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ORIGINAL PAPER

Analysis of alternative non-catalytic processes for the production of biodiesel fuel

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Abstract One of the most common supercritical processes for the production of biodiesel fuel involves the use of methanol as reactant. Besides obtaining biodiesel fuel, glycerol is also produced. To avoid the production of glycerol as by-product, alternative reactants for the production of the biofuel have been proposed in recent years. As expected, the use of different reactants may have an impact on the separation processes required to obtain biodiesel fuel complying with international standards. Thus, in this work flowsheets for the different supercritical processes for the production of biodiesel are proposed and analyzed in a simulation environment. The analyzed processes are then compared in terms of energy requirements, total annual costs, and environmental impact. It has been found that the two-step processes show advantages in terms of CO_2 emissions, but in terms of total annual cost the one-step processes are better, showing potential for low CO_2 emissions. Nevertheless, the processes in one-step (with methanol or methyl acetate) result in lower CO_2 emissions and TAC if they are operated at lower temperature. Acetic acid process is the more energy-intensive and expensive of the four processes.

Keywords Biodiesel production · Alternative non-catalytic processes · Process simulation · Supercritical reactions

List of symbols

r_i (mol of component i/s)	Reaction rate for component i
k_j (1/s)	kinetic constant for reaction j
C_i (mol/L)	Molar concentration of component i
HE	Heating efficiency
Q_{prod} (kJ/h)	Heat produced by the fuel
Q_{req} (kJ/h)	Heat required to produce the fuel
TAC (USD/year)	Total annual cost
CC (USD)	Capital cost
OC (USD/year)	Operation cost
n (years)	Payback period
A	Pre-exponential factor
E_a (kJ/kmol)	Activation energy
Q_T (MJ/h)	Total thermal energy requirements

Introduction

Human activity is characterized by a high energetic consumption. Particularly on the industrial and transport sectors, high quantities of fossil fuels are burned to satisfy such energy requirements; this represents a significant contribution to environmental detriment. Furthermore,

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since petroleum is not a renewable energy source, worldwide dependency on fossil fuels is unavoidable (Brondani et al. 2015); also, its price varies considerably depending on availability and even political factors. Thus, different alternatives for energy sources have been proposed in recent years. Renewable liquid fuels figure among those alternative sources of energy. Biodiesel is a liquid fuel which is considered as a potential substitute for conventional, petroleum-based diesel. Among the main advantages of biodiesel over petroleum diesel, we can mention its renewability, its lower emissions of greenhouse gases, and its non-toxicity (Van Gerpen 2005; Bernal et al. 2012). Also, different types of biomass can be used as raw materials for its production such as waste chicken fat (Gurusala and Selvan 2014), spent coffee grounds (Caetano et al. 2014), or mustard oil (Chakraborty et al. 2014).

The most common method to produce biodiesel involves the use of a basic catalyst. Nevertheless, such kind of catalysts is very sensitive to the presence of water and free fatty acids in the feedstock; thus, low-cost oils cannot be processed with basic catalysts because such oils have high amounts of free fatty acids. This represents a disadvantage considering that a great amount of biodiesel could be generated from waste oils (Igliński et al. 2014). Therefore, other alternatives have been explored in terms of catalysts, such as the use of homogeneous and heterogeneous acid catalysts (Lotero et al. 2005; Semwal et al. 2011; Halek et al. 2013; Sing et al. 2014), and the use of enzymes to promote the transesterification reactions (Ranganathan et al. 2008). Modern technologies have also been proposed for the production of biodiesel, e.g., the use of membrane reactors, micro-channel reactors, microwave reactors, helicoidal reactors assisted with ultrasound (Qiu et al. 2010; Kiss and Bildea 2012; Delavari et al. 2015), reactive distillation columns (Kiss et al. 2006; Marchetti and Errazu 2008; de Lima da Silva et al. 2010; Kiss 2010, 2011), and thermally coupled reactive distillation systems (Miranda-Galindo et al. 2011; Kiss et al. 2012), among others. Also, the synthesis of biorefineries to produce biodiesel has been tackled considering the modeling of uncertainties with robust optimization (Tan et al. 2013) and stochastic optimization (Abbasi and Diwekar 2014), including the assessment of sustainability of the production process via fuzzy optimization (Liew et al. 2014).

Another alternative which has obtained special attention on recent years is the use of alcohols under supercritical conditions. This approach commonly uses methanol as reactant to simultaneously perform the transesterification and esterification reactions under pressures between 8.4 and 40 MPa and temperatures about 320–350 °C, with no catalyst required (He et al. 2007; Demirbas 2009; Hawash et al. 2009; Samniang et al. 2014). Some studies, nevertheless, report data for pressures up to 105 MPa (Kusdiana and Saka 2001). Other approach has been proposed by Saka (2005), in which a hydrolysis reaction occurs in a first reactor, and then, in a second reactor the esterification of fatty acids takes place. For both alternatives, the presence of fatty acids has no negative effect on the yield on the reaction; thus, low-price feedstock (such as used or waste oils and fats) can be used as raw material (Saka 2011), reducing up to 60–80 % the total cost of biodiesel production (Glisic et al. 2009; Lee et al. 2011). It has also been proved that the difference in total energy requirements between the basic catalyst process and the one-step supercritical process is small (Glisic and Skala 2009). In terms of environmental impact, it has been reported that the one-step supercritical process causes higher impact than the catalytic process (Kiwjaroun et al. 2009), but in terms of costs, the supercritical process has the potential to be better than the catalytic process (Marchetti and Errazu 2008; West et al. 2008). Other works establishes that, in order to make supercritical processes competitive, their costs and thermal energy requirements must be reduced (Sawangkeaw et al. 2010; Tan and Lee 2011). As an attempt to achieve such reductions, the use of reactive distillation has also been proposed for the two-step process (Gómez-Castro et al. 2013).

The supercritical processes on which methanol acts as solvent as well as the conventional basic-catalyzed process produce glycerol as by-product; an excess on the production of glycerol may cause a reduction on its selling price (Johnson and Taconi 2007). Therefore, other reactants have been tested to produce biodiesel under supercritical conditions, such as methyl acetate (Saka and Isayama 2009; Campanelli et al. 2010) and acetic acid (Saka et al. 2010).

In this work, industrial-scale processes are proposed for the production of biodiesel by different supercritical technologies using as reactants methanol in single-step and two-step processes: methyl acetate and acetic acid. The last two processes have only been analyzed in a laboratory scale in previous works (Saka and Isayama 2009; Campanelli et al. 2010; Saka et al. 2010). Thus, in this contribution their potential as alternatives for the production of biodiesel is analyzed in terms of energy, total annual cost, and environmental impact; to the authors' knowledge, there is not a formal analysis to compare the use of different reactants is supercritical processes for biodiesel production. The proposed processes are studied through the use of the process simulator Aspen Plus.

Study cases

The production of biodiesel fuel by four different high-temperature, high-pressure processes has been studied. For all processes, a mixture of triolein (70 mol%) and oleic acid (30 mol%) has been used as raw material. This composition of fatty acids is an average of the values reported for different vegetable oils (King et al. 1998). The processes analyzed in this work are described next.

Simulation of the processes

Simulations of the processes have been performed using the commercial simulator Aspen Plus V7.2. The stream with triolein and oleic acid, which is used to represent the vegetable oil, is fed to the processes at a flow rate of 10 kmol/h. A parametric analysis has been performed for each process, searching for high conversion on reactors and the desired purities on the separation equipment, but allowing low thermal energy requirements. A description of each of the processes is presented in the following sub-sections.

One-step methanol process (OSMP)

The first process under analysis is the Saka process (Saka and Kusdiana 2001), on which the transesterification and esterification reactions occur in a single vessel at 450 bar and 350 °C, using methanol as reactant according to the following reactions:

$$\mathrm{TRIO} + 3\mathrm{MEOH} \leftrightarrow 3\mathrm{MEOL} + \mathrm{GLY}, \tag{1}$$

$$\mathrm{OLAC} + \mathrm{MEOH} \leftrightarrow \mathrm{MEOL} + \mathrm{H_2O}, \tag{2}$$

where TRIO is trioleine, MEOH stands for methanol, GLY is glycerol, OLAC is oleic acid, H_2O represents water, and MEOL stands for methyl oleate, which represents biodiesel fuel.

In this process, the feed stream enters to a tubular reactor and it reacts with a stream of methanol, with an approximate ratio of 42 mol of methanol/mol of oil. This ratio has been reported as optimal by Kusdiana and Saka (2001). In the reactor the transesterification of the triolein and the esterification of the oleic acid occur simultaneously, according to the kinetic model provided by Kusdiana and Saka (2001):

$$-r_{\mathrm{MEOL}} = k_1 C_{\mathrm{TRIO}}, \tag{3}$$

$$-r_{\mathrm{MEOL}} = k_2 C_{\mathrm{OLAC}}. \tag{4}$$

Kinetic constants at basis reaction temperature are shown in Table 1. The pressure of the stream leaving the reactor is reduced to 1.013 bar, and the resulting stream enters to a distillation column where methanol is recovered. Then, methyl ester is separated in a decanter from the aqueous phase, which consists of glycerol and water. Finally, glycerol is obtained in a distillation column with a purity of 99.5 wt%. In this process, the vapor–liquid equilibrium (VLE) on the reaction zone has been modeled using the RK-Aspen model, as proposed by Glisic et al. (2007) for mixtures of triglycerides and methanol under supercritical conditions. The use of a reliable thermodynamic model is very important for supercritical systems, due to the strong dependence of the reaction kinetics with the distribution of the phases (Glisic et al. 2007). For the purification zone, which is operated under low-pressure conditions, vapor–liquid–liquid equilibrium (VLLE) has been simulated using the UNIFAC-LL model, since two liquid phases are obtained in the decanter. To the best knowledge of the authors, there are no reported data for the ternary system water–glycerol–methyl oleate. There are, however, available data for the methanol–glycerol–methyl oleate system, and it has been reported that the UNIFAC model fits properly the experimental data for phase equilibrium (Negi et al. 2006); thus, the UNIFAC-LL model has been used on the simulations involving the separation of glycerol and methyl oleate. The quaternary VLLE plot for the methanol–glycerol–methyl oleate–water system is shown in Fig. 1, where shadowed regions are heterogeneous. Ternary and binary plots for the subsequent separations

Table 1 Kinetic constants for the reactions involved

Symbol	Value	Source
k_1 (s^{-1})	0.0190 (at 350 °C)	Kusdiana and Saka (2001)
k_2 (s^{-1})	0.0280 (at 350 °C)	Kusdiana and Saka (2001)
k_3 (s^{-1})	0.0028 (at 270 °C)	Saka (2005)
k_4 (s^{-1})	0.0029 (at 270 °C)	Saka (2005)
k_5 (s^{-1})	0.0020 (at 350 °C)	Saka and Isayama (2009)
k_6 ($L^2\ mol^{-2}\ s^{-1}$)	0.0700 (at 350 °C)	Saka and Isayama (2009)
k_7 (s^{-1})	0.8000 (at 300 °C)	Saka et al. (2010)
k_8 (s^{-1})	0.0029 (at 270 °C)	Saka et al. (2010)

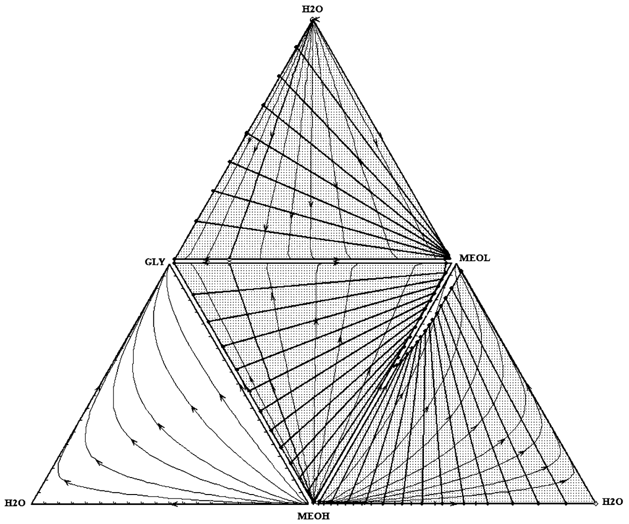


Fig. 1 Quaternary phase equilibrium plot for the system methanol–glycerol–methyl oleate–water at 1 at. (UNIFAC-LL)

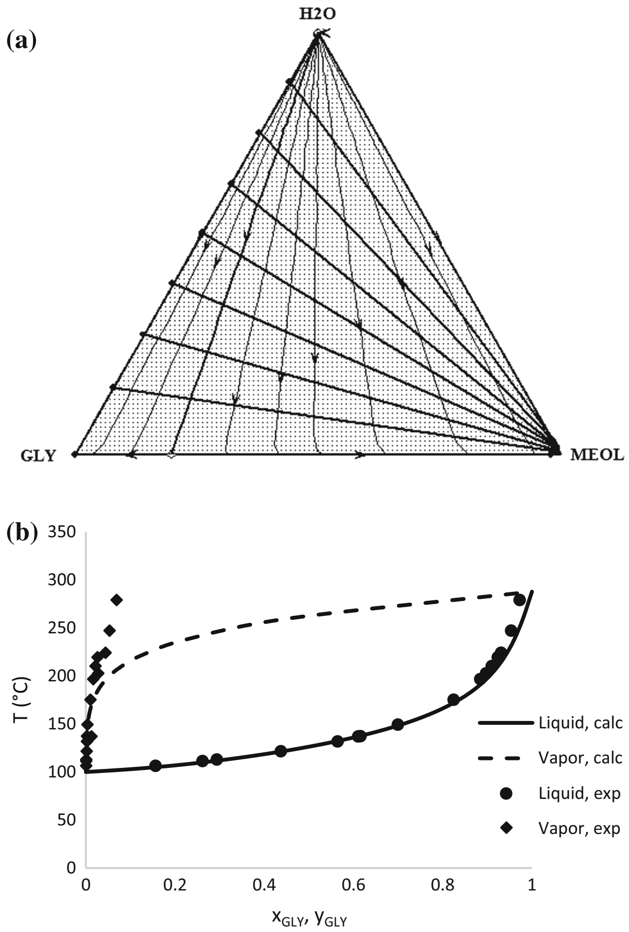


Fig. 2 Equilibrium plots at 1 atm using the UNIFAC-LL model. **a** Ternary phase equilibrium plot for the system methyl oleate–water–glycerol, **b** Binary phase equilibrium plot for the system glycerol–water

(methyl oleate–water–glycerol and water–glycerol) are presented in Fig. 2. Experimental data for the water–glycerol system has been taken from the work of Chen and Thompson (1970). It can be seen in Fig. 1 that two phases are formed in almost all the range of compositions for water/glycerol and methyl oleate. According to the calculated data, an heterogeneous azeotrope is formed between glycerol (80.14 mol%) and methyl oleate (19.86 mol%) at 279.3 °C. The whole process is shown in Fig. 3.

Two-step methanol process (TSMP)

The second process under study is the Saka–Dadan process (Saka 2005), on which a hydrolysis reaction takes place in a first reactor, and then, in a second reactor, esterification with methanol occurs. The reactions involved in this process are

$$\mathrm{TRIO} + 3\mathrm{H_2O} \leftrightarrow 3\mathrm{OLAC} + \mathrm{GLY}, \qquad (5)$$

$$\mathrm{OLAC} + \mathrm{MEOH} \leftrightarrow \mathrm{MEOL} + \mathrm{H_2O}. \qquad (6)$$

Both reactions take place at 70 bar and 270 °C.

In the two-step methanol process, the oil stream enters to a tubular reactor where a hydrolysis reaction occurs. The ratio between reactants is approximately 153 mol of water/mol of oil (Minami and Saka 2006). In this first reactor, the triolein is separated into oleic acid and glycerol, according to the kinetic model given by Saka (2005):

$$-r_{\mathrm{OLAC}} = k_3 C_{\mathrm{TRIO}}. \qquad (7)$$

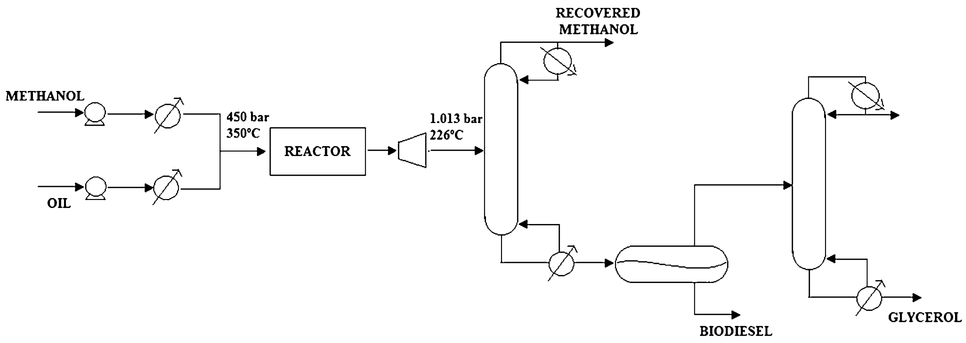
The stream leaving the hydrolysis reactor enters to a decanter, where the phase containing fatty acids is separated from the aqueous phase, which contains mainly water and glycerol. The stream with the oleic acid enters to a second reactor, where an esterification with methanol occurs. The ratio between reactants is about 28 mol of methanol/mol of oil (Minami and Saka 2006). In this reactor the products are methyl oleate and water. This reaction was modeled by using the expression proposed by Saka (2005):

$$-r_{\mathrm{MEOL}} = k_4 C_{\mathrm{OLAC}}. \qquad (8)$$

Kinetic constants for Eqs. (7) and (8) are shown in Table 1. The pressure of the stream leaving the esterification reactor is then reduced to 1.013 bar, and introduced into a decanter. The first stream obtained on the decanter goes to a distillation column where methanol is recovered. The second stream goes to a flash drum where methyl oleate is further purified to reach specifications.

The stream containing water and glycerol (obtained on the decanter which follows the hydrolysis reactor) enters a flash drum where the excess of water is vaporized. Then, glycerol is further purified in a distillation column, reaching 99.5 wt% of glycerol purity. VLE is simulated as follows: for the hydrolysis reactor, the RK-ASPEN model is

Fig. 3 One-step methanol process (OSMP)



used. For the glycerol and methyl oleate purification sections (which operate at 1 atm), the UNIFAC-LL model is used. Finally, for the esterification reactor, Peng–Robinson equation of state is used, since it fits the experimental data reported by Gómez-Castro et al. (2013) as well as the COSMO-SAC model. The ternary liquid–liquid equilibrium (LLE) plot for the system water–glycerol–methyl oleate at 70 bar is shown in Fig. 4a, whereas the VLLE plot for the system methanol–water–methyl oleate is presented in Fig. 4b. The plot shown in Fig. 4a is computed at 70 bar, since the decanter is still in the high-pressure zone. The flowsheet for the whole process is shown in Fig. 5.

Methyl acetate process (MAP)

The third process uses methyl acetate as reactant (Saka and Isayama 2009) at 200 bar and 350 °C, where the following reactions take place in a single vessel:

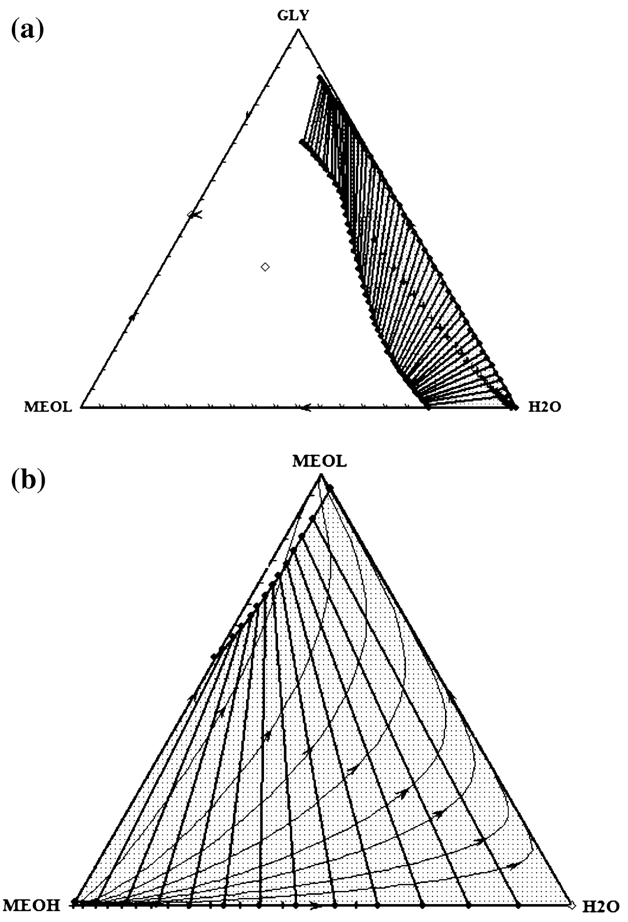


Fig. 4 Equilibrium plots. **a** Ternary phase equilibrium plot for the system methyl oleate–water–glycerol at 70 bar (RK-Aspen), **b** Ternary phase equilibrium plot for the system methanol–water–methyl oleate at 1 bar (UNIFAC-LL)

$$\mathrm{TRIO} + 3\mathrm{MEAC} \leftrightarrow 3\mathrm{MEOL} + \mathrm{TRIAC}, \qquad (9)$$

$$\mathrm{OLAC} + \mathrm{MEAC} \leftrightarrow \mathrm{MEOL} + \mathrm{AAC}. \qquad (10)$$

In reactions (9) and (10) MEAC is methyl acetate, TRIAC stands for triacetin and AAC represents acetic acid.

In this process, the feed stream enters a tubular reactor and it reacts with a stream of methyl acetate, with a ratio of 42 mol of methyl acetate/mol of oil, which has been reported as the optimal ratio (Saka and Isayama 2009). In the reactor, triolein is converted to methyl oleate and triacetin; simultaneously, oleic acid produces methyl oleate and acetic acid. The reactions occur according to the kinetic model provided by Saka and Isayama (2009):

$$-r_{\mathrm{MEOL}} = k_5 C_{\mathrm{TRIO}}, \qquad (11)$$

$$-r_{\mathrm{MEOL}} = k_6 C_{\mathrm{OLAC}}^2 C_{\mathrm{MEAC}}. \qquad (12)$$

Kinetic constants for Eqs. (11) and (12) are shown at Table 1. Once the stream leaves the reactor, its pressure is reduced to 1.013 bar. The resulting stream enters a flash drum, where the methyl acetate in excess is recovered. Then, further purification of methyl oleate takes place in a distillation column, in order to comply with purity specifications. In this process, the VLE on the reaction zone has been modeled using the RK-Aspen model, following the proposal of Glisic et al. (2007) for methanol under supercritical conditions; similarly, VLE has been simulated using the UNIFAC-LL model for the low-pressure purification zone. Equilibrium plots for the mixtures involved are shown in Fig. 6, while the whole process is presented in Fig. 7.

Acetic acid process (AAP)

In the fourth process, acetic acid is used as reactant to produce oleic acid at 200 bar and 300 °C. Then, in a second vessel, methanol esterifies the oleic acid, obtaining methyl oleate, at 170 bar and 270 °C (Saka et al. 2010). The reactions are as follows:

$$\mathrm{TRIO} + 3\mathrm{AAC} \leftrightarrow 3\mathrm{OLAC} + \mathrm{TRIAC}. \qquad (13)$$

$$\mathrm{OLAC} + \mathrm{MEOH} \leftrightarrow \mathrm{MEOL} + \mathrm{H_2O}. \qquad (14)$$

In this process, the oil stream enters a tubular reactor where it reacts with acetic acid. The ratio between reactants is approximately 38 mol of acetic acid/mol of oil (Saka et al. 2010). In this first reactor, oleic acid and triacetin are obtained as products, following the kinetic model proposed by Saka et al. (2010):

$$-r_{\mathrm{OLAC}} = k_7 C_{\mathrm{TRIO}}. \qquad (15)$$

The stream leaving the first reactor is treated with water, obtaining a stream rich in acetic acid, water, and triacetin and a second stream containing mainly oleic acid. The

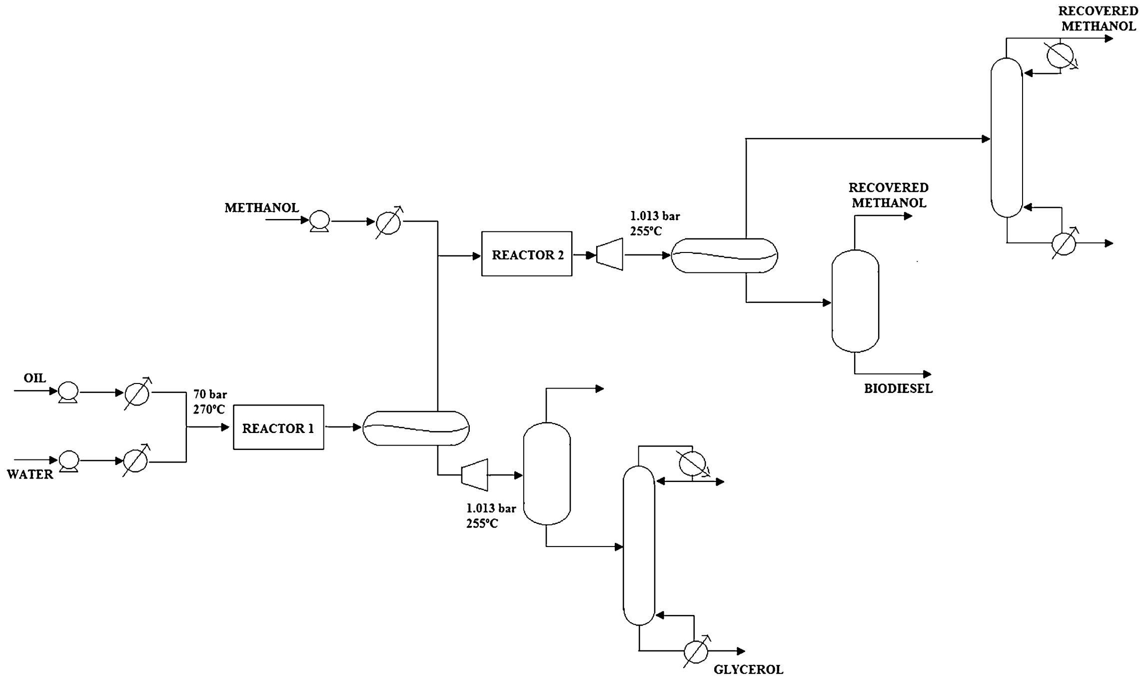


Fig. 5 Two-step methanol process (TSMP)

stream with oleic acid enters an esterification reactor, where methyl oleate and water are obtained. The ratio between reactants is about 33 mol of methanol/mol of oil (Saka et al. 2010). This reaction proceeds according to the kinetic model given by Eq. (16):

$$-r_{\mathrm{MEOL}} = k_8 C_{\mathrm{OLAC}}. \tag{16}$$

Kinetic constants for Eqs. 15 and 16 are shown in Table 1. Pressure of the stream leaving the esterification reactor is reduced to 1.013 bar, and then the stream enters a decanter. The first stream is sent to a distillation column, where methanol is separated from water. The second stream enters to a flash drum, where methyl oleate is obtained with the desired purity. Back to the washing column, the stream containing water, acetic acid, and triacetin is conditioned to atmospheric pressure, and then the stream enters a distillation column, where triacetin is obtained with a purity of 97 mol%. The mixture of acetic acid and water represents a difficult separation; thus, azeotropic distillation is used to purify acetic acid, with isobutyl acetate as entrainer (Luyben and Chien 2010). Acetic acid is obtained with a purity of 99 mol%. VLE is simulated as follows: for the first and second reactors, the RK-ASPEN model and the Peng–Robinson equation of state are used, respectively. For the purification systems, the UNIFAC-LL model is used, except for the azeotropic distillation column, where the NRTL/Hayden-O'Connell equation is used, according to the proposal of Luyben and Chien (2010). In Fig. 8 ternary plots for the mixtures involved in the acetic acid recovery step are presented. The flowsheet for the whole process is shown in Fig. 9.

Kinetic constants presented in Table 1 are reported at a basis reaction temperature. Nevertheless, changes on reaction rate constants with temperature have been also considered through an Arrhenius approach:

$$k(T) = A \cdot \exp(E_a/RT). \tag{17}$$

Values for the pre-exponential factor and energy of activation have been obtained through regression of previously reported experimental data, and are shown in Table 2, together with the source of the experimental information.

Analysis tools

To compare the different processes for the production of biodiesel at high temperature and pressure, three parameters have been used: total heat duty, emissions of CO_2, and total annual costs. Total heat duty considers all the thermal energy inputs to the equipment, and it is an indirect measurement of the quantity of steam required by the process. The other two parameters will be discussed in the following sub-sections. In order to determine if the fuel obtained has potential to produce more energy than that used to produce it, heating efficiency (HE) is also computed as defined by Gómez-Castro et al. (2011):

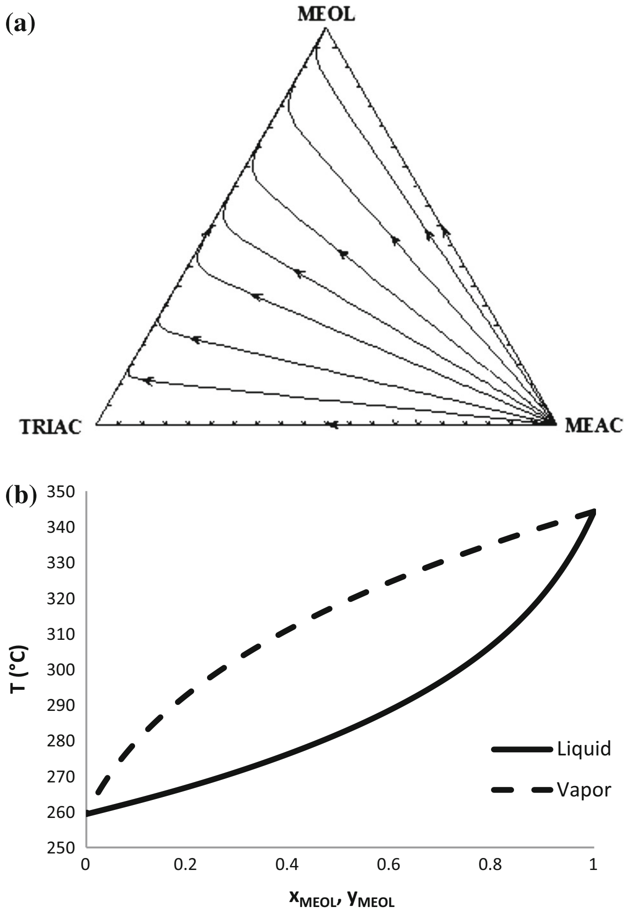


Fig. 6 Equilibrium plots at 1 bar using the UNIFAC-LL model. **a** Ternary phase equilibrium plot for the system methyl oleate–methyl acetate–triacetin, **b** Binary phase equilibrium plot for the system methyl oleate–triacetin

$$HE = \frac{Q_{\text{prod}}}{Q_{\text{req}}}, \tag{18}$$

where Q_{prod} is the quantity of thermal energy produced by the fuel and Q_{req} is the quantity of thermal energy required to produce the fuel. Thus, values for heating efficiencies higher than 1 imply that the fuel delivers more energy than that required for its production. A value of 3980 kJ/kg for the heating capacity of biodiesel has been used (Demirbas 2008).

CO_2 emissions

Most of the process equipment need an external heat input to perform its operations. This heat is provided by steam, at a given pressure and temperature, which must be enough to allow a proper temperature difference on the heat exchanging device. Steam is produced in a boiler where a fossil fuel is usually burned, producing greenhouse gases, particularly carbon dioxide (CO_2). The CO_2 produced will depend mainly on the heat required by the process, and also on the pressure of the steam. To estimate the emissions for each process, the method proposed by Gadalla et al. (2005) is used, where natural gas has been selected as fuel to obtain the steam.

Total annual costs

Total annual costs (TAC) are calculated as the sum of annualized capital costs (CC) and operation costs (OC), as reported by Luyben and Luyben (1995):

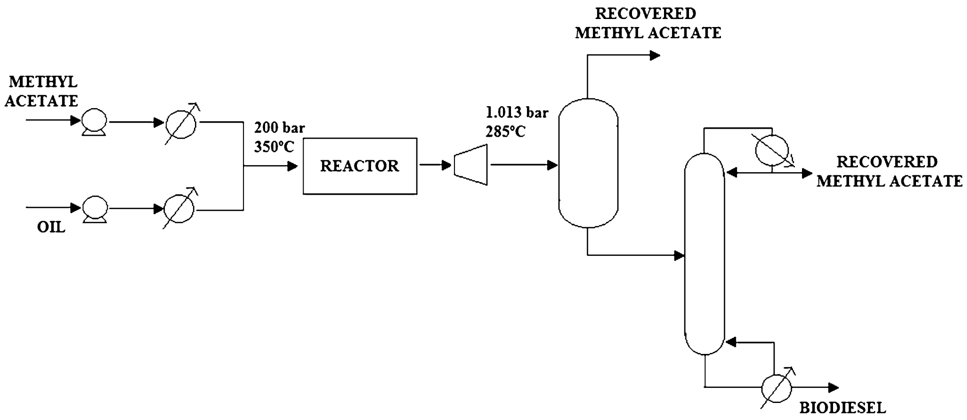
$$TAC = \frac{CC}{n} + OC, \tag{19}$$

where n is the payback period, i.e., the time after which the fixed capital investment is recovered. The value of n has been taken as 5 years to annualize the capital costs.

Capital costs are calculated by considering the purchase cost for each piece of equipment, which is estimated following the Guthrie's method as shown by Turton et al. (2009). The costs obtained from the data presented by Turton et al. (2009) are updated by using the Chemical Engineering Cost Index of October of 2011, with a value of 594.

Operation costs are calculated by considering the cost of steam, water, and electricity. Steam is used as heat source, whereas water is used where cooling is required. Electricity

Fig. 7 Methyl acetate process (MEAP)



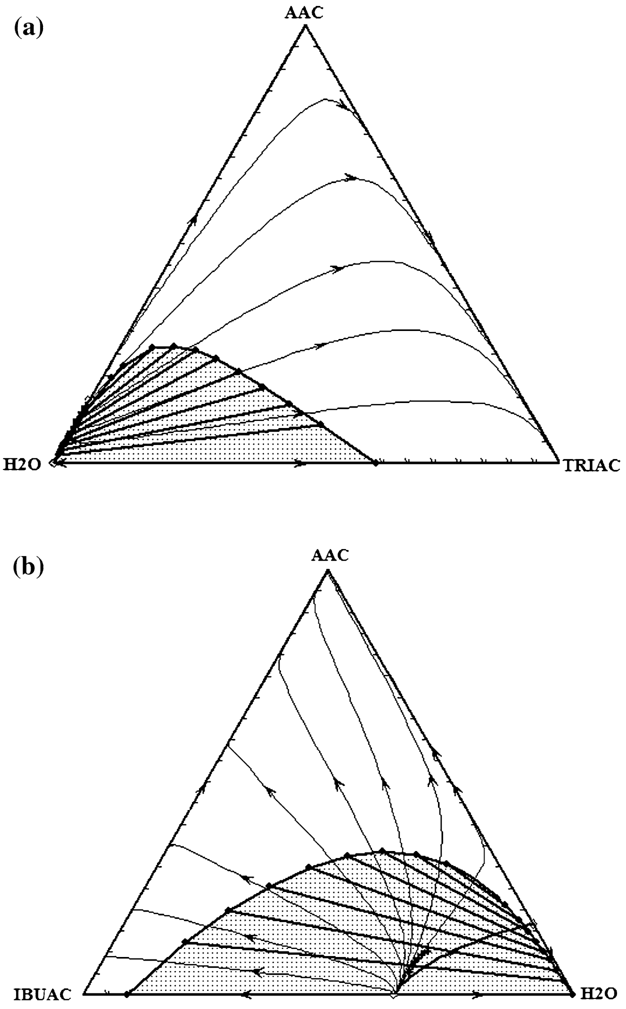


Fig. 8 Equilibrium plots. **a** Ternary phase equilibrium plot for the system acetic acid–water–triacetin at 1 bar (UNIFAC-LL), **b** Ternary phase equilibrium plot for the system acetic acid–water–isobutyl acetate at 1 bar (NRTL/Hayden-O'Connell)

is used mainly in the pumps. A cost of 0.0000148 USD/kg is used for cooling water, with its temperature being increased from 25 to 35 °C. Since different heating levels are required on the processes, three kinds of steam are used: high pressure, medium pressure and low pressure. Low-pressure steam (2.5 bar) has a saturation temperature of 127 °C and a cost of 0.02929 USD/kg. Medium-pressure steam (26.5 bar) has a saturation temperature of 227 °C, with a unitary cost of 0.02959 USD/kg. Finally, high-pressure steam has a cost of 0.02997 USD/kg and a saturation temperature of 316 °C for the TSMP and AAP processes, whereas a steam with a saturation temperature of 366 °C is required for the OSMP and MAP processes. High-pressure steams are at 107 and 200.5 bar, respectively. Costs for water and steam have been taken from the work of Turton et al. (2012). Cost for electricity has been taken as the mean unitary cost for the central zone of Mexico in October of 2013, with a value of 0.079 USD/kWh. Annual operation costs have been calculated by assuming that the plant operates 8500 h per year.

Results

A sensitivity analysis of the design parameters for all supercritical processes has been performed, in order to reduce as much as possible the thermal energy requirements. Then, considering the heat required for all the pieces of equipment of these processes, the total energy requirements have been computed. Operating conditions for the pumps for all the processes are shown in Table 3, while in Table 4 operating conditions for the heat exchangers are shown. It can be seen that, even though one-step processes require higher temperatures, total energy duty in exchangers is higher for two-step processes, mainly due to the energy required for heating the water. In Table 5, the operating for the reactors are presented, where the conversion corresponds to the limiting reactant; it can be seen that the hydrolysis reaction is the slowest one. Also, in Table 5, two values of conversion are shown for the one-step processes; the first value corresponds to the conversion of triolein, while the second value is the conversion of oleic acid. When reducing the pressure of the streams entering to the separation section, the use of hydraulic turbines is proposed to obtain some electricity. Potential electricity production in those devices is as follows: 395 kW for the OSMP, 208 kW for the TSMP, 331 kW for the MAP, and 408 kW for the AAP. Operating conditions for the distillation columns (Table 6) show that most of the energy required in the two-step methanol process is used in recovering the alcohol. In the case of the acetic acid process, high quantities of energy are required for the recovery of methanol, and for separating the water–acetic acid azeotrope. Total steam and energy requirements are shown in Table 7, from where we observe that the OSMP is the process with the lowest thermal energy requirements, while the processes taking place in two steps (TSMP and AAP) have considerably high energy requirements (about 4.5 and 7.4 times the energy required by the OSMP, respectively). It is important to notice that the whole MEAP requires high-pressure steam. If the emissions of carbon dioxide are considered (they are also shown in Table 7), the TSMP process shows the lowest carbon dioxide emissions, followed by the AAP. The processes taking place in a single step (OSMP and MEAP) show high CO_2 emissions, because they require steam at a higher temperature; thus more fuel is burned to obtain that steam, releasing more greenhouse gases. Results for the calculations of heating efficiency are also shown in Table 7. It can be seen that, if only the energy due to the process in considered, the

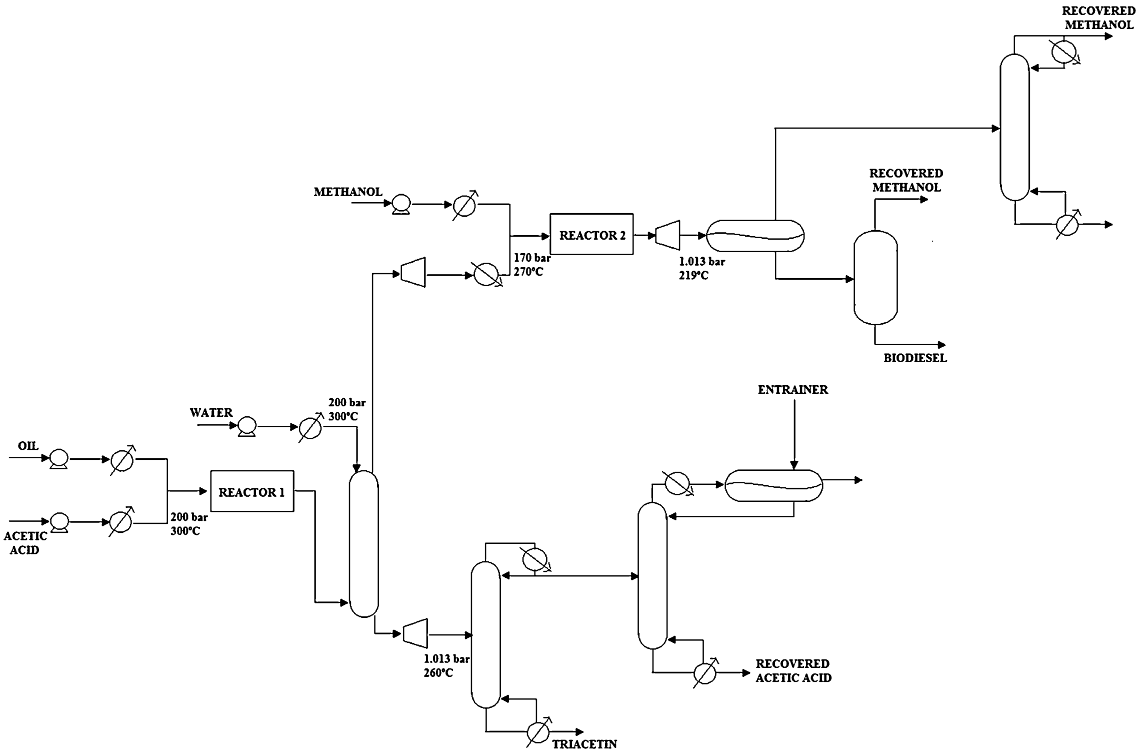


Fig. 9 Acetic acid process (AAP)

Table 2 Variation of kinetic constants with temperature

Symbol	A	E_a (kJ/kmol)	Source
k_1 (s^{-1})	0.6724 ($T < 290$ °C)	31,859 ($T < 290$ °C)	Kusdiana and Saka (2001)
	302.6 ($T \geq 290$ °C)	50,208.2 ($T \geq 290$ °C)	
k_2 (s^{-1})	59,754.5	75,372.2	Saka (2005)
k_3 (s^{-1})	3158.9	70,543.9	Saka (2005)
k_4 (s^{-1})	59,754.5	75,372.2	Saka (2005)
k_5 (s^{-1})	1.32×10^{11} ($T < 340$ °C)	164,858 ($T < 340$ °C)	Saka and Isayama (2009)
	13.6 ($T \geq 340$ °C)	45,735.3 ($T \geq 340$ °C)	
k_6 ($L^2\ mol^{-2}\ s^{-1}$)	5.97×10^{32} ($T < 320$ °C)	384,007 ($T < 320$ °C)	Saka and Isayama (2009)
	4×10^9 ($T \geq 320$ °C)	128,327 ($T \geq 320$ °C)	
k_7 (s^{-1})	3.63×10^{10}	28,180	Saka et al. (2010)
k_8 (s^{-1})	59,754.5	75,372.2	Saka (2005)

processes in two steps require much more energy than that delivered in the fuel. The OSMP and MEAP processes have a heating efficiency higher than 1; thus, it delivers more energy than that required by the process. Nevertheless, it must be considered that, for the MEAP process, the biofuel obtained consists not only on methyl esters but also triacetin.

Equipment costs, utilities costs, and total annual costs (TAC) are shown in Table 8. It can be seen that the one-step processes (OSMP and MEAP) show the lowest values of TAC. The one-step processes show low TAC's, because they require fewer pieces of equipment; nevertheless, they must be constructed on special materials (e.g., Ni alloys) to resist the hard reaction conditions. On the other hand, the TSMP configuration requires more pieces of process equipment, but the conditions for the reaction are less severe. Thus, stainless steel can be used for the construction of the reactor, but high quantities of energy are required to recover the methanol on the stream leaving the esterification reactor. The AAP has the highest values for TAC because of the difficult separation between water and acetic acid (about 96 % of the total requirements for mid-pressure steam), and the separation of the triacetin (about 62 % of the total requirements of high-pressure steam).

An additional factor has to be considered to decide which process may be feasible in practice: it has been

Table 3 Operating conditions for the pumps

	OSMP		TSMP		
	Oil pump	Methanol pump	Oil pump	Water pump	Methanol Pump
Inlet pressure (bar)	1.01	1.01	1.01	1.01	1.01
Outlet pressure (bar)	450	450	70	70	70
Volumetric flow rate (m^3/h)	9.02	16.97	9.02	36.51	15.02
Electricity (kW)	277.40	426.20	42.62	117.72	60.00

	MEAP		AAP			
	Oil pump	Methyl acetate pump	Oil pump	Acetic acid pump	Methanol pump	Water pump
Inlet pressure (bar)	1.01	1.01	1.01	1.01	1.01	1.01
Outlet pressure (bar)	200	200	200	200	170	200
Volumetric flow rate (m^3/h)	9.02	33.41	9.02	21.16	13.49	28.61
Electricity (kW)	122.94	316.34	122.94	222.31	136.28	279.01

Table 4 Operating conditions for the heat exchangers

	OSMP		TSMP		
	Oil exchanger	Methanol exchanger	Oil exchanger	Water exchanger	Methanol exchanger
Inlet temperature (K)	360.33	317.92	308.27	299.84	302.57
Outlet temperature (K)	623.15	623.15	543.15	543.15	543.15
Heat duty (MJ/h)	4718.49	16,078.40	3456.40	34,706.40	13,551.80

	MEAP		AAP			
	Oil exchanger	Methyl acetate exchanger	Oil exchanger	Acetic acid exchanger	Methanol exchanger	Water exchanger
Inlet temperature (K)	326.75	310.46	326.75	319.67	306.442	303.49
Outlet temperature (K)	623.15	623.15	573.15	573.15	543.15	573.15
Heat duty (MJ/h)	4806.27	22,180.80	3918.06	6377.59	11,230.8	30,378.10

reported that biodiesel may show thermal instabilities, isomerizing into its trans form, for temperatures higher than 300 °C. A consequence of these instabilities is that they might cause a reduction on the yield (Imahara et al. 2008). Furthermore, it has been reported that glycerol may show decomposition under temperatures of 350–400 °C and pressure of 100–300 bar (Anitescu et al. 2008). Thus, it appears that the TSMP is the best option, showing low environmental impact and ensuring the thermal stability of the methyl esters. Nevertheless, alternatives must be proposed for reducing the energy requirements of the two-step methanol process, because steam costs have a high impact on its TAC. One of those alternatives is the use of reactive distillation, as proposed in a previous work (Gómez-Castro et al. 2013). Further, although it is unavoidable producing glycerol, it may be treated to obtain high-value products within a biorefinery configuration. Other alternative is operating the one-step processes at a lower temperature to avoid biodiesel and glycerol decomposition. This will have as a consequence a reduction on the rate of reaction, requiring a bigger reactor to achieve the conversion requirements. An analysis on the impact of reducing reaction temperature for the one-step processes has been performed. Total annual costs and CO_2 emissions for the modified OSMP and MEAP are shown in Table 9. In the case of the OSMP, the reduction on the utilities costs due to the lower requirements of steam has a higher impact on total annual costs than the increasing on equipment costs because of the need for bigger reactors for temperatures between 290 and 350 °C. Thus, when temperature is lowered, TAC is also reduced. Nevertheless, for temperatures lower than 290 °C, TAC is slightly increased, which means that the capital costs for reactors began to be more important. It can be also observed that, for temperatures lower than 300 °C,

Table 5 Operating conditions for the reactors

	OSMP	TSMP	
	Transesterification/Esterification	Hydrolisis	Esterification
Length (m)	4.0	8.0	3.5
Diameter (m)	1.3	3.0	1.0
Residence time (hr)	0.09	0.69	0.07
Heat duty (MJ/h)	−1749.89	4762.26	1515.54
Conversion (%)	99.85/99.96	99.10	99.70

	MEAP	AAP	
	Methyl acetate reactor	Acetic acid reactor	Esterification
Length (m)	7.5	3.5	4.0
Diameter (m)	4.5	1.5	2.0
Residence time (hr)	1.33	0.11	0.29
Heat duty (MJ/h)	−2499.46	−6068.25	1401.19
Conversion (%)	99.98/97.45	99.87	97.52

Table 6 Operating conditions for the distillation columns

	OSMP		TSMP	
	Methanol recovery	Glycerol purification	Methanol recovery	Glycerol purification
Number of stages	30	10	18	6
Feed stage	13	2	4	4
Distillate rate (kmol/h)	396.0	2.59	248.1	36.83
Main product purity	0.997	0.98	0.99	0.98
Reflux ratio	0.66	0.1	2.2	0.1
Heat duty (MJ/h)	6117.9	552.8	29,518.4	1955.09

	MEAP	AAP	
	Methyl acetate recovery	Methanol recovery	Triacetin purification
Number of stages	20	18	15
Feed stage	17	9	5
Distillate rate (kmol/h)	25.5	303.39	1552.51
Main product purity	0.999	0.99	0.969
Reflux ratio	0.38	0.52	0.04
Heat duty (MJ/h)	5248.8	18,010.40	37,007.00

	AAP Azeotropic column
Number of stages	20
Feed stage	10
Bottoms rate (kmol/h)	510.29
Entrainer flow rate (kmol/h)	3.63
Main product purity	0.985
Reflux ratio	0.56
Heat duty (MJ/h)	96,760.20

emissions of CO_2 are dramatically reduced. This is because lower temperature steam can be used; thus, less fuel is required. In the case of the MEAP process, it can be seen that total annual costs are increased for temperatures between 320 and 340 °C, if compared with the basis temperature. This occurs because, for temperatures lower than

Table 7 Steam and thermal energy requirements, CO_2 emissions, and efficiency for the analyzed processes

Process	Steam requirements (Ton/h)			Q_T (MJ/h)	CO_2 emissions (kg/h)	HE
	High pressure	Medium pressure	Low pressure			
OSMP	34.9	0.5	3.4	27,468	23,349	1.03
TSMP	46.7	1.6	30.3	129,099	10,556	0.21
MEAP	53.1	0.0	0.0	32,236	35,385	1.06
AAP	46.7	52.3	8.2	203,738	16,698	0.15

Table 8 Results for the costs analysis (all the costs in USD × 10^3/year)

Process	Equipment	Utilities	TAC
OSMP	2088.8	10,386.5	12,475.3
TSMP	1385.1	20,008.2	21,393.3
MEAP	2770.0	14,311.3	17,081.5
AAP	3214.9	27,849.8	31,064.7

Table 9 Variation of the TAC and environmental impact with the temperature for the one-step processes

Temperature (°C)	TAC (USD × 10^3/year)		CO_2 emissions (kg/h)	
	OSMP	MEAP	OSMP	MEAP
270	9007.5	–	2062	–
280	8906.4	–	2265	–
290	7393.1	30,078.5	2391	7951
300	7393.2	20,319.5	2443	8339
310	11,589.4	24,779.5	20,101	31,202
320	11,812.6	19,236.3	20,902	31,724
330	12,718.6	19,256.5	23,557	33,140
340	12,233.4	16,799.0	22,535	34,261
350	12,475.3	17,081.5	23,349	35,385

340 °C, reaction rate for triolein is slower. For temperatures lower than 320 °C, reaction rate for oleic acid also changes, and the required reactors are bigger. Due to the special material required, the effect of reactor capital cost is more important when temperature is decreased. Emissions of CO_2 are considerably reduced for temperatures lower than 300 °C, but TAC is very high. Data for 280 °C and 270 °C are not shown because very big reactors would be required to achieve the desired conversion, and the TAC would be considerably increased. According to this study, one-step methanol process can be operated at temperatures of 290 °C with the lowest TAC and CO_2 emissions when compared to the same processes at 350 °C. Nevertheless, TAC for methyl acetate process increases for temperatures lower than 340 °C, because of the high impact of temperature over reaction rates. Emissions of CO_2 for this process can be reduced at 300 °C, but total annual cost makes this alternative economically non-viable.

Table 10 Molar flow rates for the biodiesel produced

Component	Molar flow rate (kmol/h)			
	OSMP	TSMP	MEAP	AAP
Triolein	0.016	0.007	0.0012	0
Water	0.040	0.007	0	0.08
Glycerol	0.014	1.34×10^{-6}	0	0
Oleic acid	0.0003	0.068	0.077	2.59×10^{-5}
Methanol	0.269	0.43	0	1.00
Methyl oleate	23.95	23.75	23.92	23.71
Methyl acetate	0	0	0.23	0
Acetic acid	0	0	0.55	2.8×10^{-8}
Triacetin	0	0	6.91	2.55
TOTAL	24.32	24.27	31.68	27.35

Molar flow rates for the biodiesel fuel obtained on the different processes are shown in Table 10. These results correspond to the base case for the one-step processes (350 °C), but care has been taken to obtain the same flow rates when reducing the temperature. Production for the OSMP, TSMP, and AAP is quite similar. In the case of the MEAP process, production is slightly higher. Nevertheless, it must be taken into account that biodiesel fuel obtained through the MEAP approach contains not only methyl esters but also triacetin. Production of methyl esters is almost the same as that for the other processes. An additional stage of purification could be required if pure methyl esters were desired; nevertheless, this could be senseless because the mixtures methyl ester/triacetin has been proved as reliable fuels (Saka and Isayama 2009). Finally, a comparison between the amounts of biofuel obtained by the different processes and the requirements defined by American and European standards is shown in Table 11. Data for the standards have been taken from the work of Demirbas (2007). The biodiesel obtained by the OSMP comply with almost all of the standards but that corresponding to the maximum composition of water. The TSMP configuration satisfies all of the standards. In the case of the MEAP process, all of the standards are also achieved, but although the biodiesel stream contains no free glycerol, it has acetic acid and methyl acetate; these compounds are not considered in the standards for biodiesel, and its impact on the performance of the biodiesel

Table 11 Comparative of the biofuel obtained with the standards ASTM/EN 14213

Component	Standard	OSMP	TSMP	MEAP	AAP
Water and sediment	0.05 max vol%	0.16	0.02	0	0.28
Free glycerol	0.020 max wt%	0.018	1.74×10^{-6}	0	0
Total glycerol	0.25 max wt%	0.21	0.09	0.01	0
Triglyceride	0.2 max wt%	0.19	0.09	0.01	0
Methanol	0.2 max wt%	0.12	0.19	0	0.42

fuel must be tested. Finally, even though the AAP configuration is the most expensive alternative, it fails on achieving the standard for methanol.

Conclusions

A comparative study on the performance of different supercritical processes for the production of biodiesel fuel has been presented. Industrial-scale flowsheets for the production of biofuel have been proposed, and they have been compared in terms of energy requirements, CO_2 emissions and total annual costs. The processes in one step show in general lower energy requirements but high environmental impact; also, the process with methanol in two steps has the lowest value for CO_2 emissions. Furthermore, a process with moderate conditions for temperature and pressure is necessary to avoid decomposition of biodiesel; thus, the two-step methanol process is preferred, but intensification alternatives must be used to reduce its energy and methanol requirements. The performance of the one-step methanol process can be significantly enhanced if the operation temperature is reduced below 300 °C, which causes a slight increment in equipment costs, but a high reduction in utilities costs and CO_2 emissions, also avoiding methyl esters and glycerol decomposition. Finally, the process with acetic acid has high environmental impact and total annual costs, mainly because of the difficulty to separate the mixture acetic acid–water.

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Conflict of interest The authors declare that they have no conflict of interest.

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