Batch Study of Glycerol Decomposition in One-Stage Supercritical Production of Biodiesel

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The objective of this work was to assess some of the points that need to be elucidated in order to define the economic viability of the noncatalytic supercritical biodiesel process. Net yield of the supercritical process, consumption of methanol, and the quality of the fuel issuing from the reactor were studied. Biodiesel was prepared by reacting refined soy oil with supercritical methanol at $T = 280$ °C and methanol-to-oil molar ratios of 15 and 20. After the reaction, unreacted methanol, water, and other volatile compounds were removed from the product by stripping with nitrogen at 110 °C. Biodiesel production by the reaction of oils in supercritical methanol under the conditions used in this work produces practically no glycerol byproduct. This fact simplifies the downstream refining of the produced biodiesel. Glycerol is transformed into products of smaller molecular size and water. At first this water reacts with the triglycerides of the reacting mixture to form free fatty acids (FFA), thus increasing the acidity of the product. At longer reaction times the acids are converted into methyl esters again. Glycerol methanolysis reactions increase the methanol consumption. The small amount of glycerides and FFA contaminants in the biodiesel product makes a final step of refining by silica adsorption convenient. No liquid effluents are issued with such a refining step. After the FFA and glycerides are recycled, the yield of the process is 94–96%.

Introduction

The benefits of biodiesel cannot be overemphasized.[1–3] Growth expectations of the capacity installed worldwide for biodiesel production have increased in recent years because of the continuous rise of petroleum prices and legislation in developed countries forcing refiners to add biofuels in the formulations of gasoline and diesel fuels. Nowadays an increase in the production of biodiesel or bioethanol is possible only by increasing the yield of planted croplands or by increasing the planted areas. This carries the threat of exhausting the current croplands, taking croplands used for food purposes, or irreversibly damaging the environment if natural forests are transformed into croplands. Experience with the third alternative in Argentina, Paraguay, and Brazil indicates that such a policy ends up with a negative carbon dioxide balance. A better solution for increasing the production of biofuels would be the use of all currently unexploited feedstocks.

Most of the final biodiesel fuel price is dictated by the price of the raw material. In this sense, beef tallow and yellow grease are inexpensive feedstocks discarded by some industries that could be advantageously used in the making of a cheaper biodiesel fuel. However, they contain high amounts of free fatty acids (FFA, 5–30%) that react with the dissolved alkalis used as catalysts in the most common industrial processes. For this reason they cannot be directly processed by these facilities.

Initially pioneered by Japanese researchers,[4–6] the noncatalytic supercritical process has lately become an intensively researched process due to its tolerance to FFA and water and its seemingly multifeedstock capacity. The process comprises one-stage transesterification with supercritical methanol, in the absence of any catalyst. The many advantages of the reaction with supercritical methanol have been previously discussed:[1,7–11] Disadvantages of the one-stage supercritical method are related to the drastic conditions needed to sustain the supercritical state: the high temperatures demand high heating and cooling duties in the reaction stage; the very high pressures (20–40 MPa) involve costly pumping requirements;[4,5] and the high methanol: oil ratios (42–52)[12] involve high costs for evaporation, recovery, and recycling of unreacted methanol. In spite of these drawbacks, many patents have been issued for the production of biodiesel with this process.[6,12,13]

It seems obvious that, in order to assess the economic viability of the noncatalytic supercritical biodiesel process, some points need to be elucidated by further research: (a) The price of biodiesel depends 80–90% on the value of the raw material, and for this reason the net yield of fatty acid methyl esters must

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be high to be competitive. European alkali-catalyzed processes using high-quality oils display yields of about 97% when the glycerol phase with dissolved glycerides and soaps is recycled. The net yield of the supercritical process needs to be determined, and it can be said in advance that yields lower than 95% are not competitive. (b) Net consumption of methanol in the supercritical process is determined not only by the stoichiometry of transesterification but also by its consumption in lateral reactions with glycerol. Supercritical methanol is highly reactive; it performs a nucleophilic attack on carbon atoms bonded to oxygen and may even break the carbon chain. Ethers seem the most likely products, though other products like acrolein are not ruled out. In any case, these lateral reactions increase the specific consumption of methanol and the production costs. (c) The overall economic balance of the biodiesel process demands the valorization or price maintenance of the issued byproduct. The problem is obviously concentrated on the valorization of glycerol. Nowadays, though multiple products can be made from glycerol, its market value has dropped due to the saturation of the market, especially in Europe. Free fatty acids (FFA) are another possible byproduct. If they cannot be marketed, their recycle to the reactor feed is a viable and commonly used solution. (d) The last issue is the quality of the biodiesel fuel. This is very important because the quality of the fuel issuing from the reactor defines the complexity and dimension of the downstream refining facilities.

The objective of this work was to assess some of the points a–d raised above. Refined soy oil was reacted with supercritical methanol under typical process conditions. Yield values were measured and the amount and type of byproduct were determined.

Experimental Section

Materials. Refined edible soy oil was supplied by COTO s.a.cif with 0.21% free fatty acid (FFA) content, 0.03% water, and a iodine value (IV) of 134. Methanol (99.9+%) was supplied by Dorwil with 0.001% FFA and 0.06% water.

Transesterification Reaction. 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, similar to other reported experiments.[14] The thermocouple was located on the axis of the cylindrical reactor, 1 mm from the bottom and in contact with the liquid phase. The methanol:oil molar ratio (R) was set at 15 and 20. After being charged, the autoclave was purged with nitrogen and closed. Then it was heated at 30 °C min^{-1} to the target temperature (280 °C), and paired values of temperature and pressure values were recorded. After reaction, the reactor was put in an ice bath in order to quench the reaction. Once it got cold, the reactor was opened and the content was transferred to an erlenmeyer and weighed. Then it was stirred gently and unreacted methanol was stripped by heating to 110 °C and bubbling nitrogen for 1 h. The methanol-stripped solution was again weighed and then left unstirred to allow the formation of an upper organic layer and a lower polar one. The upper biodiesel layer was sampled for analysis.

Biodiesel Analysis. Each liquid sample was analyzed by different techniques. The water content was assessed by means of Karl Fischer potentiometric titration, according to EN ISO 12937 and ASTM D 2709, for samples of reaction products before and after the stripping treatment. The Karl Fischer reagent was supplied by Merck, and the titration was performed with an Altronix apparatus with a glass electrode.

FFA (free fatty acid) content was determined by volumetric titration with a solution of NaOH as indicated in the ASTM D664 test. Kinematic viscosity values were determined with Cannon-Fenske viscometers (Cannon Instrument Co) at 40 °C following the standard method ASTM D445 by employing a thermostat. All

viscosity data reported here are means of duplicate determinations. Reproducibility of the viscosity data was very good. The iodine value was assessed by AOCS Cd 1−25. The concentrations of glycerol, methanol, methyl esters, and mono-, di-, and triglycerides were determined by the chromatographic method of Plank and Lorbeer.[15] Pyridine (Merck, 99.9%) was used as a solvent and silylation catalyst for preparation of the samples. These were derivatized with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MST-FA, Aldrich). 1,2,4-Butanetriol (>95%, Fluka) and tricaprin (>99%, Fluka) were added as internal standards. After 15 min at room temperature, the silylated samples were dissolved in *n*-heptane (Merck, 99,5%) and injected in the GC for their analysis. The analysis were performed with a Varian Star 3400 CX gas chromatograph equipped with an on-column Supelco injector and a flame ionization detector (FID). The column was a Zebron ZB-5 (Phenomenex), 25 m × 0.25 mm i.d. fused-silica capillary column. The samples were injected manually at an oven temperature of 50 °C. After an isothermal period of 1 min, the chromatograph oven was heated at 15 °C min^{-1} to 180 °C, at 7 °C min^{-1} to 230 °C and ballistically to 300 °C (where it was held for 20 min). Nitrogen was used as carrier gas at a flow rate of 3 mL min^{-1}. The detector temperature was 350 °C; nitrogen served as detector makeup gas at an inlet pressure of 0.5 bar. The total run time was 90 min.

Analysis of Light Fraction. To identify the light compounds being formed by glycerol decomposition, the product mixture of one of the runs ($R = 20$, 60 min, 280 °C) was distilled in a batch distiller with heating from room temperature up to 80 °C. The distillate was analyzed by GC-MS in a Varian CP-3800 coupled to a Varian Saturn 2000 high-sensitivity mass spectrometer with ionic trap.

Results and Discussion

In each run, the total pressure of the system depended mainly on the methanol:oil ratio and not the reaction time. Before the target reaction temperature was achieved, pressure varied almost linearly in accord with previous results.[16] Once the reaction was started, the pressure varied only slightly with reaction time and it can be considered as constant. For $R = 15$, the initial pressure at the point that 280 °C was reached was 68 bar and the final pressure was 62.5 bar. For $R = 20$, the initial pressure was 75.5 bar and the final pressure 74.1 bar.

The most noteworthy feature in all the samples analyzed was that the glycerol content was negligible. At first it was thought that the reaction did not proceed due to some experimental problem, but it was soon discovered that fatty acid methyl ester (FAME) yield values were high. The analysis indicated that in some cases transesterification of the samples proceeded almost to completion. The system was closed and leakproof, and therefore the glycerol either decomposed and was incorporated into long-chain molecules or decomposed into light compounds that were stripped away with water and methanol in the purifying steps. The lack of glycerol as a byproduct was noticeably reflected by the smallness or absence of the glycerol bottom layer after the decanting step.

The mass balance performed after the supercritical reaction of each sample indicated that a net mass loss occurred in the feedstock. This mass loss depended on reaction time and on the methanol-to-oil molar ratio (R). Its value was about 1−3% of the initial feedstock mass (including methanol).

In all cases, not only the initial mass was varied but also the FFA and water content of the reacting mixture were increased (Figure 1). For $R = 1,5$ the water content increased approximately linearly with reaction time. For $R = 20$, the pattern

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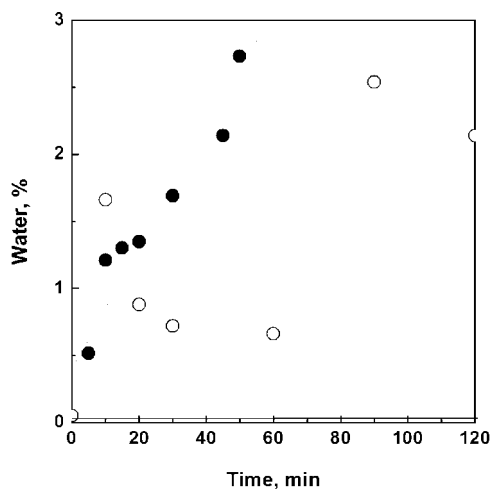
Figure 1. Water content as a function of the reaction time for two different methanol-to-oil molar ratios: (●) $R = 15$; (○) $R = 20$.

was different and not clearly defined. Water content first decreased to about 0.6%, but after 1 h it began to increase and reached 2.4% at the end. In any case it is clear that water is a reaction product and that the final water content is 2–3%.

The ASTM 6751 and EN 14214 norms establish a maximum water content in biodiesel of 0.05%. The supercritical biodiesel process thus does not produce a biodiesel ready for commercialization but one that has to be further treated to comply with the standards. According to the mass balance, the formed water would amount to 1–3%. At a first glance this percentage could be associated with a net yield loss because the measured methyl ester yield was 94–96%. This value is smaller than that of the alkaline-catalyzed process.

Water appearance among reaction products must be related to the disappearance of glycerol. Recently, Anitescu et al.[17] reported that they did not obtain glycerol in stoichiometric amounts as byproduct of the transesterification reaction with supercritical methanol. They postulated that glycerol reacted to produce compounds of smaller molecular weight. Degradation of glycerol to light fuel components eliminates the costly steps of glycerol separation. These authors supposed that the glycerol decomposition products could be directly used as part of the biodiesel fuel. This situation would simplify the production process greatly since glycerol no longer needs to be separated from the final product and some additional fuel could be produced.

Glycerol can react in several ways:

(a) Decomposing to produce products of smaller molecular weight: acrolein, acetaldehyde, acetic acid, etc. Some of these products can be gaseous at room temperature and pressure and could have been lost when the reactor was opened at the end of the reaction tests.

(b) Polymerizing to form polyglycerols. Condensation reactions are known to occur at high temperatures, forming hydroxylated chains capable of further reaction. Polyglycerols negatively affect biodiesel properties since they are thickeners and increase the viscosity of the solutions they are dissolved in.

(c) Etherification with methanol to produce glycerol ethers. This reaction would yield methyl glycerol, dimethyl glycerol, and trimethyl glycerol depending on the degree of reaction. Glycerol methyl ethers have been recently reported as conve-

nient components of biodiesel.[18] Etherification with subcritical methanol usually demands an acid catalyst.[19,20] Methanol in the supercritical state loses its hydrogen bridge bonds and can therefore perform a nucleophilic attack on the carbon of the C–O bonds of glycerols without the aid of a catalyst. For example, supercritical methanol is known to noncatalytically perform the depolymerization of polyethers.[21] The presence of these glycerol ethers dissolved in biodiesel could positively affect the viscosity and the pour point of the fuel. The increase in oxygen content would promote total combustion and the decrease of particulate emissions.[18]

Options b and c do not involve a net weight loss since the organic products formed are not removed from the biodiesel pool due to their high boiling point. Option b necessarily involves a phase separation due to the low solubility of polyglycerols in solvent of relatively low polarity such as biodiesel. Due to the reduction or absence of a decanted phase after the reaction, it might be supposed that glycerol is consumed in reactions a and c.

We made mass balances in each of the reaction tests in order to determine the fate of the glycerol. Inspection of the methyl ester yield values confirmed that glycerol decomposition products did not contribute to the ester phase; that is, no reaction between glycerol and methyl esters occurred.

Light compounds in the product mixture after one reaction ($R = 20$, 60 min, 280 °C) were separated by distillation with an end temperature of 80 °C. Analysis of the distillate by GC-MS showed peaks related to methanol, methyl esters, glycerol, and a polar compound of uncertain nature. The computer database gave two possible compounds that fitted the fragmentation pattern of this compound closely. One was 1-methoxy-2-propanol (A) and the other one was formic acid ethyl ester (B). A balance of atoms in compound A indicates that it is a product of condensation and reduction. It can be formed by reaction of glycerol and methanol with the loss of one water molecule and one oxygen atom. While water loss by condensation of -OH groups of glycerol is widely reported, reports on reduction are scarce. Recently Daimon et al.[22] have reported that α,β-unsaturated aldehydes can be reduced in supercritical methanol to give the corresponding unsaturated alcohols. The hydrogen for the reduction is provided by methanol. In the case of compound B, the atomic balance indicates that this compound can be formed by water loss and subsequent internal molecular rearrangement.

The equilibrium concentration of glycerol in biodiesel downstream of an alkali-catalyzed transesterification reactor depends on the content of residual methanol.[23,24] When methanol is removed, the solubility is a function only of the temperature. It is 0.2% at 25 °C and increases linearly at higher temperatures. In order to adjust the glycerol content to the values specified in the quality norms, biodiesel must be washed with 3–5 g of water (g of biodiesel)$^{-1}$ as suggested by Karaosmanoglu et al.[25] In the case of the supercritical biodiesel process, such washing

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Table 1. Free Glycerol, Bound Glycerol, Methanol, and Water Content as a Function of Reaction Time at a Methanol-to-Oil Ratio of 15

reaction time (min)	free glycerol (%)	bound glycerol (%)	methanol (%)	water (%)
20			0.10	
30	0.054		0.12	
60	0.040			
90	0.031	1.89	0.05	0.04
120	0.024	0.70	0.08	0.05

requirements are much reduced or totally eliminated due to the decreased glycerol content of the supercritically produced biodiesel.

It is seen that in all cases the stripping procedure at 110 °C is effective in reducing the methanol content to values lower than those established in quality norms such as IN 141214 (0.2%). During stripping, water is also removed. The results of Table 1 show that the residual water contents are generally lower than the limits established in the quality standards. With respect to the values of residual glycerol, the results of Table 1 indicate that free glycerol is continously reduced at higher residence times. Conversely, bound glycerol is first increased and finally decreased at higher residence times. This might indicate that bound glycerol is formed from free glycerol and FFA in some circumstances. For a residence time of 120 min, the glycerol content is close to the values specified in the quality norms (free glycerol <0.02%). The results clearly indicate that the supercritical process can produce a biodiesel fuel that complies with the glycerol content requirements "as is" and almost without further refining steps downstream of the supercritical reactors. A simple adjustment of the glycerol content can indeed be done by silica adsorption as reported elsewhere,[26] thus sparing schemes of washing with their involved issue of wastewaters.

Figure 2 shows the FFA content as a function of reaction time for two *R* values. The raw materials of the reaction, refined soybean oil and methanol, had acidity values of 0.21% and 0.001%, respectively. Under the reaction conditions used, FFA are formed. For both *R* values, similar FFA versus time patterns were obtained. Acidity was first rapidly increased and then slowly decreased, thus giving rise to a maximum at middle reaction times (15−20 min). After 90 min of reaction time the FFA content is lowered to less than 0.7%. The ASTM 6751 and IN 14214 standards establish a maximum FFA of 0.25% and 0.40%, respectively. This limit could be met if longer reaction times are used. Extrapolation of the plots of Figure 2
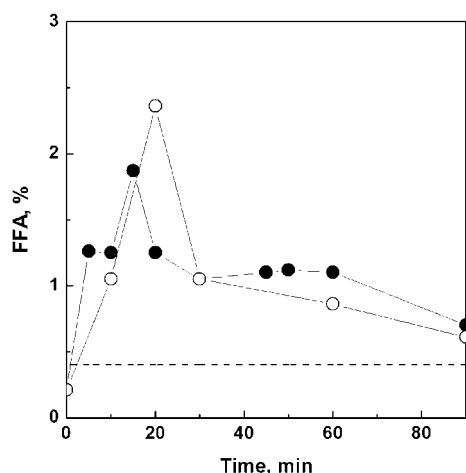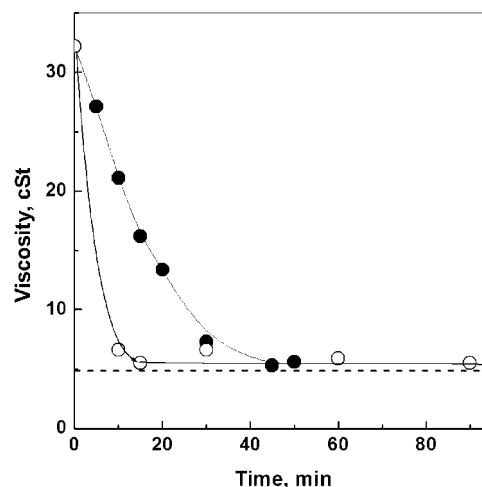
Figure 3. Kinematic viscosity of biodiesel at 40 °C as a function of reaction time. (●) *R* = 15; (○) *R* = 20. (---) Maximum content as established by ISO 3104.

at 120 min of reaction time indicate that a fuel with 0.3% can be obtained. If a shorter residence time is used, a biodiesel that does not comply with FFA requirements is produced and further acidity adjustments must be performed downstream of the supercritical reactors.

Time evolution of the FFA content follows the pattern of a serial reaction network, with FFA being intermediate products of the reaction. The decomposition of glycerol produces water. This water reacts with tri-, mono-, and diglycerides to form FFA and glycerol (hydrolysis reaction).[27] The simultaneous reactions of FFA formation and consumption lead to the volcano shape found in Figure 2 for the FFA content.

The produced biodiesel fuel also needs to meet the kinematic viscosity specifications (40 °C) that are 1.9−6.0 cSt in the ASTM D6751 American standard and 3.5−5.0 cSt in the EN 14214 European standard. Figure 3 is a plot of the values of kinetic viscosity as a function of the residence time. As the reaction proceeds and the total conversion is increased, the viscosity of the mixture is continuously reduced. At 60 min the viscosity approaches the values specified in the quality norms. The viscosity reduction is mainly due to the transformation of triacylglycerols into fatty acid methyl esters, and as expected, the viscosity reduction rate is increased at higher methanol-to-oil ratios. Nothing can be said on the possible increase of viscosity by minor amounts of dissolved polyglycerols since their contribution to the total viscosity seems to be marginal.

Figure 4 shows a scatter plot of the iodine values of the biodiesel products as a function of the residence time for two methanol-to-oil ratios (15 and 20). For *R* = 15, the iodine value is not changed during the reaction and the value of biodiesel coincides with that of the original soybean oil (IV = 134). For *R* = 20, the iodine value remains constant up to 60 min of residence time but it is decreased at higher residence time values. A 15-point decrease was recorded at 120 min residence time. The iodine value is strictly proportional to the number of unsaturated carbon−carbon bonds in the mixture. IV reduction can, a priori, be supposed to be due to two different causes. Methoxylation of the acyl chains by attack on the double bonds could be postulated but is very unlikely due to the nucleophilic nature of the reactive carboxyl moiety of supercritical methanol and the electron-rich environment of the olefinic bonds. IV

Figure 2. Biodiesel FFA content as a function of reaction time for two different methanol-to-oil molar ratios: (●) *R* = 15; (○) *R* = 20. (---) Maximum content as established by EN 14104.

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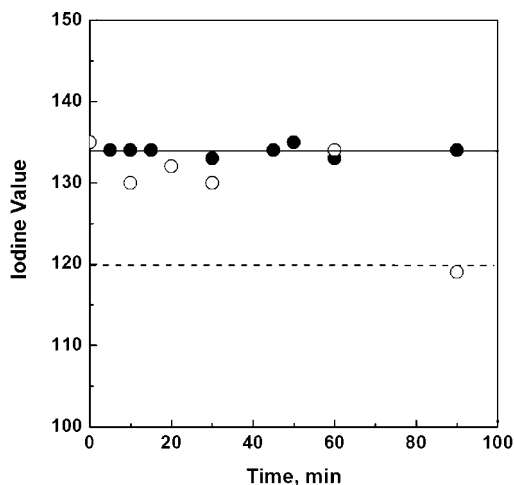(27) Minami, E.; Saka, S. *Fuel* **2006**, *85*, 2479.

Figure 4. Iodine value of biodiesel as a function of reaction time. (●) $R = 15$; (○) $R = 20$. (---) Maximum content as established by EN 14111.
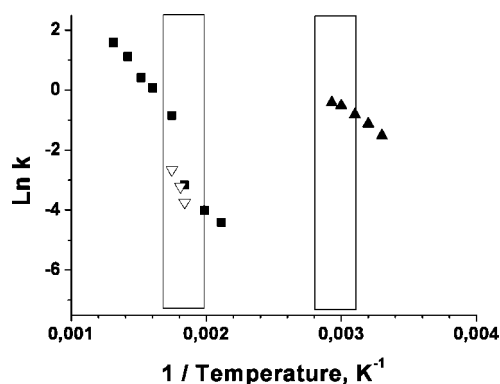

Figure 5. Transesterification pseudo-first-order kinetic constants. Supercritical process: Kusdiana and Saka[5] (■) and this work (▽). Alkaline process: Noureddini and Zhu[29] (▲).

reduction by the formation of new saturated compounds with no reactive olefinic bonds is more likely. In fact, He et al.[28] have recently reported that unsaturated FAME are lost at high reaction temperatures (greater than 300 °C) and long residence times (greater than 30 min). Their experimental setup is a continuous reactor, but the general conclusions remain.

For the sake of comparison, we have calculated average kinetic constants on the basis of a pseudo-first-order kinetic model (Figure 5). Kinetic constants were estimated from conversion values at the end of the run. The experiments were performed at high methanol-to-oil ratios (10−20), and the equilibrium constant is known to be close to unity due to the almost null value of the Gibbs free energy change. For this reason the inclusion of an inverse reaction term was disregarded. The assumption of a pseudo-first-order kinetic model follows the line of other reports on supercritical transesterification.[5] Figure 5 is a comparison of the kinetic constants of noncatalytic and alkali-catalyzed reactions. Data of Kusdiana and Saka[5]

obtained under noncatalytic supercritical conditions were also added. Values of the constants for the alkali-catalyzed reactions were taken from the report of Noureddini and Zhu[29] after conversion of their constants to pseudo-first-order. When the constants are plotted together in Arrhenius form, it is readily seen that the value of the constants is highly dependent on the temperature and that temperatures must be conveniently chosen for a fair comparison. Open bars in Figure 5 were placed in the temperature ranges of common process operation. Alkaline processes usually use atmospheric reactors or reactors with a small overpressure; therefore, the k value for this process should be the one at 80−110 °C. In the case of noncatalytic processes, a minimum temperature over the critical temperature of methanol is needed to sustain the supercritical state, but too-high temperatures may be inconvenient due to degradation of oil products. In this sense a 250−280 °C range seems most convenient for this comparison. When values in this range are compared, it becomes obvious that the kinetic constant of the alkaline process is higher than the constant of the supercritical process.

Conclusions

Biodiesel was prepared by reacting refined soybean oil with supercritical methanol at $T = 280$ °C and methanol-to-oil molar ratios of 15 and 20. Water and other volatile compounds were removed from the product by stripping with nitrogen at 110 °C. The results obtained enable us to conclude the following:

Biodiesel production by the reaction of oils in supercritical methanol at the conditions used in this work produces practically no glycerol byproduct. This fact simplifies downstream refining of the produced biodiesel. The glycerol issue is reduced from 10% in the classical alkali-catalyzed process to a negligible 0.02%. With such a small amount of residual glycerol, the washing steps for glycerol removal and the posttreatments of process wastewater can be spared.

Glycerol is transformed into products of smaller molecular size and water. At first this water reacts with the triglycerides of the reacting mixture to form free fatty acids, thus increasing the acidity of the product. At longer reaction times the acids are converted into methyl esters again. Glycerol methanolysis reactions increase the methanol consumption.

The small amount of glycerides and FFA contaminants in the biodiesel product makes a final step of refining by silica adsorption convenient. No liquids effluents are issued with such a refining step.

After the FFA and glycerides are recycled, the yield of the process is 94−96%.

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