Analysis of a Two-Step, Noncatalytic, Supercritical Biodiesel Production Process with Heat Recovery

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A two-step, noncatalytic process for the production of biodiesel is analyzed. The reaction of transesterification of triglycerides with methanol is carried out in supercritical conditions by adopting reaction temperatures of 250−300 °C, higher than the critical temperature of methanol (240 °C). Under these conditions, free fatty acids are converted into fatty acid methyl esters with similar or higher rates than the corresponding triglycerides, and therefore, the process can use high acidity, cheap feedstocks, like yellow grease or beef tallow. The reacting system is also tolerant to water, so it is much more robust than the acid or alkali catalyzed systems which need the removal of water or free fatty acids to prevent catalyst deactivation. In order to minimize the heat consumption and pumping power which are very high in the traditional one-step supercritical method, two reactors with intermediate glycerol removal are used and a heat recovery scheme composed of heat exchangers and adiabatic flash drums is proposed. A computer model was built with experimentally obtained data and with data taken from the literature. The operation mode and the process conditions were determined on the basis of the minimization of the energy consumption (heat duty, cooling services, pumping power) and the fulfillment of product quality constraints (maximum amount of bound glycerin, maximum amount of methanol, and maximum allowable temperature for free glycerol treatment). The results indicate that carrying out the transesterification reaction in two steps enables the use of a low methanol-to-oil ratio (10−15). The preferred operation mode uses a first reaction stage in the perfectly mixed state and a second reaction stage in plug flow mode. Under these conditions, not only can the total pressure of the system be reduced but also the sensible heat of the product stream coming out of the reactor can be used to completely vaporize the unreacted methanol and decrease the heat consumption of the process.

Introduction

Biodiesel has lately emerged as an alternative fuel of wide acceptance because of some comparative advantages over petroleum derived diesel: it has a lower enviromental impact,[1] a higher lubricity, a higher cetane number, and a lower flash point. Remarkable reductions in emissions other than nitrogen oxides[2,3] and an increase in lubricity have been reported with neat methyl soyate or methyl soyate/petrodiesel fuel blends. Biodiesel does not contain harmful aromatic hydrocarbons, and it does not produce sulfur oxides (SO_x). Particulate emissions are also decreased. Additionally, biodiesel has the appeal of being made from renewable resources like plant and animal triglycerides and it is biodegradable.

The use of biodiesel is however limited in spite of its significant environmental benefits. The main reason is that the processes currently in use produce biodiesel at a higher cost than petroleum diesel. Currently, the price in fuel stations can only be made competitive by means of tax incentives. The problem is associated both with the feedstocks used and the process technology involved. In the biodiesel industry, the price of the raw materials can account for up to 80% of the final cost of the fuel.[4] Plant oils like soy and sunflower oils have a highly fluctuating price, and high international prices force their use to be shifted from the making of biodiesel to the food market. In contrast, beef tallow and yellow grease are inexpensive feedstocks discarded by some industries which could be advantageously used in the making of a cheaper biodiesel fuel. They contain high amounts of free fatty acids (FFA, 5−30%) that combine with the alkaline catalysts commonly used, and for this reason, they cannot be directly processed by facilities working with the alkali catalyzed process. Many solutions have been proposed for the handling of acidic feedstocks:[5] (i) preneutralization is easy but produces a net yield loss if the soaps are not recycled; (ii) pre-esterification of the FFA with methanol or glycerol, catalyzed by strong acids (slow), and followed by esterification in alkaline medium (fast); (iii) fully acid catalyzed esterification. Acid catalysts are not as effective as the alkaline ones and take much longer reaction times, thus leading to big reactor volumes. The processes catalyzed by alkalis (NaOH, KOH) or by acids (H_2SO_4) need washing steps to eliminate the dissolved catalyst (3−5 wastewater L/L biodiesel).[6] If washing is performed without flashing the unreacted methanol the (water−methanol−glycerol) mixture

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(1) Zhang, Y.; Van Gerpen, J. H.; Lee, I.; Johnson, L. A.; Hammond, E. G.; Marley, S. J. *JAOCS* **1996**, *73*, 1549.
(2) Romig, C.; Spataru, A. *Bioresour. Technol.* **1996**, *56*, 34.
(3) Wang, W. G.; Lyons, D. W.; Clark, N. N.; Gautam, M.; Norton, P. M. *Environ. Sci. Technol.* **2000**, *34*, 933.
(4) Ma, F.; Hanna, M. A. *Bioresour. Technol.* **1999**, *70*, 1.
(5) Lotero, E.; Liu, Y.; Lopez, D. E.; Suwannakarn, K.; Bruce, D. A.; Goodwin, J. G., Jr. *Ind. Eng. Chem. Res.* **2005**, *44*, 5353−5363.
(6) Karaosmanoglu, F.; Cigizoglu, K. B.; Tuter, M.; Ertekin, S. *Energy Fuels* **1996**, *10*, 890.

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must be distilled in order to recycle the methanol, e.g., as it is done in the Lurgi process.[7]

An alternative process to the catalytic ones has been recently pioneered by japanese researchers.[8−10] The process comprises the one-stage transesterification with supercritical methanol, in the absence of any catalyst. At high temperatures, methanol is in a supercritical state ($T_c = 240$ °C) and forms a homogeneous phase with the oil phase, something that does not occur in the other conventional processes, unless a minimum level of conversion is attained.[11] Reaction by supercritical methanol has some advantages: (i) Glycerides and free fatty acids are reacted with equivalent rates.[12] (ii) The homogeneous phase eliminates diffusive problems. (iii) The process tolerates great percentages of water in the feedstock;[13] catalytic processes require the periodical removal of water in the feedstock or in intermediate stages to prevent catalyst deactivation. (iv) The catalyst removal step is eliminated.

Some disadvantages of the one-stage supercritical method are clear: (v) The high temperatures involved impose high heating and cooling costs in the reaction stage. (vi) The process operates at very high pressures (20−40 MPa).[8,9] (vii) High methanol:oil ratios (usually set at 42−52)[14] involve high costs for the evaporation of the unreacted metanol.

A new supercritical biodiesel production process is proposed in this work in order to alleviate v−vii. The one-reactor setup of the classical supercritical processes[14,15] is replaced by two reactors operating in series (see Figure 1). An intermediate step of glycerol removal between the two reaction steps is introduced in order to allow the reaction to proceed to completion with reasonably low methanol:oil ratios (e.g., 10−15). A lower methanol:oil ratio is expected to decrease the heat duty required for the evaporation of the unreacted metanol and the total pressure. Additional heat recovery equipment is introduced in order to decrease the total heat duty. Double tube heat exchangers before the supercritical reactors allow the preheating of the reacting mixture by the stream exiting the reactor. Adiabatic flash drums downstream of the reactors evaporate the unreacted methanol. Only one flash drum per reaction stage was implemented in the simulation. In the industrial practice, the flashing could be implemented in two stages to decrease the pressure difference handled by each flash drum.

The process was simulated using a computer model built from from literature reports, estimations, and experimental data. The choice of an operation mode and reactor type (plug flow in a tubular reactor and perfect mixture in tank reactor) are discussed in relation to the conversion achievable and the process pressure. The process variables were varied in order to minimize the heat and pumping duties.

Experimental

Materials. Refined edible soy oil was supplied by COTO s.a.c.i.f. Reference methyl soyate was prepared according to the standard procedure (catalytic low-temperature method using NaOH as catalyst) described elsewhere.[16] Methanol (99.9+%) was supplied by Dorwil. The components were analyzed with the method of Pland and Lorbeer.[17]

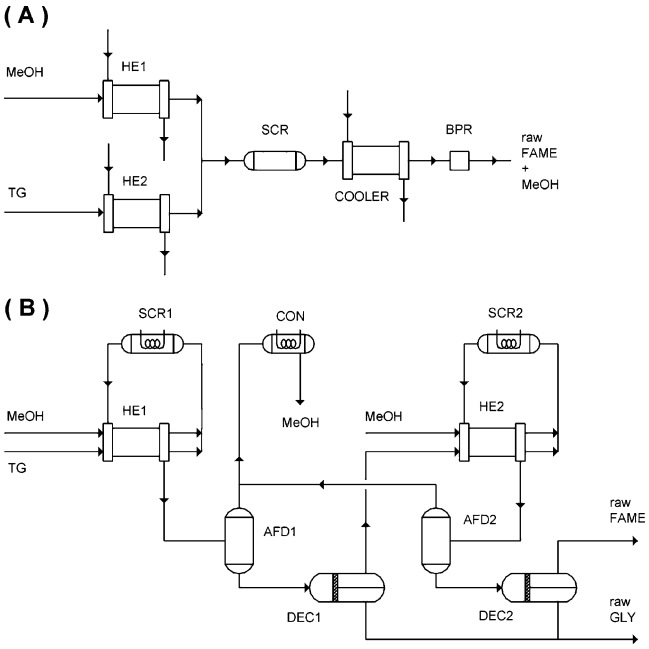

Figure 1. Flowsheets of continuous supercritical processes for the production of biodiesel. (a) 1-Stage, no heat recovery. (b) 2-Stage with heat recovery (this work). MeOH = methanol, Gly = glycerol, TG = triglycerides, SCR = supercritical reactor, HE = heat exchanger, CON = condenser, FAME = fatty acid methyl esters, DEC = decanter, AFD = adiabatic flash drum, and BPR = backpressure regulator.

***P*−*T* Curves.** In each run, a mixture of soy oil and methanol was placed in a 50 mL stainless steel autoclave having a thermocouple and a pressure gauge, similarly to other reported experiments.[18] The methanol:oil ratio was set at 6, 10, and 15. After being charged, the autoclave was purged with nitrogen and closed. Then, it was heated at 10 °C min^{-1} to the target temperature, and paired values of temperature and pressure values were recorded.

In order to make a comparison with the behavior of one-phase systems, another set of solutions of the same MeOH/TG ratios was mixed with a minimum amount of cosolvents and the *P*−*T* traces were measured. THF (Ciccarelli, 99+%) and biodiesel (99.5+%) were used as cosolvents, and they were added in small aliquotes until a single solution was formed. These solutions were charged to the autoclave, and their equilibrium vapor pressures at various temperatures were measured.

Model Development

Fluid Properties. Components are named with abbreviations throughout the text (see the Figure 1 caption). Pure component properties (methanol, glycerol) were mostly taken from the NIST on-line Webbook database. Triolein and methyl oleate were taken as model compounds for triglycerides and biodiesel. Vapor pressure was calculated with Antoine's formula from the NIST database only in the case of methanol and glycerol. In the case of biodiesel, the vapor pressure correlations of Yuan et al.[19] were used, and in the case of triolein, the Ceriani and Meirelles correlation was used.[20]

Vapor−Liquid Subcritical and Supercritical Equilibria. Subcritical activity coefficients were calculated with the UNI-

(7) Hamilton, C. *Biofuels made easy*; Lurgi Life Science Technical Brochure, 2004.
(8) Saka, S.; Kusdiana, D. *Fuel* **2001**, *80*, 225.
(9) Kusdiana, D.; Saka, S. *Fuel* **2001**, *80*, 693.
(10) Sasaki, T.; Susuki, T.; Okada, F. U.S. Patent 6,187,939, 2001.
(11) Srivastava, A.; Prasad, R. *Renewable Sustainable Energy Rev.* **2000**, *4*, 111.
(12) Warabi, Y.; Kusdiana, D.; Saka, S. *Bioresour. Technol.* **2004**, *91*, 283.
(13) Kusdiana, D.; Saka, S. *Bioresour. Technol.* **2004**, *91*, 289.
(14) Goto, V; Sasaki, T.; Takagi, K. U.S. Patent 6,812,359, 2004.
(15) Minami, E.; Ehara, K.; Kusdiana; Saka, S. *5th Biomass International Conference of the Americas*, Orlando, Florida, 2001; Session 17.
(16) Noureddini, H.; Zhu, D. *JAOCS* **1997**, *74*, 1457.
(17) Plank, C.; Lorbeer, E. *J. Chromatogr., A* **1995**, *697*, 461.
(18) Demirbas, A. *Energy Convers. Manage.* **2002**, *3*, 2349.
(19) Yuan, W.; Hansen, A. C.; Zhang, Q. *Fuel* **2005**, *84*, 943.
(20) Ceriani, R.; Meirelles, A. J. A. *Fluid Phase Equilib.* **2004**, *215*, 227.

FAC algorithm[21] with group contributions by Gmehling et al.[22] Supercritical (pressure−temperature−composition) data were either measured or taken from other reports.[8−10]

Chemical Kinetics. The transesterification of oil is known to proceed via a three-step consecutive reaction network[16] (eqs 1−3). The global reaction can be written as eq 4. The kinetic model might be enlarged to include the reaction of free fatty acids (FFA) with methanol, but this is not necessary in the supercritical reactor model. In contrast to the alkaline catalyzed system, where the FFA can react with the catalyst and produce a inhibition of the transesterication reactions, in the catalyst-free supercritical system, the FFA react only with methanol and at a similar or higher rate than glycerides as recently disclosed by Saka and co-workers.[12] The same authors have also demonstrated that the reacting system is extremely tolerant to the presence of water.[13] For this reason, we do not include FFA or water in the formulation of the kinetic model and the feedstock is considered to be composed only of oil and methanol.

$$\mathrm{TG} + \mathrm{MeOH} \underset{k2}{\overset{k1}{\rightleftharpoons}} \mathrm{DG} + \mathrm{FAME} \tag{1}$$

$$\mathrm{DG} + \mathrm{MeOH} \underset{k4}{\overset{k3}{\rightleftharpoons}} \mathrm{MG} + \mathrm{FAME} \tag{2}$$

$$\mathrm{MG} + \mathrm{MeOH} \underset{k6}{\overset{k5}{\rightleftharpoons}} \mathrm{Gly} + \mathrm{FAME} \tag{3}$$

$$\mathrm{TG} + 3\mathrm{MeOH} \underset{k^{-1}}{\overset{k}{\rightleftharpoons}} \mathrm{Gly} + 3\mathrm{FAME} \tag{4}$$

where FAME = fatty acid methyl ester, TG = triglyceride, DG = diglyceride, MG = monoglyceride, Gly = glycerol, and MeOH = methanol.

The individual reactions are well described by second-order kinetics, and values of the kinetic constants have been extensively reported, especially for the alkali catalyzed system.[16] These second-order kinetic expressions are written below in eqs 5−7.

$$r_1 = -\frac{\mathrm{d}C_{\mathrm{TG}}}{\mathrm{d}z} = k_1 C_{\mathrm{TG}} C_{\mathrm{MeOH}} - k_2 C_{\mathrm{DG}} C_{\mathrm{FAME}} \tag{5}$$

$$r_2 = -\frac{\mathrm{d}C_{\mathrm{DG}}}{\mathrm{d}z} = k_3 C_{\mathrm{DG}} C_{\mathrm{MeOH}} - k_4 C_{\mathrm{MG}} C_{\mathrm{FAME}} \tag{6}$$

$$r_3 = -\frac{\mathrm{d}C_{\mathrm{MG}}}{\mathrm{d}z} = k_5 C_{\mathrm{MG}} C_{\mathrm{MeOH}} - k_6 C_{\mathrm{Gly}} C_{\mathrm{FAME}} \tag{7}$$

Some reports indicate that the first step of formation of the diglyceride is the slowest of the three consecutive reactions,[16] with k_3 and k_5 being almost an order of magnitude higher than k_1. The same reports indicate that the equilibrium constant of reaction 3 is 2 orders of magnitude higher than the equilibrium constants of reactions 1 and 2. Therefore, the concentration of DG and MG can be considered negligible as a first approximation. If reaction 1 is considered to be rate-limiting, far from equilibrium, the rate of the global reaction can be reduced to eq 8.

$$r = -\frac{\mathrm{d}C_{\mathrm{TG}}}{\mathrm{d}z} = kC_{\mathrm{TG}} C_{\mathrm{MeOH}} \tag{8}$$

This equation is sometimes simplified further when C_{MeOH} is high; C_{MeOH} is taken as invariant, and its value is combined with the kinetic constant in order to produce a pseudo-first-order model. Kusdiana and Saka[9] develop a first-order model with this approach but they use the lumped concentration of unsterified glicerides (TG + DG + MG) as a variable instead of TG.

In this work, the full kinetic model of eqs 5−7 is employed but with two simplifications: (i) reaction 1 is considered to be the limiting step; (ii) reactions 2 and 3 are considered to be in equilibrium. The value of the equilibrium constants are estimated with a group contribution method. With these assumptions, the kinetic model has only one unknown parameter, the kinetic constant k_1 of eq 1. This kinetic constant as a function of the reaction temperature was correlated from the data of Kusdiana and Saka[8,9] and Demirbas.[18]

Sensible Heat Transfer. The scheme of Figure 1b is adopted. For the sake of simplicity, the supercritical reactor was considered to be heated by means of a jacket with a constant temperature fluid. The equation for heat transfer through the walls of the tubular reactor can therefore be written as follows:

$$\frac{\mathrm{d}T_{\mathrm{r}}}{\mathrm{d}z} = \frac{4h}{D_{\mathrm{t}}\rho C_{\mathrm{p}}}(T_{\mathrm{SCR}} - T_{\mathrm{r}}) \tag{9}$$

where D_{t} = tube diameter, h = heat transfer coefficient, ρ = fluid density, C_{p} = heat capacity, z = tube length, T_{SCR} = temperature inside the super critical reactor (SCR), and T_{r} = temperature of the heating fluid.

Downstream of the tubular reactor, the sensible heat of the product stream was used to preheat the feed to the reactor by means of a double tube heat exchanger (i = inner, hot side; o = outer, cold side).

$$\frac{\mathrm{d}T_{\mathrm{o}}}{\mathrm{d}z} = -\frac{\mathrm{d}T_{\mathrm{i}}}{\mathrm{d}z} = \frac{4h}{D_{\mathrm{t}}\rho C_{\mathrm{p}}}(T_{\mathrm{i}} - T_{\mathrm{o}}) \tag{10}$$

Latent Heat Transfer. The remaining heat content (enthalpy) of the stream issuing from the heat exchanger was supposed to be recovered by means of adiabatic flash drums placed before the decanter. They were modeled according to the classical formulations of vapor−liquid equilibrium theory.[23] The model was simulated using the Rachford−Rice algorithm. Fugacity coefficients were taken as unity, and fugacity was taken as the product of the vapor pressure multiplied by the mole fraction of each component. As mentioned before, the activity coefficients were modeled using the UNIFAC algorithm.

Heating Duty and Pumping Power. The total heat duty (HD) was calculated as the sum of the enthalpy difference between the entrance and the exit of each reactor. The pumping power (PP) was calculated as the sum of the product of the flow rate by the pressure drop in the first and second reaction stages. This pressure drop is calculated as the difference between the pressure of the reactor and the pressure of the flash drum. The pressure of the reactor was taken to be equal to the autogenous equilibrium pressure of a closed system containing a mixture of methanol and oil of the corresponding MeOH/TG ratio.

$$\mathrm{HD} = \sum F_{\mathrm{v}}\rho C_{\mathrm{p}}(T_{\mathrm{SCRexit}} - T_{\mathrm{SCRentrance}}) \tag{11}$$

(21) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor−liquid equilibria using UNIFAC*; Elsevier Publishing: Amsterdam, 1977.

(22) Gmehling, J.; Li, J.; Schiller, M. *Ind. Eng. Chem. Res.* **1993**, *32*, 178.

(23) Henley, E. J.; Seader, J. D. *Equilibrium-Stage Separation Operations in Chemical Engineering*; John Wiley & Sons: New York, 1981; p 270.

$$PP = \sum F_v(P_{SCR} - P_{flash}) \quad (12)$$

where F_v = volumetric flow rate, P_{SCR} = pressure inside the supercritical reactor, T_{SCR} = temperature of the fluid in the supercritical reactor, ρ = density of the fluid, and C_p = heat capacity of the fluid.

Model Constraints. The problem was subjected to a set of constraints worked out from the compositional limits set by current quality norms for biodiesel. According to Kimmel,[24] the equilibrium glycerol content of a biodiesel stream is a linear function of the methanol content and it is approximately 0.2% at 25 °C for a 0.0% content of methanol. Therefore, the free glycerol specification cannot be met unless the biodiesel stream is further refined downstream of the last decanter, and this restriction has no meaning for the model because the model does not include the refining operations. The total glycerol specification targets all glycerides (TG, DG, MG) and can be transformed into a minimum conversion constraint if some simplifying assumptions are made. If DG and MG are considered negligible, the total bound glycerol content is equal to the TG content and it should be lower than 0.24%. This is equivalent to saying that the conversion should be higher than approximately 99.6−99.7%. With respect to the content of methanol, a limit has not been included in many norms. However, the content of methanol is also restricted by the maximum flash point admitted. In this work, the maximum established by austrian norms was adopted (see Table 1). The restrictions can therefore be written as follows:

$$X_{TG} \geq 99.6\% \text{ (mass basis)} \quad (13)$$

$$C_{MeOH} \leq 0.20\% \text{ (mass basis)} \quad (14)$$

Results and Discussion

Kinetics. The fitting of the kinetic data produced the following results:

$$k_{subcritical} = 16.025e^{(-9164/RT)} \quad (15)$$

$$k_{supercritical} = 698.78e^{(-11215/RT)} \quad (16)$$

As it can be seen in Figure 2, the data of ref 8 were well correlated by an Arrhenius expresion while those of ref 17 were scarce and too scattered to give a god fit. In the previous equations, T is expressed in kelvin, k has units of liters per mole per minute, and the activation energy is expressed in calories per mole. The kinetic data of ref 8 correspond to mixtures of MeOH/TG = 42 and variable pressure. The small variations in the density of supercritical methanol were here disregarded, and a constant value was adopted to calculate the rate constant for the second-order model.

The activation energy for the supercritical noncatalytic transesterification is higher than that for the subcritical one, though the subcritical is 2 orders of magnitude slower. It can be seen that there are two distinctive zones of different reactivity. The noncatalytic reaction rate is negligible at temperatures lower than the critical temperature of methanol (240 °C). The lower limit is not completely defined, and different authors find different values of the temperature at which the enhanced reactivity of methanol begins. In the data of Saka et al.,[8,9] this limit is approximately 275 °C (see Figure 1) and some points of "slow kinetics" can be found at temperatures lower than 275 and higher than 240 °C. Demirbas[18] performed several experiments at 240 °C and found that the system showed the "fast kinetics" regime at MeOH/TG molar ratios higher that or equal to 9. Goto et al.[14] presented data in which methanol−oil mixtures of MeOH/TG = 52 were continuously reacted at 250 °C under supercritical conditions in the absence of catalyst and with an enhanced kinetic rate. Therefore, the limit separating the slow and fast kinetics regime seems to depend both on the temperature and the composition of the mixture. This might be related to the dual dependence of the critical point of mixtures on temperature and composition. This last reasoning has been recently used in works that try to reduce the pressure and temperature of the critical point of the reacting mixture by the addition of suitable cosolvents. Cao et al.[25] have indicated that addition of a cosolvent (e.g., propane) can depress the critical temperature and pressure of a methanol:oil mixture. They, however, remarked that the temperature of the system had to be equal or greater than 280 °C in order to react with an optimum rate.

The break in the Arrhenius plot of Figure 2 is typical of other reacting systems with supercritical methanol. A similar break can be found in the report of Huang et al.[26] on the degradation of polycarbonate. At temperatures higher than the critical one, methanol changes its viscosity, dielectric constant, density, hydrogen bonding, and polarity. In the case of the transesterification reaction, Kusdiana and Saka[13] have proposed that the direct nucleophilic attack of the sp^2 carbon of the carboxyl group by an electron pair of the oxygen atom of methanol is enhanced by the high pressure and the lower hydrogen bonding of methanol. Hydrogen bonding in subcritical methanol decreases the concentration of monomeric methanol molecules able to perform a nucleophilic attack. Yamaguchi et al.[27] studied the structure of subcritical and supercritical methanol and reported a change in hydrogen bonding from 1.93 (subcritical) to 0.7

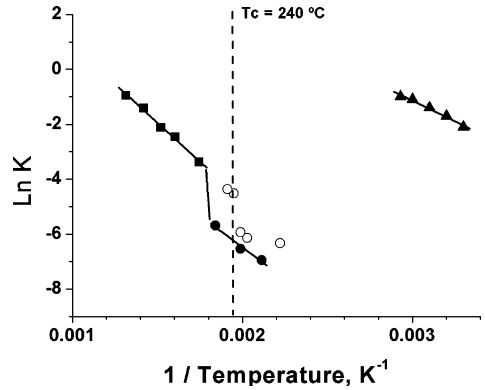

Figure 2. Arrhenius correlations of kinetic data: (■, Saka et al.;[8,9] ○, Demirbas[18]) noncatalytic, supercritical; (●) noncatalytic, subcritical; (▲) catalytic, NaOH 0.1 N.[16]

Table 1. Requirements for Methanol, Glycerol, and Glycerides Contents According to the Standards for Biodiesel Fuel

	specification	source
free glycerol	0.02% max	ASTM D6751
total glycerol	0.24% max	ASTM D6751
methanol	0.20% max	Austria Ö-NORM C-1190

(24) Kimmel, T. Doctoral Thesis, Technischen Universität Berlin, Germany, 2004.
(25) Cao, W.; Han, H.; Zhang, J. *Fuel* **2005**, *84*, 347.
(26) Huang, J.; Huang, K.; Zhou, Q.; Chen, L.; Wu, Y.; Zhu, Z. *Polym. Degrad. Stab.* **2006**, *10*, 2307.
(27) Yamaguchi, T.; Benmore, C. J.; Soper, A. K. *Chem. Phys.* **2000**, *112*, 8976−8987.

(supercritical). Chalaris and Samios[28] reported that the change in hydrogen bonding is responsible for the increase of 2 orders of magnitude of the molecular diffusivity. In Figure 2, the main change in the Arrhenius plots is not in the activation energy but in the preexponential factor. Therefore, it can be supposed that the preexponential factor of the noncatalytic reaction rate constant k is related to the concentration of monomeric, non-hydrogen-bonded methanol molecules and that this concentration is increased by about 1 order of magnitude in the supercritical region.

A comparison between the Arrhenius plots of the supercritical noncatalytic rate constant and the catalytic constant of the alkaline process seems mandatory. The data of Noureddini and Zhu[16] (NaOH 0.1 N catalyst) indicate that the catalytic rate is equal to 0.05 L mol^{-1} min^{-1} at 50 °C. The noncatalytic rate is 0.036 L mol^{-1} min^{-1} at 300 °C. Therefore, the reaction rates in the supercritical and the alkaline processes are similar or can be equalled if the temperatures are properly adjusted. One interesting consequence is that reactor volumes and residence times should then be also approximately equal for the same value of conversion and if similar MeOH/TG ratios are used. With respect to the activation energy, the data of Noureddini and Zhu[16] indicate that E_a = 13145 cal mol^{-1} which is also similar to the 11 200 cal mol^{-1} value of the noncatalytic reaction.

Thermodynamics. The values of the equilibrium constants of eqs 1−4 have never been reported for the transesterification of oils in supercritical methanol. If a group contribution method is used to estimate the global equilibrium constant, the result is exactly $K_{eq} = 1$ because the same kind and amount of groups are likely to appear in both terms of the summation used to calculate the Gibbs free energy of the reaction. Group contributions cannot capture the small chemical differences occurring in a transesterification reaction, but the value of K_{eq} is in fact close to unity. In the case of the alkali catalyzed methanolysis of soybean oil, Kimmel[24] adopts $K_{eq} = 1$. For the same reaction, Noureddini and Zhu[16] report that $K_1 = (k_1/k_2) = 0.45$, $K_2 = (k_3/k_4) = 0.18$, $K_3 = (k_5/k_6) = 34.5$, and $K_{eq} = K_1K_2K_3 = 2.7$, at atmospheric pressure and 60−70 °C. According to Kimmel,[24] transesterification equilibrium constants show only a negligible dependence on temperature, and other authors report that they are also nearly independent of solvent and salt effects.[29] Taking compositional data for the transesterification in supercritical methanol from papers and patents and calculating K_{eq} yields values both lower and higher than one. In this work, we adopt $K_{eq} = 1$ and calculate the individual equilibrium constants for each step with group contribution methods.[30,31]

***P*−*T* Composition Curves.** The results are summarized in Figure 3. The results corresponding to the MeOH−oil mixtures of MeOH/TG = 42 and 15 were plotted in raw form. All others were correlated with Antoine-like correlations, and only the correlation is plotted. In the case of the subcritical range, the experimental results indicate that for MeOH/TG = 6−42 with no cosolvent, the system splits into two immiscible phases consisting essentially of pure MeOH and pure oil. When heating from room temperature to the critical temperature of methanol, the total pressure of the system reaches values very close to the vapor pressure of pure methanol. These results are due to the immiscibility of methanol and oil mixtures. Two liquid phases are formed, and each of them exerts a vapor pressure independently of the other. As the vapor pressure of the oil is negligible, the pressure of the system is very similar to the pressure of pure methanol. The pressure of the MeOH−oil mixture of MeOH/TG = 42 (taken from ref 8) is plotted as scattered data in Figure 3. With respect to the supercritical range, Antoine's formula for pure methanol is no longer valid and predicts a higher pressure than that displayed by any of the mixtures tested. A small discontinuity in the slope of the curve of MeOH/TG = 15 at the critical temperature of methanol can be detected. Also, the $P-T$ curves of the MeOH−oil mixtures which were close in the subcritical range were more separated in the supercritical range especially in the case of the curve of MeOH/TG = 6 that had a much lower pressure than those of MeOH/TG = 15 and 10 (not plotted). At 265 °C, it was 6.5 MPa for MeOH/TG = 6 and 8.2−8.5 MPa for MeOH/TG =10−15.

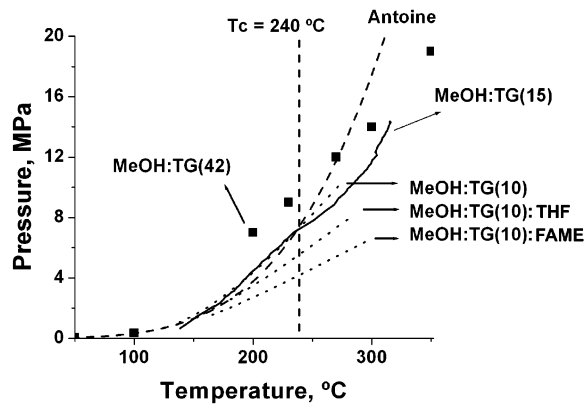

Figure 3. Pressure−temperature curves, MeOH−oil mixtures of MeOH/TG = 10 and 42 with and without cosolvent. The dashed line corresponds to Antoine's correlation for the vapor pressure of pure methanol.

The vapor pressure of the mixtures that contained THF or FAME was smaller than the pressure of the mixtures without cosolvent. These mixtures had the minimum content of THF and FAME needed for the formation of a single phase at room temperature. The resulting mixtures had different THF and FAME contents depending on the MeOH/TG ratios. For MeOH/TG =10, THF = 26% and FAME = 41% (vol/vol). THF had a stronger cosolvent effect than biodiesel. For lower MeOH/TG ratios, the needed amount of cosolvent was lower. Higher MeOH/TG ratios demanded higher amounts of cosolvent. Only the $P-T$ curves of MeOH/TG = 10 are plotted to make a comparison and to avoid overcrowding in Figure 3. The lower pressure of the MeOH−oil−cosolvent solutions is readily explained by the formation of true solutions in which the components do not exert their pressure independently but they contribute proportionally to their composition in the mixture. The volatility of THF is lower than that of methanol, and the volatility of FAME is negligible; for this reason, the pressure of these systems is lower than the pressure of the corresponding MeOH−oil solutions of equal MeOH/TG ratio.

At this point, some remarks can be made on the flowsheet of the first reaction stage and the mode of operation of the reactor. If the cosolvent effect is to be used to reduce the pressure of the first reaction, each possibility should be analyzed. THF addition produces a one-phase system without diluting the mixture too much. It can also be recycled together with methanol because its volatility is similar to the volatility of MeOH. It is also supposed that THF addition does not alter the kinetics of the MeOH−oil mixture. The disadvantage seems to be the

(28) Chalaris, M.; Samios, J. *Pure Appl. Chem.* **2004**, *76*, 203−213.
(29) Pereira, W.; Close, V.; Patton, W. *J. Org. Chem.* **1969**, *34*, 2032−2034.
(30) Joback, K. G.; Reid, R. C. *Chem. Eng. Commun.* **1987**, *57*, 233−243.
(31) Dalmazzone, D.; Salmon, A.; Guella, S. *Fluid Phase Equilib.* **2006**, *242*, 29−42.

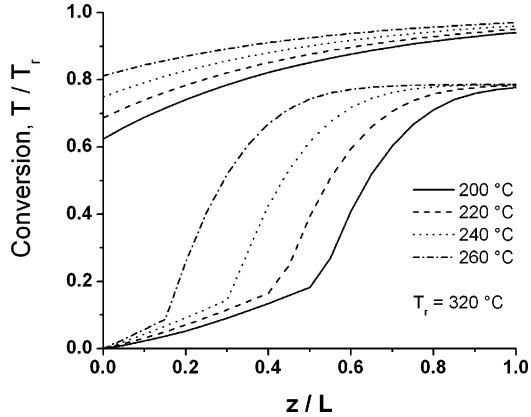

Figure 4. Temperature and conversion values in the first tubular reactor as a function of the temperature of the feed (T_{inlet}). MeOH/TG = 6, T_r = 320 °C, oil flowrate = 1000 L h^{-1}.

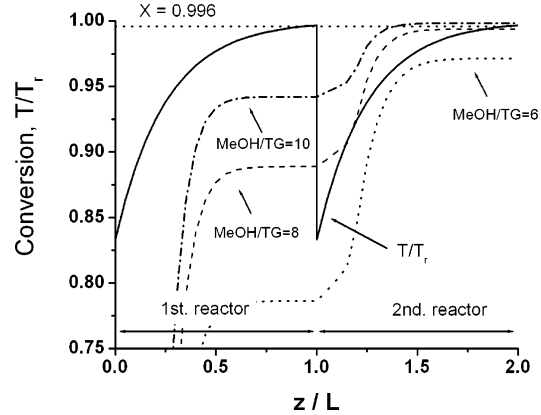

Figure 5. Temperature and conversion values along both tubular reactors as a function of the MeOH/TG molar ratio. T_r = 320 °C, feed temperature T_{inlet} = 250 °C, oil flowrate = 1000 L h^{-1}.

control of the feeding rate of MeOH which now requires the knowledge of the composition of the polar phase. The addition of FAME is less effective for eliminating the splitting into two phases but produces a more effective pressure decrease and brings no additional problems for separation and recycling. The best option however is seemingly not to recycle FAME from the product stream to the feed of the first reactor if this is a tubular reactor but to use a tank reactor working in the perfectly mixed state instead with no recycle. The first stage of transesterification for the production of biodiesel usually has an 80−90% conversion level, and therefore, a maximum pressure decrease can be obtained provided the mixing degree is good. This is not a problem because if temperatures in the 250−300 °C are used the gaslike mobility of supercritical methanol should produce high mixing even in the absence of mechanical stirrers.

In spite of these remarks regarding the possible use of a continuously stirred tank reactor (CSTR) in the first reaction stage in what follows, the simulation results will be related to the use of tubular reactors in both stages.

Conversion and Temperature Profiles in Tubular Reactors. With respect to the feeds of the first and second reactor, it was assumed that only methanol and oil were fed to the first reactor. In order to calculate the composition of the feed to the second reactor, it was assumed that total separation of glycerol occurred in the first decanter, an approximation that is valid if the content of residual methanol is sufficiently low. The small amount of glycerol entrained in the oil phase in the first decanter should also have a negligible effect on the conversion of the second reactor. The MeOH/TG molar ratio of the first reactor was set equal to 6, 8, 10, and 15 for the simulation runs. The molar ratio of the feed to the second reactor was set equal to that of the first stage, but in this case, the molar ratio was defined as follows: MeOH/(TG + DG(2/3) + MG/3 + FAME/3). In this way, the methanol volumetric feed flowrate was the same in both reaction stages, and the number of parameters of the model was decreased.

Figure 4 contains the value of conversion and temperature along the first tubular reactor as a function of the temperature of the feed for a given temperature of the heating fluid (T_r = 320 °C) and an MeOH/TG = 6. The conversion profiles have a discontinuity when the temperature of the mixture reaches 275 °C because the limit between the subcritical and supercritical regimes was established at this temperature and all the feed temperatures are lower. It can also be seen that at high residence times the conversion curves converge to the thermodynamic limit. The residence time (or reactor length) needed to achieve equilibrium depends on the MeOH/TG ratio and the reaction temperature. If the first and second reactor are sized in order to provide a sufficiently high residence time and reach equilibrium, the level of conversion at the exit of the second reactor is only determined by the MeOH/TG ratio.

The higher the feed temperature, the closer the system approaches the supercritical state and the smaller the reactor size. A feed temperature of 240−250 °C seems most convenient.

The effect of the temperature of the heating fluid, T_r, is more important than that of the feed temperature, T_{inlet}. The value of T_r dictates the value of the pressure of the reactor, because at the exit of the reactor T_{out} approaches T_r very closely. The pressure dependence on the temperature is very high as was discussed previously, and therefore, a small value above the threshold limit of the supercritical state seems the most convenient, i.e., T_r = 280−290 °C.

Figure 5 contains temperature and conversion profiles as a function of the residence time (or reactor length) for different values of the MeOH/TG ratio. For the adopted value of the equilibrium constant a minimum MeOH/TG ratio of 10 is needed in order to fullfil the FAME purity specification of the quality norms. However due to the high order of the mass action formula of reaction 4, the influence of K_{eq} on the final conversion (for 2 reactors in series) is not high. For K_{eq} = 0.3, the minimum MeOH/TG ratio to achieve 99.6% conversion is 12. An MeOH/TG = 10−12 seems convenient because higher ratios involve bigger volumes of excess methanol to be evaporated downstream of the reactor.

With respect to the convenience of using a perfectly mixed tank reactor instead of tubular reactors working in plug flow (axial Pèclet number higher than 1000), a similar conversion value in the first reactor should be achievable with slight variations in the MeOH/TG ratio and/or the reaction temperature. In the case of the second reactor, the problem is different because the value of conversion required is very high and the extreme backmixing would prevent achieving conversion values higher than 99%, even if long residence times are used.

Adiabatic Flash Drums. In the flash drums, the MeOH content must be reduced to a sufficiently small value in the first decanter in order to reduce MeOH losses and decrease the solubility of glicerol in the oil phase. In the second flash drum, the methanol content must be reduced to 0.2% in order to keep the flash point and cetane values inside the diesel range. A plot of the content of MeOH in the liquid phase in the first flash drum as a function of the MeOH/TG ratio and T_{fl}, the temperature of the flash drum, is shown in Figure 6. The results indicate that a minimum value of T_{fl} = 140−160 °C at MeOH/TG = 6−10 is needed in order to keep a maximum methanol

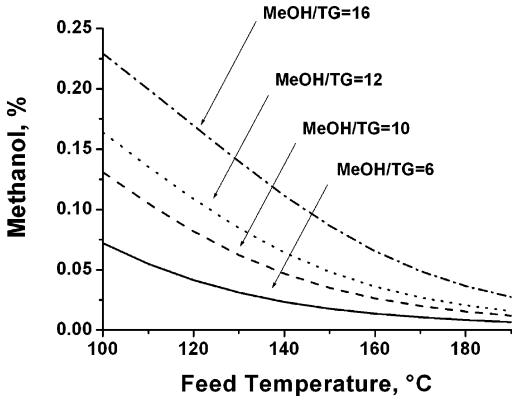

Figure 6. MeOH content (weight %) in the liquid downstream of the first flash drum as a function of the MeOH/TG ratio and the feed temperature before the flashing valve (T_v).

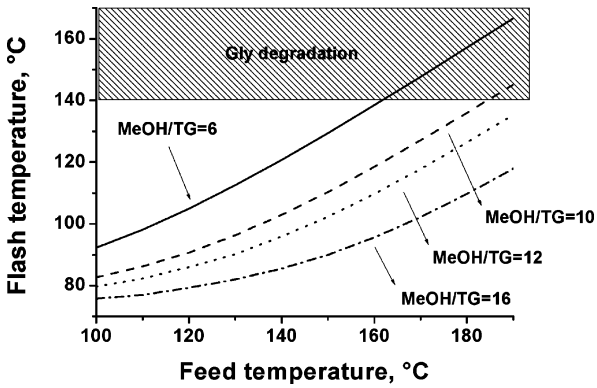

Figure 7. Flashing temperature (T_{fl}) in the liquid downstream of the first flash drum as a function of the MeOH/TG ratio and the feed temperature before the flashing valve (T_v).

content of 3% in the liquid stream issuing from the first flash drum. Higher MeOH/TG ratios, e.g., greater than 20, are not possible because, in this case, methanol cannot be completely adiabatically flashed even if the heat exchanger is eliminated.

Another concern is that of the degradation of glycerol (see Figure 7). At high temperatures, polymerization occurs, the quality is decreased, and the purification becomes difficult due to the increase in viscosity. Ueoka and Katayama[32] have suggested that flash towers for glycerol purification should operate at $T_{fl} < 140$ °C. Upstream, the flashing valve temperature is not a concern because glycerol is highly solvated by methanol.

The second flash drum has a similar behavior, and therefore, it can be inferred from Figure 6 that a 0.2% MeOH result cannot be obtained with a single flashing stage under the chosen conditions. The limit value of 0.2% can be, however, attained by operating the second flash drum at a reduced pressure (e.g., 28.5 in. Hg, the vacuum pressure obtained with simple water-ring pumps) and $T_v = 190$ °C.

Heat Duty and Pumping Power. It can be deduced that the heat duty in the reactor depends directly on the inlet temperature of the flashing valve (T_{fl}). If we consider that the temperature at the outlet of the reactor is practically equal to T_r and that there are no heat losses in the heat exchanger, the energy balance in the heat exchanger gives

$$T_{SCR\_inlet} \approx T_{HE} + T_r - T_v \qquad (17)$$

T_{HE} is the temperature of the feedstock entering the preheating heat exchanger (20−60 °C). T_r should be set at 285−290 °C, i.e., 10−15 °C just above the sub/supercritical threshold, in order to have high conversion values in the reactor. Higher temperatures are prohibitive because they generate increasingly higher pressures. T_v should be set at 140−150 °C. This is the minimum temperature that ensures low methanol levels in the liquid streams entering the decanters. Greater temperatures are discouraging because they increase the heat duty in the reactors, as explained below. A value of MeOH/TG =10 was adopted in order to allow a total conversion value of 99.6%. Higher MeOH/TG values are discouraging because they increase the total mass flowrate and the heat duty. With the use of (12) and (17) and considering $T_r \approx T_{SCR\_outlet}$,

$$Q_i = FC_p(T_{SCR\_outlet} - T_{SCR\_inlet}) \approx FC_p(T_v - T_{HE}) \qquad (18)$$

$$Q = Q_1 + Q_2 \qquad (19)$$

Q_1 is the heat duty of the first stage, and Q_2, the heat duty of the second stage. Q_2 is higher than Q_1 because of the higher value of T_v needed to almost completely flash the methanol. Now, we can compare the pumping power and heat duties of the one-reactor setup with no heat recovery with the corresponding values of the process just analyzed. Such comparative values are included in Table 2. It can be seen that the process with two tubular reactors in series does not work at a much lower pressure, but the extra cost of pumping the same flowrate through two reactors is compensated by the much higher total flowrate of the one reactor setup that needs a high excess of methanol to achieve full conversion. The difference is much greater in the case of the heating duty which is greatly improved by lowering the excess of methanol and making use of the sensible heat of the products to vaporize the unreacted methanol.

Table 2. Comparison of Heat and Pumping Duties of One-Stage and Two-Stage Supercritical Processes

	one reactor	two reactors
MeOH/TG ratio	42	10
cosolvent	none	none
yield, %	≈100	≈100
temperature, °C	300	285−290
pressure, MPa	14	10−11
total flowrate (MeOH + TG)	2.74 L L^{-1}	1.41 L L^{-1}
heat recovery	no	yes
excess methanol removal	no	yes
pumping power	8.3 kW h L^{-1}	6.4 kW h L^{-1}
Heat duty	2166 kJ L^{-1}	1382 kJ L^{-1}

Conclusions

The operating pressure for the production of biodiesel by the reaction of oils in supercritical methanol can be reduced if the reaction is allowed to proceed in two successive steps with intermediate removal of glycerol. The one-reactor setup works with molar ratio of methanol/oil = 42 and a pressure of 14−40 MPa (270−350 °C). In the two-reactor setup, the decrease of the methanol/oil ratio to 10 and the decrease of the reaction temperature to 275−290 °C results in a reduction of the working pressure to about 10−11 MPa. The final reduction in pumping power is approximately 23%.

If the first tubular reactor is changed to a perfectly mixed tank reactor, the cosolvent effect of the fatty acid methyl esters produces a great decrease of the total pressure with a parallel decrease of the pumping power associated with this stage. A similar reactor in the second reaction stage is not recommended because the extreme backmixing would prevent achieving a 99+% conversion as required by the quality standards for biodiesel fuel.

(32) Ueoka, H.; Katayama, T. U.S. Patent 6,288,287, 2001.

A low methanol/oil ratio also enables the use of adiabatic flash drums to vaporize the unreacted methanol at the outlet of the reactor with no additional heat input, with a substantial decrease of the heat duty of the process. An additional heat exchanger contacting the streams entering and exiting the reactor enables an additional recovery of heat. The final heat duty when compared to the one-reactor setup with no heat recovery is 36% lower. The two-reactor setup has the additional advantage that no additional heat is necessary to vaporize the unreacted methanol. The values of the process parameters ensure that the equilibrium temperature of the flash drums is low enough to prevent the degradation of the glycerol byproduct.

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