase first and then decrease. Since the decrease on the thermal duty is not significant for a large number of non-reactive stages, the number of non-reactive stages has been specified as 4 in our design. Finally, Fig. 12 shows the effect of the residence time for the liquid phase. As the residence time changes, conversion remains at 99.96% and the diameter of the column varies only slightly. It is clear that a residence time of 0.3 h allows the lower energy requirement for the column, although the variation is not considerable. 0.3 h was selected as the residence time in this work. Residence times lower than 0.3 h do not achieve the desired conversion and purity for methyl oleate.

Once a feasible design for the reactive column has been achieved, the design is tested with two specifications for the purity of the methyl ester at the bottoms product, 80% and 90% mass purity, respectively. The design parameters and some of the results of the simulations are shown in Table 5. Moreover, after the reactive distillation column, additional equipment is required for further

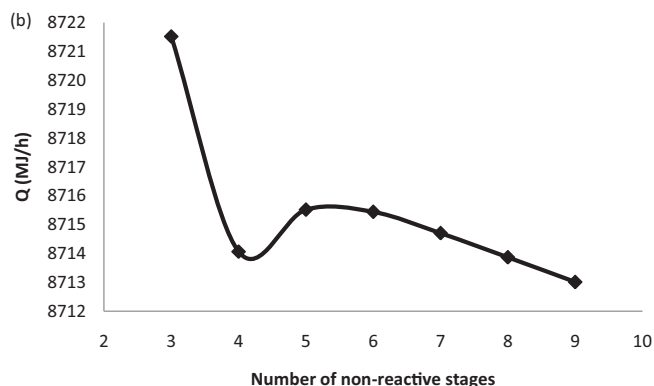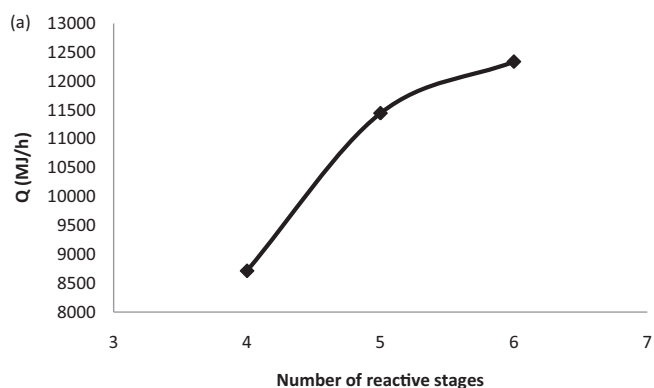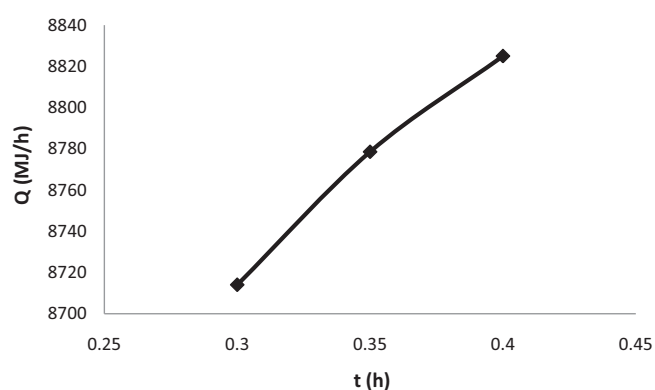Fig. 11. Effect of the number of stages on the energy requirements of the reactive distillation column: (a) reactive stages and (b) non-reactive stages.

Fig. 12. Effect of residence time for the reactive stages on the energy requirements of the reactive distillation column.

Table 5
Results for the reactive distillation columns in the esterification section of the intensified process.

	RD90	RD80
Number of stages	10	10
Oleic acid feed stage	3	3
Methanol feed stage	6	6
Reactive stages	6–9	6–9
Residence time (h)	0.3	0.3
Diameter (m)	1.36	1.28
Height (m)	3.16	3.16
Pressure on top (bar)	70	70
Condenser	Total	Total
Purity of methyl oleate	90% mass	80% mass
Reflux ratio	0.1194	0.1464
Reboiler duty (MJ/h)	8714.0	5442.9

Table 7
Comparison of the obtained biodiesel fuel with international standards.

	Standard	SR	TR	RD80	RD90
Triolein (wt%)	0.2 max	0.17	0.17	0.17	0.17
Water (vol%)	0.05 max	0.011	0.009	0.008	0.008
Free glycerol (wt%)	0.02 max	0.04	0.04	0.04	0.05
Total glycerol (wt%)	0.25 max	0.20	0.21	0.22	0.22
Methanol (wt%)	0.2 max	0.18	0.16	0.18	0.19

Table 8
Costs estimation results (USD $\times 10^3$/year).

	Whole process			Esterification		
	C_F	C_V	TAC	C_F	C_V	TAC
SR	2501.5	23,288.4	25789.9	1035.4	8948.7	9984.1
TR	2154.5	21725.7	23880.2	664.9	7645.3	8310.2
RD90	1873.3	20780.7	22654.0	344.7	6814.9	7159.6
RD80	1858.8	19,395.8	21,254.6	330.5	5550.9	5881.4

purification of the products. The design parameters for the flash drums used in both cases are shown in Table 3. Table 6 presents the results for the distillation columns used to purify the remaining methanol. Notice that, when purity of methyl oleate in the reactive distillation column is reduced, the DIST2 distillation column receives a higher feed flowrate, thus requiring a slightly higher energy input.

6.4. Purification of glycerol

Since the stream leaving the decanter has a high concentration of water, the purification of glycerol has to be performed in two steps. First, the excess of water is eliminated in a flash drum. Results for this flash unit are shown in Table 3; these results are common for all the configurations analyzed. Table 4 provides the results for the distillation column used to purify the glycerol up to 99.5% mol. The separation of the excess of water results in a large energy demand. The flash drum contributes with 81% of the total energy requirements on the glycerol purification section, achieving a purity of 17.4 mol% (51.8 wt%).

Table 7 shows a comparison of the biodiesel obtained on the simulations with respect to international standards (Vicente et al., 2004). It can be seen that the biodiesel satisfies almost all of the standard requirements, only exceeding the free glycerol contents. Nevertheless, the total glycerol requirements are also satisfied. Energy requirements for the different sections of the alternative configurations (SR, TR, RD90 and RD80) are the same, except for the esterification step. The hydrolysis step involves mainly the heating requirements on the hydrolysis reactor; such requirements are equal to 11,374.1 MG/h in the four configurations. Similarly, the glycerol purification step considers the flash drum and the distillation column and requires 58,246.9 MJ/h also for the four configurations. Finally, the esterification step involves the reaction and the subsequent purification. Requirements for this step

are different for each configuration: 23,845.9; 18,186.4; 15,679 and 11,143.3 MJ/h for SR, TR, RD90 and RD80, respectively.

In the case of the conventional process, the two-reactor configuration presents smaller energy requirements. In addition, the use of a reactive distillation column further reduces the energy demand. The reduction is more significant when the mass purity specification for the product is low. Moreover, the purification of glycerol is the step with the higher impact on energy demand, requiring about 62–72% of the total energy needed by the process. That is mainly due to the large amount of water to be removed from a small proportion of glycerol.

Table 8 shows the results of the costs estimations. The total cost of the whole process as well as the individual cost for the esterification step is presented. In terms of total annual cost, using two esterification reactors is better than using a one-reactor configuration; that is because of the high investment required for installing a large reactor to achieve the desired conversion. The use of reactive distillation reduces considerably the total annual cost for the esterification step; a more significant reduction results when a mass purity of 80% for the methyl oleate is obtained in the reactive distillation column. However, the savings for the intensified configurations are smaller when the whole process is considered. That obeys to the fact that the glycerol purification step consumes a high proportion of the total energy requirements for the whole process, and energy costs have a great impact on the total annual cost, with a contribution of 90% or higher of the TAC.

Next, we provide a comparison between the processes obtained in this work and those proposed by Gomez-Castro et al. (2011). The results obtained for the conventional process using the esterification reactors are not quite different. Nevertheless, given the importance of the ELV calculations for the design of reactive distillation systems, a subtle but important difference on the designs

Table 6
Results for the distillation columns in the esterification section of the intensified process (methanol purification step).

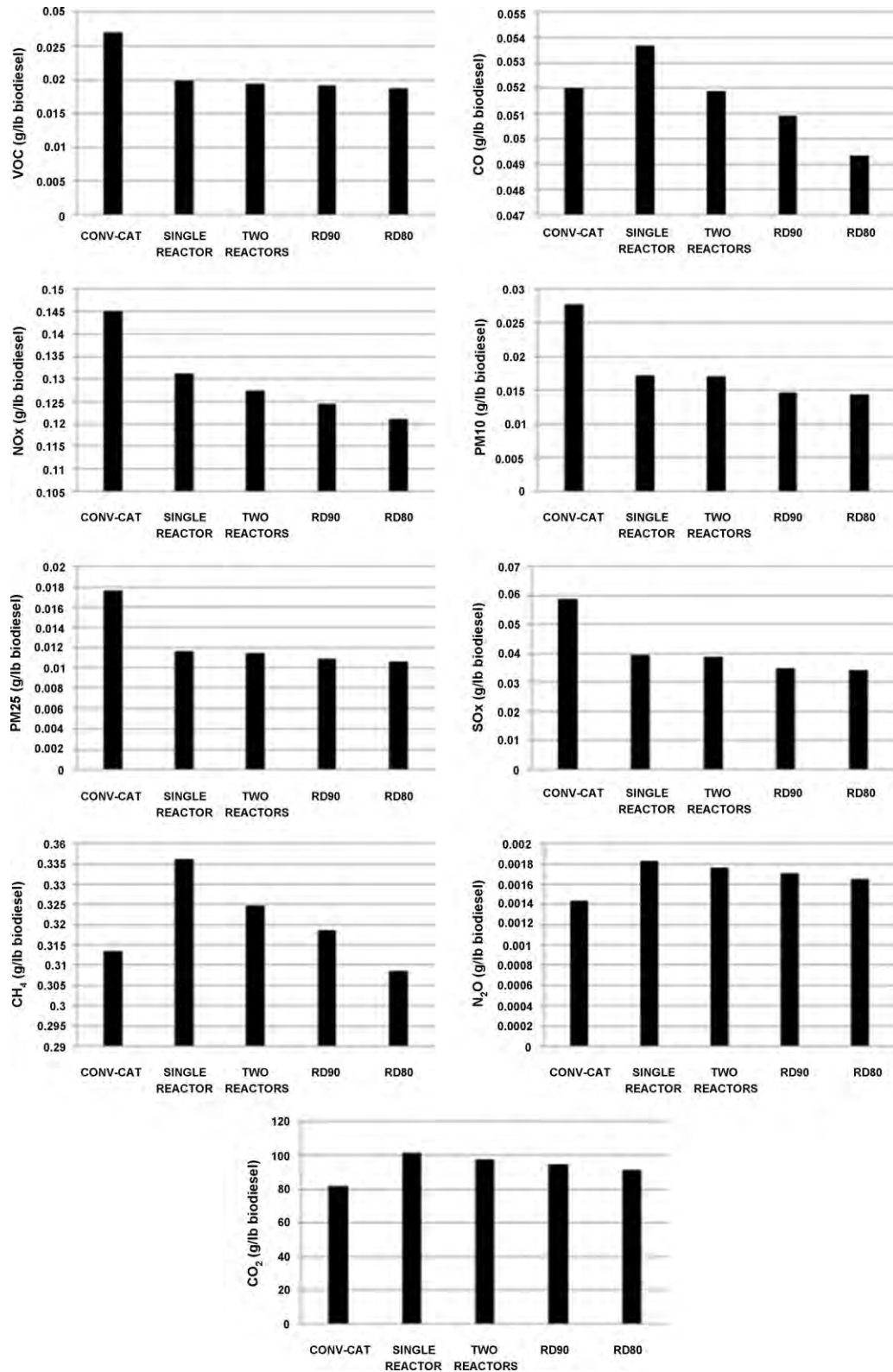|	RD90			RD80		
	DIST1	DIST2		DIST1	DIST2	
Number of stages	20	17		20	20	
Feed stage	16	12		15	15	
Diameter (m)	1.29	1.11		0.60	1.63	
Height (m)	5.02	4.46		5.02	5.02	
Pressure on top (bar)	1.00	1.00		1.00	1.00	
Condenser	Partial-vapor	Partial-vapor		Partial-vapor	Partial-vapor	
Purity of methanol	99.5%	99.5%		99.5%	99.5%	
Purity of water	98.5%	98.5%		98.5%	98.5%	
Reflux ratio	1.2673	1.4517		1.8378	1.3366	
Reboiler duty (MJ/h)	3980.7	2984.4		764.9	4935.4	

Fig. 13. Emissions of the conventional and supercritical process with methanol recirculation.

has been found by using the NRTL model and using the COSMO-SAC model. According to the results reported by using the NRTL model (Gomez-Castro et al., 2011), it is possible to perform a separation in a reactive distillation column with a side stream and then use flash drums to purify the methanol. Nevertheless, when using the COSMO-SAC model, it is predicted that two additional distillation

columns must be used to separate the methanol–water mixture obtained from the top and the side stream of the reactive distillation column. Thus, in this work the use of conventional reactive distillation systems is proposed as a better alternative.

NRTL parameters are usually fitted from experimental data. However, there are no experimental data available for all of the

binary pairs of the components involved in the process at the conditions of the reaction. Further, COSMO-SAC predictions are based on quantum chemistry, and the parameters required for its use are of molecular and electronic nature and do not depend on the temperature. Thus, if those parameters are available (as it occurs on the simulator for the compounds under analysis), the COSMO-SAC mode represents a useful alternative for the prediction of VLE at the conditions needed in the process. In summary, since the NRTL model depends on its parameters, which strongly depends on the temperature, the predictions obtained by this model may be affected by the changes on the temperature occurring across the process. Thus, the predictions obtained by the COSMO-SAC model are expected to be more reliable.

6.5. Estimation of emissions

Given the large amount of methanol required to perform the esterification reaction, it results mandatory to recycle the excess methanol recovered after the esterification step. Otherwise, the use of fresh methanol to satisfy the reactant requirements would be translated into high costs and high pollutant emissions for the analyzed process. Emissions for the different pollutants under study are presented in Fig. 13, where CONV-CAT refers to the emissions for the conventional catalytic process. Since requirements for fresh methanol are low, pollutant emissions due to the production of fresh methanol are also low and supercritical processes shows lower emissions than the catalytic process for the most of the pollutants, except for the nitrous oxide and carbon dioxide. Nevertheless, it is important to recall that, additionally to the analyzed pollutants, there are also emissions of wastewater from the purification stages on the catalytic process, which does not occur on the supercritical processes. In the case of methane, only the process with the reactive column RD80 shows lower emissions than the rest of the alternatives. In summary, it is clear that, if methanol is reused, the levels of emissions for the supercritical process are comparable with those of the conventional catalytic process.

7. Conclusions

A simulation analysis of a biodiesel production process with methanol at high pressure and temperature is presented. The study considers aspects of energy, costs and environmental impact. Modifications to the original process have been proposed and tested; the modifications proposed consist on the intensification of the esterification section by using reactive distillation systems. Alternative configurations analyzed include the use of a single esterification reactor and two reactors with a purification step between them. It has been found that, in terms of energy requirements for the conventional alternatives, the use of two reactors represents lower energy requirements for the feed flow rate considered, possibly due to the increasing on the concentration of oleic acid when the by-product water is removed on the purification step between the reactors. Moreover, using a reactive distillation column further reduces the total heat input required by the process, due to the constant removal of the by-products and the excess methanol. In terms of costs, a similar result was found. The use of a reactive distillation column with a mass purity of 80% for the biodiesel represents the lower costs for the process. This implies that reactive distillation is a useful and an interesting alternative for supercritical process only as a pre-purification step, since achieving high purities for the products, even when is feasible, requires considerably high thermal energy input and, as a consequence, high production costs.

Analysis of environmental impact for the studied process shows that emissions due to the production of methanol have a high impact on the total emissions for the supercritical processes; thus, recycling excess methanol is mandatory to allow the supercritical method emissions being comparable or even lower than those of the conventional catalytic method. Using a single reactor for the esterification also results in higher emissions, because of large energy requirements. When using reactive distillation systems, the pollutants emissions are reduced with respect to the conventional supercritical processes, especially for carbon monoxide, nitrogen oxides, sulfur oxides and methane.

When compared to the catalytic process, emissions of methane, nitrous oxide and carbon dioxide of the supercritical process with reactive distillation are higher, but the difference is small.

In summary, when simultaneously considering energy requirements, production costs and pollutant emissions, the use of reactive distillation for biodiesel production with methanol at high pressure and temperature appears as an interesting and convenient alternative in terms of costs and environmental impact. Finally, the working parameters of the reactive distillation column for the supercritical processes are ambiguously extreme for a reactive distillation setup. So, the operation of the biodiesel production process at the conditions of pressure and temperature needed by the Saka–Dadan method is still to be investigated. This work does not deal with that issue; additional analysis is required to determinate if such system can be successfully operated in practice and at industrial scale.

Acknowledgements

Appendix A: Utilities cost.

To calculate the utilities cost for the processes, estimated unitary cost values have been used. For the cooling water, a unitary cost of 0.0011 U\$/kg has been considered (assuming a temperature increment from 25 to 35 °C). The high pressure steam unitary cost is assumed as 0.0123 U\$/kg, with a saturation temperature of 307 °C. The medium pressure steam unitary cost is 0.0101 U\$/kg, with a saturation temperature of 207 °C. In the case of electricity, a unitary cost of 0.099 U\$/kWh was used; this cost is the mean value reported in Mexico (September, 2010).

Symbols

C_i	concentration of the component i (mol/L)
C_F	fixed costs (U\$)
C_V	variable costs (U\$/year)
$\dot{E}$	electricity required by the process (BTU/lb biodiesel)
f_L	factor for energy losses in the production of natural gas
k_E	rate constant for the esterification reaction (s^{-1})
k_H	rate constant for the hydrolysis reaction (s^{-1})
$\dot{M}$	energy content of methanol (BTU/lb biodiesel)
$\dot{Q}_{NG}$	energy provided by natural gas to produce steam in the biodiesel process (BTU/lb biodiesel)
t	expected payback period for an investment (years)
TAC	total annual cost (U\$/year)
X_T	total emissions of pollutant X (g/lb biodiesel)
X_{QP}	emissions due to production and burnt of natural gas (g/lb biodiesel)
X_E	emissions due to electricity production (g/lb biodiesel)
X_{MEOH}	emissions due to methanol production (g/lb biodiesel)
$X_{NG,LB}$	emissions due to natural gas burnt in a large boiler (g/BTU)
$X_{NG,SB}$	emissions due to natural gas burnt in a small boiler (g/BTU)
$X_{P,NG}$	emissions due to the production of natural gas used as energy source for biodiesel production (g/BTU)

$X_{E,FP}$ emissions due to the production of fuel for electricity (g/BTU)

$X_{E,FB}$ emissions due to the fuel burnt for electricity generation (g/BTU)

$X_{NG,M}$ emissions due to the production of natural gas used as feedstock for producing methanol (g/BTU)

$X_{EN,M}$ emissions due to the natural gas burnt for methanol production (g/BTU)

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