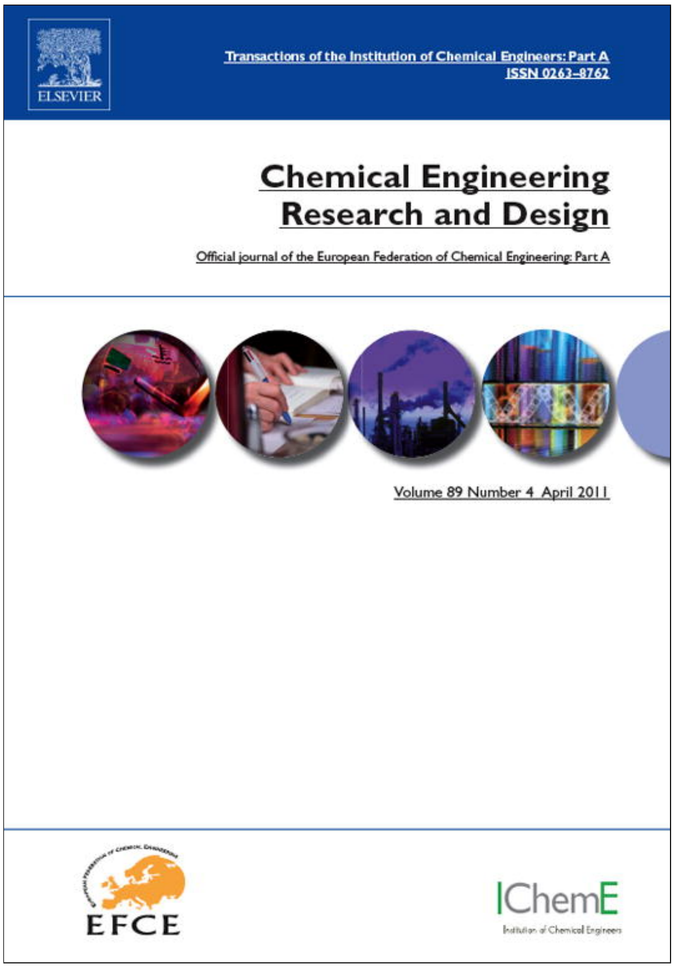

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Esterification of fatty acids in a thermally coupled reactive distillation column by the two-step supercritical methanol method

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ABSTRACT

Biodiesel fuel has been shown as a clean energy alternative to petroleum diesel. Conventional biodiesel production involves the use of catalyst, which implies high energy consumptions for the separation of both the catalyst and the by-products of the reaction, including those of the undesirable reaction of saponification. Recently, a process involving the use of short-chain alcohols at supercritical conditions has been proposed (Saka-Dadan process); one of the main advantages of that process is that it avoids the need for a catalyst as well as the occurrence of the saponification reaction. However, although the process requires less pieces of equipment than the conventional one, its energy requirements are still high, making biodiesel fuel more expensive than petroleum diesel. This work proposes the use of reactive distillation and thermally coupled reactive distillation configurations to produce biodiesel fuel by the supercritical methanol method. First-order kinetics is used to represent the esterification reaction, obtaining high conversions in a single shell. Both of the configurations proposed reduce energy requirements when compared to the conventional (Saka-Dadan) process. Calculations were also performed to estimate CO_2 emissions, thermodynamic efficiency and cost. The thermally coupled reactive distillation configuration shows to be the best alternative in terms of energy consumption, CO_2 emissions and thermodynamic efficiency. Further, cost estimations also show that the use of a thermally coupled scheme considerably reduces both utilities and capital costs.

Keywords: Biodiesel production; Thermally coupling; Reactive distillation

1. Introduction

Extensive research is being conducted to develop renewable and clean fuels that can replace fossil fuels. Fuels obtained from natural sources are known as biofuels. Among biofuels, bioethanol and biodiesel have been largely studied because of their direct application to engines. Bioethanol is used as a substitute for gasoline, and biodiesel as a substitute of petroleum diesel. Many countries are now using biofuels mixed with fossil fuels to reduce greenhouse emissions. Brazil is considered as the main producer of bioethanol, whereas the U.S. and the European Union are the main producers and consumers of biodiesel.

Biodiesel is produced from vegetable oils such as sunflower oil, safflower oil, rapeseed oil, castor oil, and coconut oil. The main disadvantage of using edible oils to produce biofuels is that they are currently a part of the human food chain. Then, research is being focused on finding new oil sources, such as algae, waste vegetable oils, non-edible oils and animal fats containing triglycerides (Demirbas, 2007; Canakci, 2007). Biodiesel is defined as a mixture of fatty acid methyl or ethyl esters, used as fuel in diesel engines and heating systems (Demirbas, 2007; Canakci, 2007). Biodiesel has many advan-

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Nomenclature

$(CO_2)_{Emiss}$ (kg/s)	CO_2 emissions by production of steam
b (kJ/h)	exergy function
C% (%)	carbon content of a fuel
C_i (mol/L)	concentration of component i
h (kJ/kmol)	molar enthalpy
h_{Proc} (kJ/kg)	enthalpy of steam delivered to the process
HE	heating efficiency
k (s^{-1})	first-order reaction rate constant
LW (kJ/h)	lost work
n (kmol/h)	mole flow
n_{mol} (kmol)	number of moles
NHV	net heating value
Q_{Fuel} (kJ/h)	heat delivered by a fuel to produce steam
Q_{Proc} (kJ/h)	heat delivered to the process
Q_{prod} (kJ/h)	heat produced by a fuel
Q_{req} (kJ/h)	heat required to produce fuel
s (kJ/kmol K)	molar entropy
T_0 (K)	temperature of surroundings
T_s (K)	temperature of the system
W_{min} (kJ/h)	minimum work for the separation
W_s (kJ/h)	shaft work

Greek symbols

η	second law efficiency
λ_{Proc} (kJ/kg)	heat of vaporization of steam delivered to process

tages over petroleum diesel: it is non-toxic, biodegradable, free of sulfur and carcinogenic compounds, and can be used directly on diesel engines (Vicente et al., 2004). Its main disadvantages are its high viscosity, low energy content and high nitrogen oxide emissions (Al-Zuhair, 2007).

Conventional production of biodiesel consists on the transesterification of triglycerides, which are the main components of oils and fats used as raw materials, with a short-chain alcohol, usually methanol, in the presence of a catalyst. The catalysts more commonly used are basis, such as sodium hydroxide or potassium hydroxide; but acids such as sulfuric acid and enzymes are also used. Depending upon the temperature and the amount of catalyst used, reaction yields can be superior to 95% (Demirbas, 2008b). The main problem of using basic catalysts is the saponification reaction occurred when the raw material contains high concentrations of water or free fatty acids. In the case of acid catalysts, the problem is that the reaction rate usually becomes very slow. Moreover, the use of either type of catalyst implies an additional separation which requires high energy consumptions to get biodiesel and glycerin (by-product) with an adequate purity. Finally, in the case of using enzymes as catalysts, a key disadvantage is that they are expensive, making this alternative infeasible for industrial production.

Biodiesel can also be produced through transesterification of triglycerides in vegetable oils or animal fats with methanol at supercritical conditions, i.e. 350 °C and 20–50 MPa (Kusdiana and Saka, 2001). The conditions of such a reaction are severe and special materials are required, but it avoids the use of a catalyst and reduces the number of separation units needed in the process. A two-step process has also been proposed to avoid the need for supercritical conditions (Minami and Saka, 2006). In the two-step process (known as the Saka-Dadan process), the triglycerides are first treated with water (hydrolysis) to get fatty acids and glycerol, which is immediately removed. The fatty acids react then with methanol at 270 °C and 7 MPa to get methyl esters (biodiesel) and water. Since the hydrolysis reaction produces free fatty acids, the presence of these on the feed to the esterification reactor does not cause undesirable reactions. Fig. 1 shows the two reactions involved; R^1, R^2, R^3 and R^4 correspond to fatty acid chains of variable length. In the hydrolysis reaction triglycerides are converted to di- and monoglycerides, finally producing fatty acids. It has been shown that the presence of water on the raw material does not affect the yield of methyl esters as it occurs with the catalytic process (Kusdiana and Saka, 2004). This feature makes the Saka-Dadan process a convenient way to deal with animal fats and waste oils, as they contain high concentrations of free fatty acids and water. Even so, because of the temperature and pressure conditions, the Saka-Dadan process involves high energy consumptions, which impact on the final cost of biodiesel.

2. Thermally coupled reactive distillation

In a conventional process, a chemical reaction requires a separation sequence to purify the products, by-products and remaining reactants. This usually takes place in several separation devices. A common intensification alternative to these operations involves a reactive distillation column, in which the reaction and the separation take place in just one shell. There are many studies on reactive distillation process; some of them deal with the design of reactive columns (Giessler et al., 2001; Sanchez-Daza et al., 2003; Thery et al., 2005) for mixtures up to 4 components, and some others analyze reactive distillation columns with equilibrium and non-equilibrium stage models (Baur et al., 2000).

To reduce the energy demand in distillation processes, additional configurations have been proposed. One of the most studied systems is the Petlyuk column, also known as fully thermally coupled column. The Petlyuk column uses vapor–liquid interconnecting streams to achieve heat transfer by direct contact; then, these interconnections avoid the need for two condensers and two reboilers required by the conventional three-column sequence (Gómez-Castro et al., 2008). Another thermally coupled configuration is the thermally coupled direct sequence, in which a vapor stream flows from the main column to a rectification column, eliminating one reboiler of the conventional sequence. It has been demonstrated that thermally coupled systems provides energy savings up to 50% when compared to conventional distillation trains (Triantafyllou and Smith, 1992).

New intensification schemes combine the advantages of reactive distillation and thermally coupling. Such systems are known as the reactive Petlyuk column and the reactive thermally coupled direct sequence (Mueller and Kenig, 2007; Barroso-Muñoz et al., 2007). These columns appear to be an excellent alternative to reduce energy consumptions on processes where chemical reactions occur (Barroso-Muñoz et al., 2007). In a previous work (Gómez-Castro et al., 2010), we use chemical equilibrium models to approximate the hydrolysis and esterification reaction on the Saka-Dadan process. We then study the feasibility of using reactive distillation and thermally coupled reactive distillation for biodiesel production with the two-step supercritical methanol process. In this paper, as an improved approximation, we analyze the pro-

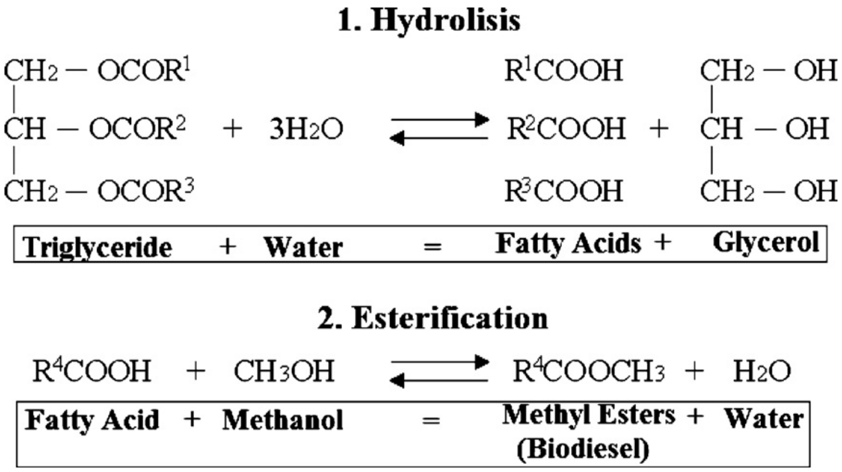

Fig. 1 – Reactions involved in the two-step supercritical methanol method for biodiesel production.

cess by using first-order kinetics to represent the esterification reaction. The accuracy of this kinetic model is successfully compared with the experimental data of Minami and Saka (2006). Furthermore, we perform calculations to evaluate CO_2 emission in the esterification step. Thermodynamic efficiency and costs of the reactive distillation systems are also estimated. Simulations were developed on AspenOne^{TM} process simulator and results are compared with those obtained by using an equilibrium model.

3. Thermodynamic efficiency and CO_2 emissions

A useful measure of the performance of energy-consuming separation processes is the thermodynamic efficiency. Thermodynamic efficiency compares the minimum work of separation with the actual amount of separation work (minimum work plus lost work). A high value of thermodynamic efficiency indicates reduction in lost work. Since distillation is by nature a low-efficiency process, it is important to obtain efficient separation schemes. It is already known that thermally coupled distillation sequences are usually more efficient than conventional distillation systems because of the better use of the heat contained on the internal streams of the columns. Appendix A summarizes the equations involved in the calculation of the thermodynamic efficiency (Henley and Seader, 2006).

In addition, another performance index of a clean process is represented in terms of its carbon dioxide emissions. In the case of distillation columns, steam is used to satisfy the energy requirements on the reboilers; also, for endothermic reactions, steam can be used to provide the required heat input. Fuel oil and natural gas are the most commonly used fuels to produce steam on industry and considerable amounts of CO_2 are sent to the atmosphere in the combustion process. As CO_2 is one of the most important greenhouse effect gases, chemical process should be designed to reduce the emissions of this gas (which implies reducing the energy consumptions of the systems). In this work, the methodology proposed by Gadalla et al. (2005) is used to calculate CO_2 emissions (see Appendix B).

4. Design and simulations

4.1. *Reaction kinetics*

A first-order kinetic model was tested to represent the esterification reaction. The rate equation is given by Eq. (1).

$$\frac{dC_{MEOL}}{dt} = kC_{OLAC} \tag{1}$$

Activation energy was calculated by using the values of the rate constant proposed by Saka (2007). Then, simulations of a batch reactor were developed to test this kinetic model. The reaction under analysis is as follows:

$$OLAC + MEOH \leftrightarrow MEOL + H_2O$$

where OLAC corresponds to oleic acid, MEOH is methanol, MEOL is methyl oleate and H_2O is water. The reaction was performed at 7 MPa and 270 °C, using a volumetric ratio of 0.9/1 (methanol/oleic acid). The thermodynamic models used were the NRTL equation to represent the liquid phase behavior and the Redlich–Kwong equation for the gas phase. Results were

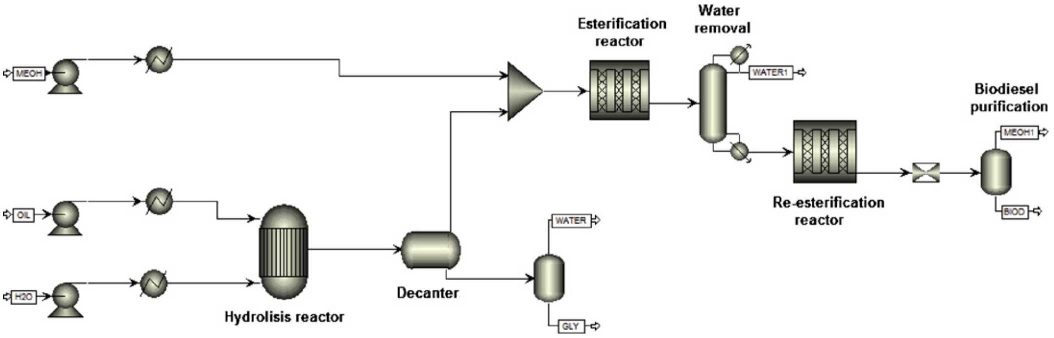

Fig. 2 – Diagram of the simulation of biodiesel production by the conventional supercritical methanol method.

successfully compared with those published by Minami and Saka (2006).

4.2. *Designing the reactive thermally coupled systems*

Once the kinetic model was obtained and verified, simulations of the process were developed on the AspenOne^{TM} process simulator. The oil was simulated as pure triolein, a triglyceride contained in high concentrations on many vegetable oils such as rapeseed oil, sesame seed oil, peanut oil, and palm oil. The use of pure triolein is consistently assumed for all the configurations analyzed in this paper.

4.2.1. *The conventional (Saka-Dadan) process*

As in a previous work (Gómez-Castro et al., 2010), the hydrolysis reactor of the Saka-Dadan process was simulated as a chemical equilibrium reactor with the RGibbs module. After this step, a decanter was used to separate the two phases formed: 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 an esterification reactor along with the methanol stream at

Table 1 – Standard requirements for biodiesel fuel.

Component	Requirement/standard
Water and sediment	0.05 max vol.% (ASTM)
Free glycerol	0.020 max wt.% (ASTM/EN14214)
Total glycerol	0.25 max wt.% (ASTM/EN14214)
Monoglyceride	0.8 max wt.% (EN14214)
Diglyceride	0.2 max wt.% (EN14214)
Triglyceride	0.2 max wt% (EN14214)
Methanol	0.2 max wt% (EN14214)

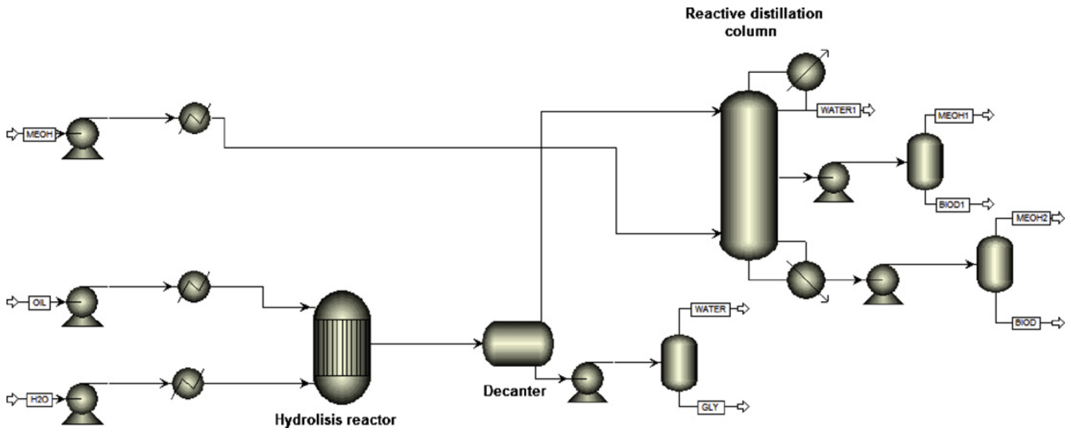

Fig. 3 – Diagram of the simulation of biodiesel production by the supercritical methanol method using reactive distillation.

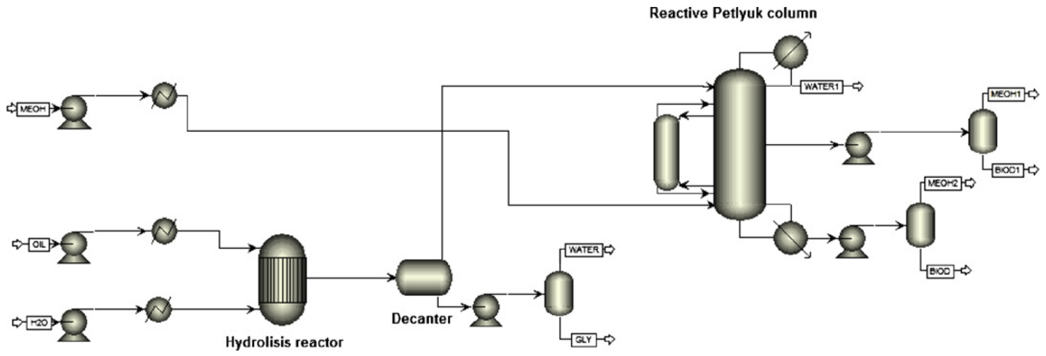

Fig. 4 – Diagram of the simulation of biodiesel production by the supercritical methanol method using the reactive Petlyuk column.

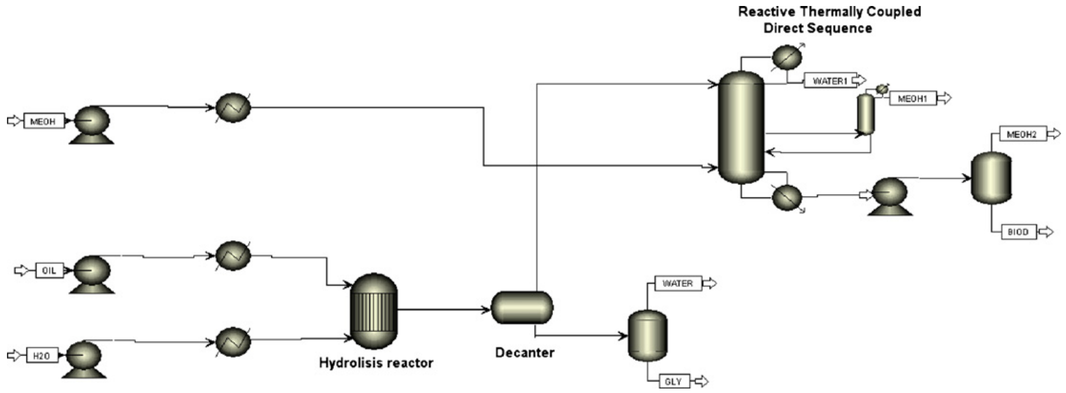

Fig. 5 – Diagram of the simulation of biodiesel production by the supercritical methanol method using the reactive thermally coupled direct sequence.

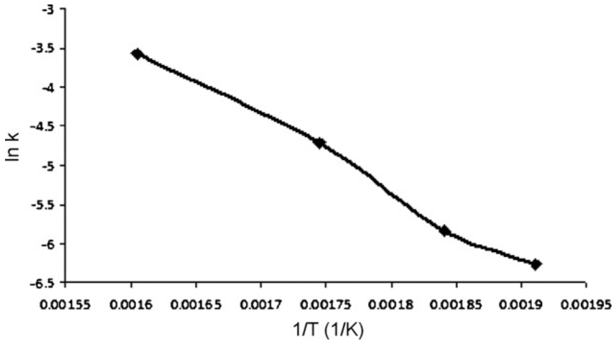

Fig. 6 – Arrhenius plot for the esterification reaction.

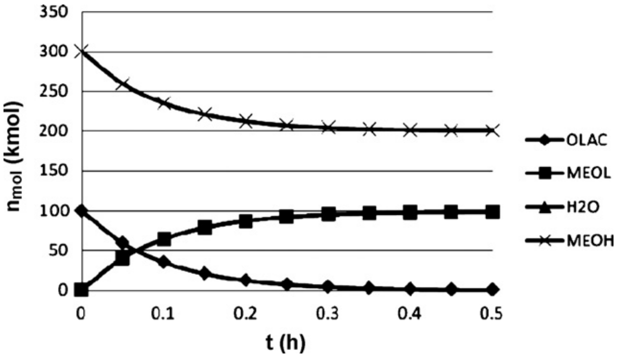

Fig. 7 – Variation of the number of moles in the batch-type reactor.

7 MPa and 270 °C. The esterification reactor was simulated as a plug flow reactor using the kinetic model previously discussed. Since the rate of reaction becomes slower as the concentration of fatty acid decreases, the reactor conversion was targeted as 97.3% to avoid an excessively large reactor. The stream leaving the reactor is then introduced into a distillation column to eliminate the water contained on it. The bottoms stream is sent to a second esterification reactor, where the remaining acetic acid is converted to methyl acetate. The stream leaving the second reactor goes through an expansion valve and is then sent to a low-pressure flash drum, where the methanol is vaporized and biodiesel is obtained in the liquid stream. The diagram of the simulation is shown in Fig. 2.

4.2.2. *The reactive distillation process*

Once the conventional Saka-Dadan process was simulated, a reactive distillation column (RDC) was introduced; the esterification reactor is no longer considered since the reaction and the separation take now place on the same shell. The same first-order kinetic model was used to represent the reaction rate. The design strategy for the reactive distillation column has already been reported (Gómez-Castro et al., 2010). The system consists of a reactive stripping section and a non-reactive rectification section. It is assumed that the reaction occurs on the stripping section because it occurs on liquid phase; also, since the reactant oleic acid and the product methyl oleate are among the heaviest components of the mixture, they will be concentrated on the bottoms of the column. To ensure the appropriate distribution of liquid and vapor flow throughout the column, the liquid feed stream was fixed on the top of the column and the vapor phase methanol stream enters on the reboiler. Other selections for the feed flow distribution cause drying on the column trays. The number of non-reactive and reactive stages was then defined and modified by analyzing the change on conversion and heat duty for a target purity of biodiesel on the bottoms. The column with the lowest energy requirements consists on a 15-stages system which separates water as the top product, part of the methanol is obtained as the side-stream product and a mixture of methanol and methyl oleate constitutes the bottoms product. A lower number of stages results on an increment in the heat duty with no improvement on the conversion. Temperature in the reactive distillation column is lower than 300 °C to avoid methyl oleate isomerization. The product obtained is 90% (mass) biodiesel, and does not satisfy standard requirements; Table 1 shows the values of the requirements as given by Demirbas (2007). Therefore, a low-pressure flash unit was used to improve product purity. To avoid wasting kinetic energy, hydraulic turbines are introduced to reduce pressure, then obtaining some electric energy that may be useful for the operation of pumps at high-pressure. The diagram for the RDC process is shown in Fig. 3.

4.2.3. *The thermally coupled reactive distillation approach*

The reactive distillation column configuration is then used to design a reactive Petlyuk column (TCRD) and a reactive thermally coupled direct sequence (RTCDS). The reactive Petlyuk column was designed taking as a basis the number of stages of the reactive column. A number of non-reactive stages

Table 2 – Specifications of the esterification step for the conventional process.

Reactor 1		Reactor 2	
Total mole flow (kmol/h)	680.28	Total mole flow (kmol/h)	415.04
Total mass flow (kg/h)	54,490.09	Total mass flow (kg/h)	49,675.42
Conversion	97.27%	Conversion	69.26%
Heat duty (kJ/h)	12,756,013.6	Heat duty (kJ/h)	795,609.0
Pressure (MPa)	7	Pressure (MPa)	7
Reactor volume (m^3)	96.9	Reactor volume (m^3)	10.7
Residence time (h)	0.36	Residence time (h)	0.11
Flash drum		**Distillation column**	
Vapor fraction	0.6631	Stages	25
Temperature (K)	433.15	Bottoms rate (kmol/h)	415.04
Pressure (MPa)	0.1013	Bottoms rate (kg/h)	49,675.42
Heat duty (kJ/h)	−10,916,364	Reflux ratio	2.8
		Top stage pressure (MPa)	7
		Feed stage	15
		Biodiesel purity (mass%)	79.85%
		Heat duty (kJ/h)	28,074,296.5

Table 3 – RD column performance with respect to retention time.

t (h)	Q (kJ/h)	Conversion	Diameter (m)
0.1	35,671,491.7	0.9879	3.2038
0.2	35,196,869.3	0.9880	3.2100
0.3	35,053,076.2	0.9915	3.2117
0.4	34,971,909.9	0.9934	3.2119
0.5	34,919,834.7	0.9946	3.2118
0.6	34,883,643.2	0.9954	3.2116
0.7	34,856,625.9	0.9960	3.2114
0.8	34,835,871.4	0.9965	3.2112
0.9	34,819,409.4	0.9969	3.2110
1.0	34,806,035.9	0.9972	3.2109

corresponding to the RDC were taken to form the Petlyuk column prefractionator, the other stages were considered as a part of the main column. This approach for the design of the thermally coupled configurations has been described by Gómez-Castro et al. (2010). The reactive Petlyuk column is depicted in Fig. 4. The locations of the interlinking flows were selected as to allow a reduction on the energy consumption of the system. In the case of the RTCDS system, a similar design approach was used. One subsection of the RDC was removed and became the side rectifier. The remaining stages conform the main column. The locations of the interlinking flows were modified until the lowest heat duty was achieved. The RTCDS is shown in Fig. 5. Once the four processes (conventional, RD, TCRD and RTCDS) were successfully simulated, calculations were performed to estimate thermodynamic efficiencies, CO_2 emissions and total costs. The calculations involved in those estimations are described in Appendices A–C, respectively. As a way to show the capacity of biodiesel as a fuel, a heating efficiency is defined as:

$$HE = \frac{Q_{prod}}{Q_{req}}$$

where HE is the heating efficiency, Q_{prod} is the energy produced by the fuel (kJ/h) and Q_{req} is the energy required to produce the fuel (kJ/h). The heating capacity value for the biodiesel is taken as 3980 kJ/kg, as reported by Demirbas (2008a).

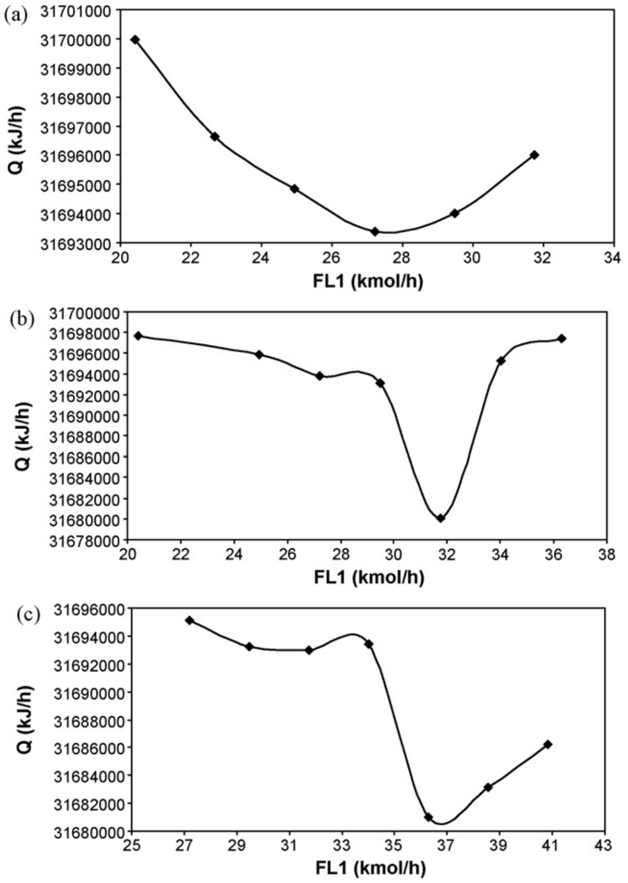

Fig. 8 – Optimization of the interconnecting flows of the reactive Petlyuk column (a) FV2 = 29 kmol/h, (b) FV2 = 32 kmol/h, (c) FV2 = 34 kmol/h.

5. Results and discussion

5.1. *Kinetic model*

Reaction rate constants were taken from Saka et al. (2006) and were used to construct an Arrhenius plot for the esterification reaction (see Fig. 6). Fig. 6 depicts the natural logarithm of the rate constant (ln *k*) versus 1/*T* (where *T* is the temperature in K). A lineal regression was applied to such data ($R^2 = 0.9911$), obtaining the value of E_A/R (slope) as 9065.7, which corresponds to a value of the activation energy of 75,372.23 J/mol.

Table 4 – Specifications of the reactive distillation configurations.

	RD column	Reactive Petlyuk column (TCRD)		RTCDS	
		Prefractionator	Main column	Main column	Rectificator
Stages	15	4	11	10	5
Bottoms rate (kmol/h)	255.83	43.48	255.83	255.62	6.80
Bottoms rate (kg/h)	41,817.11	2487.88	41,801.84	44,338.62	380.63
Reflux ratio	2.2504	1.7439	1.9374	1.36	0.06
Heat duty (kJ/h)	35,053,076.2	0	31,680,293.7	27,745,592.9	0
Methanol feed stage	15	–	11	10	–
Oleic acid feed stage	2	–	2	2	–
Side product extraction stage	10	–	8	–	–
Reactive stages	10–15	–	7–11	7–10	–
Conversion	99.15%	–	99.15%	99.15%	–
Biodiesel purity (mass%)	90.00%	–	90.00%	91.29%	–
Interlinking stages	–	1,4	3,4/6,7	8,9	5
Interlinking vapor flow (kmol/h)	–	–	32	181	–
Interlinking liquid flow (kmol/h)	–	–	32	–	–

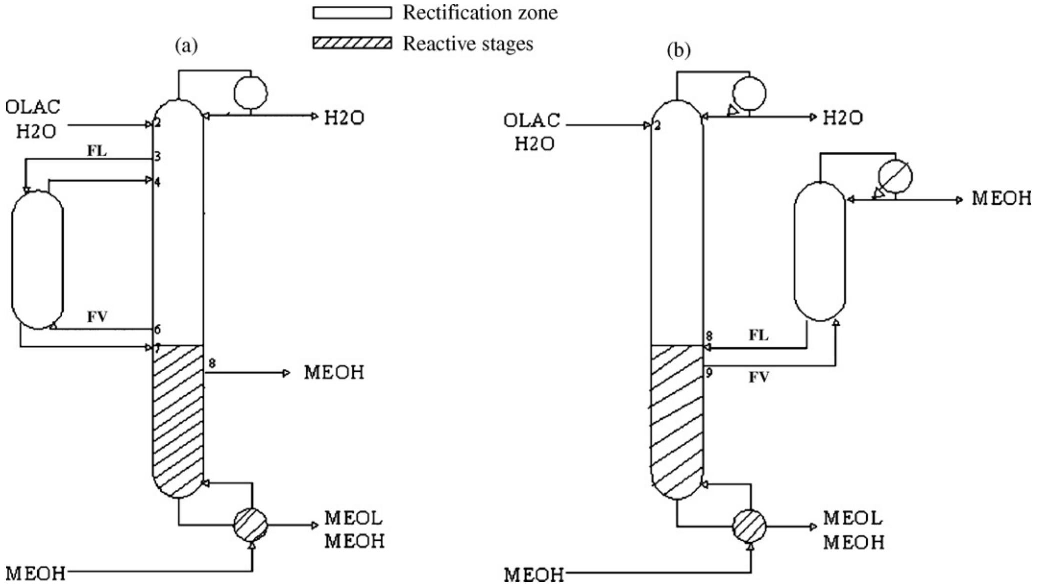

Fig. 9 – Stage distribution for the thermally coupled reactive systems. (a) Reactive Petlyuk column, (b) reactive thermally coupled direct sequence.

The value of the reaction rate constant at 270 °C was then calculated as $2.90 \times 10^{-3}\ s^{-1}$. To test the kinetic model, simulations were performed on AspenOne® by using a batch-type reactor. For a simulation time of 30 min at 7 MPa and 270 °C, a conversion of approximately 94% is obtained. Fig. 7 shows the changes on the number of moles, n_{mol}, against time for the batch-type reactor. The conversion achieved is similar to that reported by Minami and Saka (2006) for the same reaction time. In the light of the results, we then used this kinetic model for the simulation of the continuous processes.

5.2. *Simulation*

A 46 kmol/h (40,637 kg/h) stream of triolein is fed to the hydrolysis reactor, reacting with an excess of 2476 kmol/h (44,615 kg/h) of water to shift the reaction equilibrium to the products. The reaction results in 138 kmol/h (38,890 kg/h) of oleic acid and 46 kmol/h (4227 kg/h) of glycerol. The water-rich stream of the decanter contains 2209 kmol/h (39,762 kg/h) of water and 46 kmol/h of glycerol. A molar purity of 96.7% is obtained for glycerol once the water is eliminated. This purity for glycerol remains the same for all the analyzed configuration alternatives. The oil-rich phase is sent to the first esterification reactor. Some design parameters of the esterification reactor on the conventional process are shown in Table 2. Total conversion of oleic acid to methyl acetate is 99.16%. The separation of water demands a high percentage of the energy needed in this step.

Table 5 – Thermal energy consumptions for the esterification step.

Process	Q_T (kJ/h)	Energy savings
Conventional	30,709,555.1	0% (base case)
RD	25,124,307.4	18.19%
TCRD	21,551,773.5	29.82%
RTCDS	14,104,223.9	54.07%

For the simulation of the reactive distillation configuration, a preliminary analysis is needed to find appropriate values for the retention time. Table 3 shows the performance of the reactive column with respect to retention time for the reactive stages (considering the same value of the retention time for all of the stages). As the retention time increases, heat duty decreases and higher conversions are achieved, whereas the diameter of the column is not affected. For operational purposes, retention times for all of the reactive stages were assumed as 0.3 h, with a conversion of 99.15%. The same value of retention time is assumed for the reactive stages on the reactive Petlyuk column. Although this value for the retention time was not experimentally verified, the value is consistent with our assumptions about the kinetic model and our simulation results provided in Fig. 7.

Systems involving reactive distillation achieve the same conversion as the conventional process in a single shell and with a lower retention time. Table 4 provides the design para-

Table 6 – Composition of the biodiesel fuel obtained by the different analyzed processes.

	Conventional	RD	TCRD	RTCDS
Composition (mass%)				
Triolein	0.0000	0.0000	0.0000	0.0000
Diolein	2.472×10^{-9}	2.471×10^{-9}	2.471×10^{-9}	2.486×10^{-9}
Monoolein	0.0000	0.0000	0.0000	0.0000
Water	6.844×10^{-5}	3.2127×10^{-5}	3.3428×10^{-5}	5.9879×10^{-5}
Glycerol	0.0284	0.0469	0.0467	0.0569
Oleic acid	0.7994	0.8047	0.0992	0.0065
Methanol	0.2049	0.2073	0.2055	0.2054
Methyl oleate	98.9672	98.9410	99.6485	99.7311

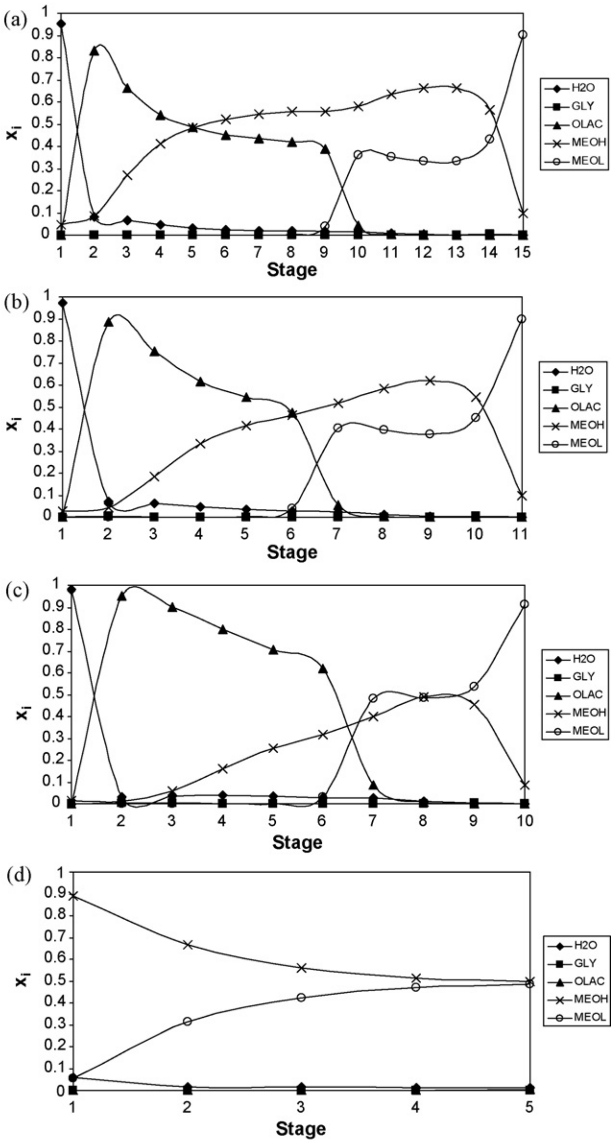

Fig. 10 – Composition profiles for the intensified systems, mass%. (a) Reactive distillation column, (b) main column of the reactive Petlyuk column, (c) main column of the RTCDS system, (d) side rectifier of the RTCDS system.

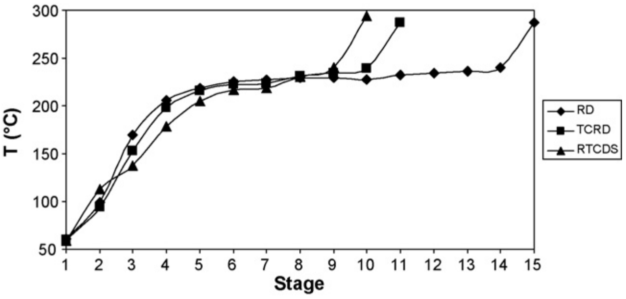

Fig. 11 – Temperature profiles of the intensified systems.

Table 8 – Thermodynamic efficiencies.

Process	W_{min} (kJ/h)	LW (kJ/h)	η (%)
RD	6,244,711.9	9,316,676.6	40.13
TCRD	6,462,773.6	7,600,664.4	45.95
RTCDS	6,522,811.2	5,796,641.9	52.95

meters of the RD column, the TCRD column (reactive Petlyuk column) and the RTCDS system. The results of the reactive Petlyuk column correspond to a local optimum with respect to energy consumption, as shown in the optimization curves for that column in Fig. 8. Fig. 9 shows a schematic representation of the stage distribution for the thermally coupled reactive systems. In addition, Table 5 shows a comparison of total energy requirements for the esterification step of the different configurations. In Table 5, total energy consumption to achieve a high-purity biodiesel fuel and methanol (to be recycled) is considered, i.e. the requirements of the esterification reactors, the distillation column and the flash unit in the case of conventional process are included; similarly, the consumptions of the reactive column and the two flash units in the cases of the reactive distillation and the thermally coupled reactive distillation processes are considered. The RTCDS column presents the lowest energy consumptions out of the four analyzed reactive systems. Table 6 presents the composition of the biodiesel product for the different analyzed processes, including the remaining free fatty acids content. Finally, Fig. 10 presents the composition profiles (%mass) and Fig. 11 shows the temperature profiles. As shown by Fig. 10, the reaction occurs mainly on the stripping section of the columns, obtaining high-purity biodiesel as the bottoms product of such columns. Also, the maximum temperature of the systems, i.e. the reboiler temperature, does not exceed the limit of 300 °C.

5.3. *CO_2 emissions, efficiencies and costs calculations*

The results of the calculations of CO_2 emissions are shown in Table 7. To evaluate the impact of using intensificated systems, the emissions for both the whole process and the esterification step are presented. For the esterification step, in the case of the conventional process, the CO_2 emissions correspond to the production of steam to satisfy the energy requirements of the two esterification reactors and the distillation column. In the case of the RD, TCRD and RTCDS processes, the CO_2 emissions correspond to the production of steam for the RD column and the flash units linked to the column. Steam is assumed to be produced at temperatures of 480 and 580 K. From Table 7, CO_2 emissions of the reactive Petlyuk column and the RTCDS

Table 7 – Carbon dioxide emissions.

Process	Whole process			Esterification		
	Q_{Fuel} (kJ/h)	CO_2 (kg/h)		Q_{Fuel} (kJ/h)	CO_2 (kg/h)	
		Fuel oil	Natural gas		Fuel oil	Natural gas
Conventional	332,861,455.0	26,569.2	17,850.5	77,211,796.5	6163.1	4140.7
RD	323,314,585.1	25,807.2	17,338.5	67,664,926.6	5401.1	3628.7
TCRD	316,718,134.7	25,280.7	16,984.8	61,068,476.3	4874.5	3274.9
RTCDS	307,114,878.1	24,514.1	16,469.8	51,465,219.7	4107.9	2759.9

Table 9 – Utilities costs and cost indexes.

Steam cost @ 580 K (U$/lb)	Steam cost @ 480 K (U$/lb)	Water cost (U$/lb)	Electricity cost (U$/kWh)	Cost index (1996)	Cost index (2009)
0.0056	0.0046	0.0005	0.057	382	539.7

Table 10 – Costs analysis results.

Process	Whole process			Esterification		
	Utilities costs (US$/year)	Equipment costs (US$/year)	Total costs (US$/year)	Utilities costs (US$/year)	Equipment costs (US$/year)	Total costs (US$/year)
Conventional	33,165,744	3,163,726	36,329,470	23,077,579	2,135,350	25,212,929
RD	30,336,016	1,803,605	32,139,621	13,911,349	720,606	14,631,955
TCRD	29,246,936	1,668,856	30,915,792	12,822,269	585,857	13,408,126
RTCDS	28,283,587	1,597,871	29,881,458	11,855,537	514,872	12,370,409

Table 11 – Heating efficiencies.

Process	Q_{prod} (kJ/h)	Q_{req} (kJ/h)	HE
Conventional	162,062,734.6	128,854,654.3	1.26
RD	162,111,491.8	124,248,305.6	1.30
TCRD	162,148,860.5	120,622,628.7	1.34
RTCDS	161,278,860.9	114,974,328.1	1.40

are considerably smaller than those of the conventional and reactive distillation processes. The use of natural gas offers lower emissions than the fuel oil, but its cost is also 3 times larger.

Table 8 provides the results of the thermodynamic efficiency calculations. Thermally coupled systems present higher values of thermodynamic efficiency. These results are in agreement with those reported by Hernandez-Gaona et al. (2005). Thermodynamic efficiency increases due to the presence of thermal links which cause a considerably reduction in energy demands. Table 9 shows the utility costs parameters used in our calculations and Table 10 presents the results for the costs calculations. Stainless steel is assumed as the construction material for all the equipment at 7 MPa as proposed by Saka et al. (2006). Costs for steam and water were taken from Turton et al. (2004) and updated by using the Chemical Engineering Costs Index. The cost for electricity was taken as the mean reported by the Mexican Electricity Company (CFE) and converted into American dollars. A period of 5 years was considered to annualize the capital cost. Table 10 shows that capital cost for the esterification step of an intensificated scheme (either reactive distillation or thermally coupled reactive distillation) is considerably smaller than that of the conventional process; there is also a reduction in total annual costs for the whole process in the case of the intensificated configurations. Finally, Table 11 provides the results for the heating efficiencies. Energy used in the calculation does not consider the requirements for the purification of glycerol. As it can be seen, even in the conventional process, the biodiesel fuel obtained generates more energy than that required for its production.

6. Conclusions

First, a study of the kinetics for the esterification reaction to produce biodiesel fuel by supercritical methanol technologies has been presented. A first-order kinetic model has been shown to fit experimental data. Furthermore, intensification alternatives for the production of biodiesel fuel by the two-step supercritical methanol method have been tested by using the first-order kinetic model. Those configurations involve the use of either reactive distillation or thermally coupled reactive distillation to carry out the esterification reaction and the purification of the product in the same shell. These alternatives present lower energy consumptions when compared to the conventional process. The energy consumptions are similar to those predicted by the equilibrium calculations for the RD and the reactive Petlyuk column (Gómez-Castro et al., 2010). The purity of the biodiesel fuel in the reactive distillation systems was targeted as 90% (mass) to avoid isomerization of the methyl ester, which occurs when temperature is higher than 300 °C.

The RTCDS system shows the lowest values of CO_2 emissions and the lowest total annual cost. If only the esterification step is analyzed, the capital savings are considerable; but if whole process is analyzed, the difference between the three schemes becomes smaller. Then, an analysis of the purification of glycerol is also necessary to find the alternatives with the lowest energy demand. The RTCDS column has the higher thermodynamic efficiency. Nevertheless, because of its higher number of degrees of freedom, the reactive Petlyuk column remains as a feasible alternative if a more rigorous optimization strategy is used. Finally, from the heating efficiency calculations, it can be seen that the biodiesel fuel obtained is capable of providing a higher amount of energy than that required for its production.

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Appendix A. Calculation of thermodynamic efficiency

Calculations of thermodynamic efficiencies were performed by using the formulations provided by Henley and Seader (2006). The equations used are the following:

First law of thermodynamics:

$$\sum_{\text{Out of system}} (nh + Q + W_s) - \sum_{\text{Into system}} (nh + Q + W_s) = 0 \qquad \text{(A.1)}$$

Second law of thermodynamics:

$$\sum_{\text{Out of system}} \left(ns + \frac{Q}{T_s}\right) - \sum_{\text{Into system}} \left(ns + \frac{Q}{T_s}\right) = \Delta S_{irr} \qquad (A.2)$$

Exergy balance:

$$\sum_{\text{Out of system}} \left[nb + Q\left(1 - \frac{T_0}{T_S}\right) + W_s\right] - \sum_{\text{Into system}} \left[nb + Q\left(1 - \frac{T_0}{T_S}\right) + W_s\right] = LW \qquad (A.3)$$

Minimum work of separation:

$$W_{\min} = \sum_{\text{Out of system}} nb - \sum_{\text{Into system}} nb \qquad (A.4)$$

Second law efficiency:

$$\eta = \frac{W_{\min}}{LW + W_{\min}} \qquad (A.5)$$

where h is the molar enthalpy, s is the molar entropy, $b = h - T_0 s$ is the exergy function, $LW = T_0 \Delta S_{irr}$ is the lost work in the system and η is the thermodynamic efficiency. The thermodynamic properties of the streams were evaluated with AspenOne^{TM}.

Appendix B. Calculation of CO_2 emissions

The methodology proposed by Gadalla et al. (2005) was used to calculate CO_2 emissions. For a steam boiler, the heat required to produce steam is:

$$Q_{\text{Fuel}} = \frac{Q_{\text{Proc}}}{\lambda_{\text{Proc}}}(h_{\text{Proc}} - 419)\frac{T_{\text{FTB}} - T_0}{T_{\text{FTB}} - T_{\text{Stack}}} \qquad (B.1)$$

where the subscript Proc is used to indicate the steam that is delivered to the process, T_{FTB} is assumed as 1800 °C and T_{Stack} as 160 °C.

The CO_2 emissions are computed as:

$$[CO_2]_{\text{Emiss}} = \left(\frac{Q_{\text{Fuel}}}{\text{NHV}}\right)\left(\frac{C\%}{100}\right)\alpha \qquad (B.2)$$

where α is the molar ratio of CO_2 and C (3.67); NHV represents the net heating value of a fuel with a carbon content of C%. For a heavy fuel oil, NHV = 39,771 kJ/kg and C% = 86.5; whereas for natural gas NHV = 51,600 and C% = 75.4.

Appendix C. Cost calculations

Process costs were estimated by using the equations provided in Turton et al. (2004) and updated through the Chemical Engineering Cost Index. The costs calculations include the installation costs for the equipments (bombs, heat exchangers, decanter, reactors and columns). The capital cost (purchase plus installation cost) is annualized over a period which is referred to as plant lifetime (assumed as 5 years in this work):

$$\text{Annual capital cost} = \frac{\text{capital cost}}{\text{plant life time}}$$

$$\text{Total annual cost} = \text{annual operating cost} + \text{annual capital cost}$$

Operating costs were assumed to be the costs of steam, cooling water and electricity. A value of 8400 h of operation per year was considered.

References

Al-Zuhair, S., 2007. Production of biodiesel: possibilities and challenges. Biofuels Bioprod. Bioref. 1, 57.

Barroso-Muñoz, F.O., Hernandez, S., Segovia-Hernandez, J.G., Hernandez-Escoto, H., Aguilera-Alvarado, A.F., 2007. Thermally coupled distillation systems: study of an energy-efficient reactive case. Chem. Biochem. Eng. Q. 21, 115.

Baur, R., Higler, A.P., Taylor, R., Krishna, R., 2000. Comparison of equilibrium stage and nonequilibrium stage models for reactive distillation. Chem. Eng. J. 76, 33.

Canakci, M., 2007. The potential of restaurant waste lipids as biodiesel feedstocks. Bioresour. Technol. 98, 183.

Demirbas, A., 2007. Importance of biodiesel as transportation fuel. Energy Policy 35, 4661.

Demirbas, A., 2008a. Biodiesel: A Realistic Fuel Alternative for Diesel Engines. Springer, UK.

Demirbas, A., 2008b. Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. Energy Convers. Manage. 49, 125.

Gadalla, M.A., Olujic, Z., Jansens, P.J., Jobson, M., Smith, R., 2005. Reducing CO_2 emissions and energy consumption of heat-integrated distillation systems. Environ. Sci. Technol. 39, 6860.

Giessler, S., Danilov, R.Y., Pisarenko, R.Y., Serafimov, L.A., Hasebe, S., Hashimoto, I., 2001. Systematic structure generation for reactive distillation processes. Comput. Chem. Eng. 25, 49.

Gómez-Castro, F.I., Segovia-Hernández, F.G., Hernández, S., Gutiérrez-Antonio, C., Briones-Ramírez, A., 2008. Dividing wall distillation columns: optimization and control properties. Chem. Eng. Technol. 31 (9), 1246.

Gómez-Castro, F.I., Rico-Ramirez, V., Segovia-Hernández, J.G., Hernandez-Castro, S., 2010. Feasibility study of a thermally coupled reactive distillation process for biodiesel production. Chem. Eng. Process.: Process Intens. 49, 262–269.

Henley, E.J., Seader, J.D., 2006. Separation Process Principles, 2nd ed. Wiley, U.S.A.

Hernandez-Gaona, C.G., Cardenas, J.C., Segovia-Hernandez, J.G., Hernandez, S., Rico-Ramirez, V., 2005. Second law analysis of conventional and nonconventional distillation sequences. Chem. Biochem. Eng. Q. 19, 235–241.

Kusdiana, D., Saka, S., 2001. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. Fuel 80, 693.

Kusdiana, D., Saka, S., 2004. Effects of water on biodiesel fuel production by supercritical methanol treatment. Bioresour. Technol. 91, 289.

Minami, E., Saka, S., 2006. Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process. Fuel 85, 2479.

Mueller, I., Kenig, E.Y., 2007. Reactive distillation in a dividing wall column: rate-based modeling and simulation. Ind. Eng. Chem. Res. 46, 3709.

Saka, S., Kusdiana, D., Minami, E., 2006. Non-catalytic biodiesel fuel production with supercritical methanol technologies. J. Sci. Ind. Res. 65, 420.

Saka, S., 2007. The new application of the supercritical technology. Biodiesel fuel oil from oils and fats by the supercritical methanol method. Chem. Eng. (Tokyo) 52 (2), 132.

Sanchez-Daza, O., Pérez-Cisneros, E.S., Bek-Pedersen, E., Gani, R., 2003. Graphical and stage-to-stage methods for reactive distillation column design. AIChE J. 49 (11), 2822.

Thery, R., Meyer, X.M., Joulia, X., Meyer, M., 2005. Preliminary design of reactive distillation columns. Trans. IChemE 83 (A4), 379.

Triantafyllou, C., Smith, R., 1992. The design and optimization of fully thermally coupled distillation columns. Trans. IChemE 70A, 118.

Turton, R., Bailie, R.C., Whiting, W.B., Shaeiwitz, J.A., 2004. Analysis, Synthesis and Design of Chemical Process, 2nd ed. Prentice Hall, U.S.A.

Vicente, G., Martinez, M., Aracil, J., 2004. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. Bioresour. Technol. 92, 297.