Integrated Technology for Supercritical Biodiesel Production and Power Cogeneration

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Integrated Technology for Supercritical Biodiesel Production and Power Cogeneration

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A supercritical (SC) fluid technology coupled with power cogeneration is proposed to produce biodiesel fuels without the conventional complex separation/purification steps. The core of the integrated system consists of the transesterification (TE) of various triglyceride sources (i.e., vegetable oils and animal fats) with SC methanol/ethanol. Part of the reaction products can be combusted by a diesel engine integrated in the system, which, in turn, provides the power needed to pressurize the system and the heat of the exhaust gases for the TE process. This article reports laboratory-scale investigations directed to system optimum performance (i.e., near complete conversion in short processing time) in connection with the effects of process operating conditions. TE experiments have been conducted at 100–300 bar, 250–425 °C, and 0.73–8.2 min residence time with soybean/sunflower oils as triglycerides and SC methanol/ethanol at ratios of alcohol to oil from 3 (stoichiometric) to 24. Special emphasis was on reactant phase transitions from liquid to SC states. These transitions were monitored with a high-pressure, high-temperature view cell connected to the reactor outlet for the continuous TE experiments and also serving as a batch reactor. Under selected parameters, near complete oil conversion to biodiesel has been achieved with the glycerol decomposition products included in the fuel. Commercial biodiesel production by this method estimated processing costs as low as $0.26/gal for a plant capacity of 5 million gal/year, significantly lower than the current processing costs of ~$0.51/gal for biodiesel produced by conventional catalytic methods. The retail cost of biodiesel produced by the proposed method is likely to be competitive with diesel fuel prices.

Introduction

Biodiesel (BD), a mixture of fatty acid methyl/ethyl esters (FAME) derived from plant/animal triglycerides (TGs) through transesterification (TE) with an alcohol, is a fuel that is under a great deal of consideration. It has been assessed that BD yields 93% more energy than that invested in its production, and relative to fossil fuels, greenhouse gases are reduced 41% by BD production and combustion while less air pollutants are released per net energy gain.[1] While worldwide TG sources are diverse, over 90% of BD in the United States is made from soybean oil (SBO).[2] By increasing the production of soybeans, there could be a positive feedback on agriculture through a higher quantity of soybean meals and implicitly more meat for food and more TG supply for BD production.

Although these benefits are very attractive, the current BD final cost is prohibitively high without governmental subsidies. Much of the actual technological complexity, involving multiple steps on TG pretreatment and BD separation/purification, originates from contaminants in the feedstock (e.g., water and free fatty acids (FFA)) or impurities in the final product (e.g., glycerol, methanol, and soaps).[3] Compared with these conventional catalytic methods, a relatively new supercritical (SC) method was found that is capable of reducing TE time from hours to minutes through a continuous process and that requires no feed pretreatment for TGs with high FFA/water content.[4]

However, it was found that many factors affected the FAME yield in the SC method: TE temperature, pressure, and residence time, alcohol to TG ratios, feedstock composition, as well as mixing and solubility parameters. Among these factors, the most important were considered the ratio of alcohol to TG and the TE temperature. The former was found to increase the FAME yield when it was far beyond the stoichiometric molar ratio of 3:1 (up to 64:1), but it was associated with increased cost of pumping, separating, and recycling of the excess alcohol. The latter led to shorter residence time but higher energy consumption and the risk of FAME decomposition.

In order to understand these difficulties, a thorough survey has been performed on increasingly reported information regarding the SC methods of BD production,[4–20] but only the

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Table 1. Conditions and Yield for the Reported Noncatalytic TE Processes

oil/cosolvent	T (°C)	P (bar)	MeOH/TG	τ (min)	B/C	yield (%)	ref
rapeseed	350	450	42	4	B	95	7, 8
soybean	235	62	6–27	600	B	85	16
soybean	120–180	~1	3–12	<1920	B	<20	9
soybean/CO_2[a]	280	143	24	10	B	98	5
soybean/C_3H_8[b]	280	128	24	10	B	98	17
canola	420–450	400	11–45	4	C	~100	6
coconut and palm	350	190	42	7	C	95–96	10
soybean	310	350	40	25	C	77–96	15
sunflower	350	200	40	40	B	96	18
castor and linseed	350	200	40	40	B	98	19
soybean/C_3H_8[b]	288	96	64	10	B	99	24
soybean	285–290	100–110	10–12	N/A	B	~100	25
waste oil/C_3H_8[b]	280	128	24	17	C	95	26
soybean/CO_2[a,c]	350–425	100–250	3–6	2–3	C	~100	this study

[a] CO_2/MeOH = 0.1. [b] C_3H_8/MeOH = 0.05. [c] A limited number of experiments were executed with this cosolvent, as shown in Table 2.

studies closer to our method are briefly discussed here.[5,6] In one example, refined SBO was treated with SC methanol and CO_2 as a cosolvent at 280 °C and 143 bar in a batch reactor for 10 min.[5] Under these conditions, 98.5% conversion of oil to BD was reported. The other key process variables were the molar ratios of methanol to oil (24:1) and CO_2 to methanol (1:10). The reaction products were settled for 60 min for glycerol separation, and then methanol was evaporated from both phases at 70 °C. Although CO_2 lowered the P–T conditions of TE, the tradeoff between the process time and the TE temperature was not optimally balanced.

In another example, canola oil and SC methanol were preheated at 270 °C, and the mixture was then treated in a capillary reactor up to 500 °C and 400 bar for 4 min.[6] The range of methanol to oil ratios was from 11:1 to 45:1 on a molar basis. Thermal decomposition of glycerol was reported for temperatures beyond 400 °C. At these high T–P values, the unsaturated high-molecular FAME also decomposed to C_6–C_{10} smaller molecular esters. The optimum reaction temperature was considered 450 °C. The excess methanol, up to 60%, was removed from the reaction products by using a rotary evaporator.

Information on the mutual solubility of the reaction components, often an overlooked issue, is essential for the production design and process operation. The reactants (TG and the alcohol) and the products (FAME and glycerol) are partially mutually soluble in the TE process. The alcohol is soluble in both FAME and glycerol but is not significantly soluble in oil. With an increase in the mass fraction of the FAME, the alcohol solubility in the TG–FAME phase increases. The TE reaction is carried out in the alcohol phase, and consequently, the reaction advance depends on oil solubility in this phase. For example, when the FAME content increases to 70%, the TG–methanol–FAME mixture becomes a homogeneous phase.[21] Glycerol has a low solubility in both oil and FAME but high affinity for alcohol.

Kinetic studies on TG–alcohol systems revealed an unusual behavior of the reaction rate constant with increasing temperature and pressure. To explain this phenomenon, the phase equilibria of the pseudobinary system sunflower oil (SFO)–methanol were measured at different temperatures between 200

and 230 °C and pressures between 10 and 56 bar.[22] The reported data indicated a strong influence of the phase equilibrium on the reaction kinetics. High-pressure phase equilibria have also been calculated for the ternary system of C_{54} TG–ethanol–CO_2, at 40–80 °C and 60–120 bar.[23] The role of CO_2 as cosolvent in increasing the mutual solubility of oil and ethanol was revealed. More recently, images of phase transitions in a BD batch reactor equipped with transparent windows have been reported.[24] Although the importance of single phase reactions on the high yield of FAME has been stressed in this study, the optimum noncatalytic TE operating conditions for near complete TG conversion were not determined. The authors concluded that additional experimental work on continuous reactors is needed.

Also, fluid transport properties play an important role in the TE reactions. In an example, the influence of the axial dispersion on the performance of tubular reactors during noncatalytic SC TE of TGs has been studied.[11] It was found that SC TE reactors must be operated at axial Peclet numbers higher than 1000 in order to limit back-mixing effects and achieve batchlike conversions at short residence times. Otherwise, the authors concluded that high temperatures and high methanol to oil ratios were required for high conversions at lower Peclet numbers.

Overall, the reported information presents the major findings on the theoretical and technical aspects of BD production by SC methods. Given the high number of process parameters affecting SC TE conversions, many of them being competitive, it is difficult to comprehensively and cohesively grasp their effects. Indeed, there are not even two reported sets of data with similar claimed optimum TE conditions (Table 1). Also, technical and economic feasibility studies of creating an alternative to the conventional BD industry are scarce.[25,26]

Two major issues on improving the efficiency of BD production concern the oil–alcohol mixing and the separation/purification processes. While the former issue can be overcome by carrying out TE in SC states, the latter is more challenging. As BD production has risen, the excessive supply of glycerol has glutted the market, sinking its price. The price of glycerol ($0.20–$0.50/lb) could drop further as BD production increases.[27] One attractive solution herein is the decomposition

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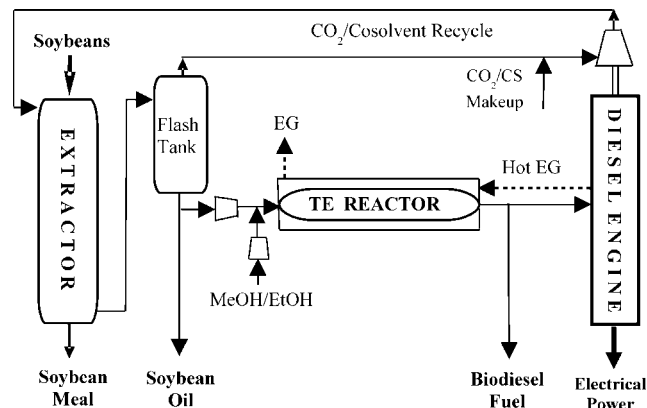(27) Rosner, H. New York Times, August 8, 2007.

Figure 1. Schematic of the integrated multistage supercritical technology to produce vegetable oils and biofuels.
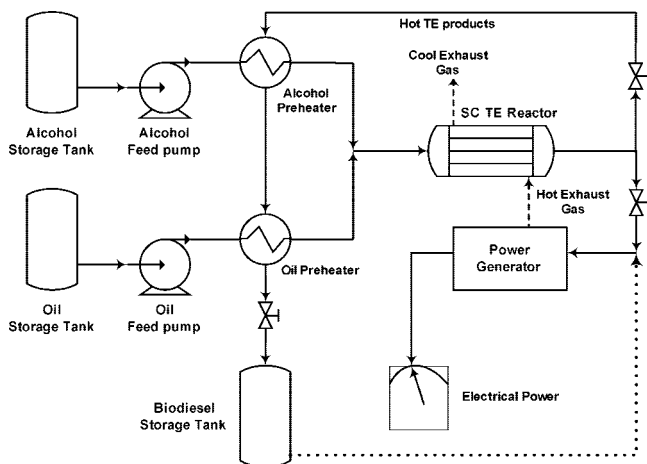

Figure 2. Flow diagram for supercritical transesterification of vegetable oils to biodiesel.

of glycerol associated with slight decomposition of FAME, which will overcome the problem of glycerol recovery in the costly separation/purification steps.

To benefit from the advantages of SC processes, we designed an integrated two-step SC technology to produce both vegetable oils by extraction with SC CO_2 and then BD through TE of the oils from the extraction step with a SC alcohol in a continuous tubular reactor (Figure 1). The mechanical/electrical power as well as the heat for these steps is provided by a power generator, which, in turn, consumes a fraction of the produced fuel. Herein, only the TE step will be discussed, which involves a simple process with no need for the multistep separations involved with acid/base catalyzed technology. When our proposed SC TE method (Figure 2) is compared with a conventional catalytic technology, the simplicity of the former is apparent.

While the overall goal of this study was to develop a simplified process for continuous and cost-effective BD production, the specific objectives were to determine optimal ranges of parameters for the TE reactions for high BD yields at laboratory scale and to compare the data of an economic analysis of the proposed technology at commercial scale with current methods.

Experimental Section

Laboratory Scale Transesterification of Vegetable Oils. The laboratory apparatus (Figure 3) consists of the following: three syringe pumps (TELEDYNE ISCO) for oil, alcohol, and CO_2 delivery; tubular reactors (coiled Hastelloy pipes of 2 and 4 m in length and 1.5 mm i.d.) heated in an electrical furnace; a view cell
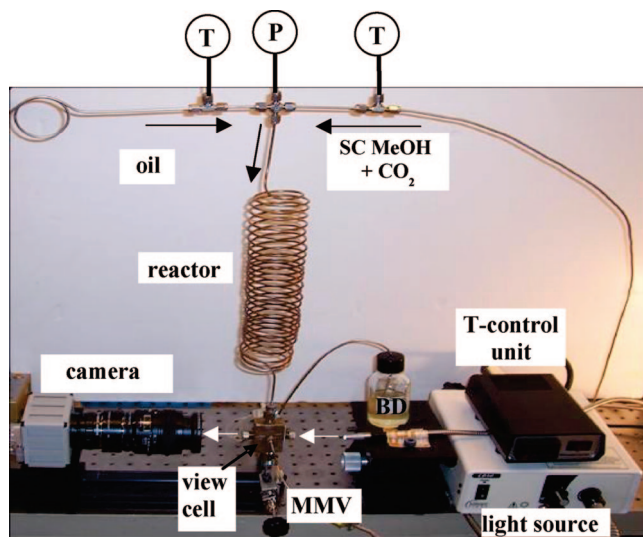

Figure 3. Photograph of the laboratory flow apparatus to study phase transitions and transesterification reactions with thermocouples (T), a pressure indicator (P), and a micrometric valve (MMV). The furnace for the reactor and the heating tapes for the feeding pipes are not shown.

(designed and constructed at Syracuse University) to monitor phase transitions, heated at the reactor temperature by four heating cartridges inserted in its 316-SS block; and a separator for liquid and gaseous TE product separation. Any of the reactor feeding streams can be preheated to the desired temperatures by using electrical heating tapes wrapped around feeding pipes that are similar to those of the reactor.

Experiments with tubular reactors (Table 2) have been executed to select ranges of $P-T$ conditions, feedstock composition, and residence time under which the highest yield of BD is obtained without requiring further separation/purification steps. It has to be noted here that the Hastelloy walls of these reactors, with high Ni content, should have a catalytic effect on TE yield and reaction product composition. To further pursue this assumption, TE experiments will also be conducted in quartz reactors similar with those reported by Savage et al.[28] for biomass noncatalytic SC gasification.

Using high pressure view cells with sapphire windows sealed on copper/gold gaskets with Belleville washers and a high-speed photo system (Photron, up to 2000 frames/s) as a diagnostic aid, it was found that the oil miscibility with methanol is crucial to attaining a high conversion of TG to FAME in a short residence time. Experiments have been carried out with this apparatus to test its capabilities regarding SBO/SFO−methanol/ethanol miscibility and phase transitions under different $P-T$ values (Table 2), under both continuous flow and batch modes.

The objective of the batch experiments was to study TG−alcohol mixing phenomena and phase transitions during a heating process regardless of the reaction time and TE conditions for optimum BD production in continuous flow reactors. For these experiments, the reactants without cosolvent were initially filled in the view cell in the amounts shown in Table 2 (runs 29 and 30), sealed, and then slowly heated to obtain SC homogeneous phases.

Experimental Conditions. Different oil−alcohol compositions have been experimentally studied (Table 2, columns 2–5). SBO and SFO have been used as the TG source, and both methanol and ethanol were the alcohols of choice. As shown in this table, small amounts of liquid CO_2 (up to 4 mol % in the alcohol) have been pumped into the reactor for some of the experiments to increase oil−alcohol mixing and their mutual miscibility as well as to lower the critical temperature of the mixture.

Experimental $T-P$ values (Table 2, columns 6 and 7) have been automatically recorded by using a HEISE digital pressure indicator

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Table 2. Laboratory Experiments on Transesterification Reactions at Different Conditions

run no.	system	FR_{oil}[a] (mL/min)	FR_{ROH}[a] (mL/min)	ROH/oil (molar)	T (°C)	P (bar)	τ (s)	comments on TE products[d]
1	SBO-MeOH	4.00	1.00	6	350	200	61	two phases, emulsive
2	SBO-MeOH	4.00	1.00	6	400	200	52	two phases, emulsive
3	SBO-MeOH[b]	2.00	0.50	6	350	200	121	two phases, emulsive
4	SBO-MeOH[b]	2.00	0.50	6	400	200	105	one phase, clear
5	SBO-EtOH	2.00	0.50	6	400	200	105	one phase, clear
6	SBO-EtOH	2.00	0.40	5	400	200	109	one phase, clear
7	SBO-EtOH	2.00	0.40	5	400	100	90	two phases, emulsive
8	SBO-EtOH[b,c]	2.00	0.40	5	400	100	89	one phase, clear
9	SBO-EtOH[b,c]	2.00	0.40	5	375	100	94	one phase, clear
10	SBO-EtOH[c]	2.00	0.40	5	400	300	131	one phase, clear
11	SBO-EtOH[c]	2.00	0.40	5	425	300	124	one phase, brown
12	SBO-EtOH[c]	2.00	0.40	5	375	300	180	one phase, clear
13	SFO-EtOH[c]	2.00	0.40	5	375	100	94	one phase, clear
14	SFO-EtOH[c]	2.00	0.40	5	400	200	119	one phase, clear
15	SFO-EtOH[c]	2.00	0.40	5	425	300	124	one phase, yellow
16	SFO-EtOH	2.00	0.40	5	350	100	129	two phases, emulsive
17	SBO-MeOH[c]	2.22	0.28	3	400	100	127	one phase, clear
18	SBO-MeOH[c]	2.00	0.50	6	400	100	72	one phase, clear
19	SBO-MeOH[c]	1.82	0.68	9	425	100	54	one phase, clear
20	SBO-MeOH[c]	1.67	0.83	12	425	100	45	two phases, emulsive
21	SBO-MeOH[c]	1.50	1.00	16	425	100	44	two phases, emulsive
22	SBO-MeOH[c]	0.80	0.10	3	325	125	159	two to three phases, emulsive
23	SBO-MeOH[c]	0.80	0.10	3	350	125	156	one phase, clear
24	SBO-MeOH[c]	0.80	0.10	3	375	150	153	one phase, clear
25	SBO-MeOH[c]	0.80	0.10	3	400	250	150	one phase, clear
26	SBO-MeOH[c]	0.70	0.10	3	300	250	133	two phases, emulsive
27	SBO-MeOH[c]	0.10	0.10	24	250	250	491	two phases, emulsive
28	SBO-MeOH[c]	0.10	0.10	24	300	150	421	two phases, emulsive
29	SBO-MeOH	batch, 3 mL each		23	26–420	1–117	3600	phase transitions observed
30	SBO-EtOH	batch, 0.5 mL each		16	26–420	1–117	3600	phase transitions observed
31	SBO only	0.10	0.0	0	27–410	100	3600	coking at $T > 400$ °C

[a] Flow rates at room temperature and system pressure. [b] 4 mol % CO_2 in alcohol. [c] Both oil and alcohol feeding streams were preheated at 350 °C. [d] One phase means near complete (>98%) TG conversion. ROH stands for MeOH or EtOH.
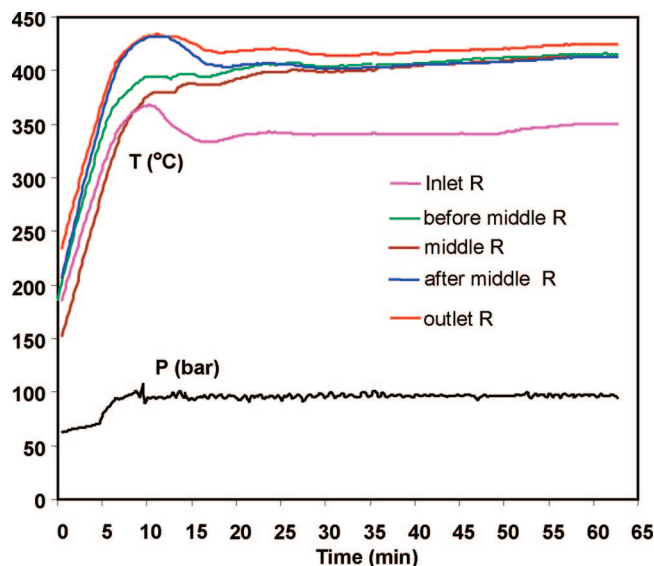

Figure 4. Typical $P-T$ conditions for the TE reactions of SBO−MeOH (runs 17–21 in Table 2 were executed between 15 and 63 min of the total recorded time). The thermocouples were located at different positions along the reactor R as shown in the legend.

and *K*-type thermocouples, respectively, and specialized software (National Instruments). A set of such typical recorded conditions are shown in Figure 4.

The residence time τ (s) was calculated based on the reactor volume V (cm³), the total volumetric flow-rate ν (mL/min), and the fluid density (g/mL) at the pump (ρ_0) and in the reactor (ρ):

$$\tau = 60V/(\nu\rho_0/\rho) \qquad (1)$$

The densities have been obtained from CHEMCAD simulations (process simulation software from Chemstations, version 5.6.4[29]) by using the Soave−Redlich−Kwong (SRK) equation of state (EOS). The calculated values have been checked with the observed residence times during the experiments, and a reasonable agreement was found, given the difficulties to obtain accurate values both theoretically and experimentally for this important TE property (Table 2, column 8).

Analytical Method. The concentrations of oil components as well as the TE reaction products were analyzed with a Thermo Electron gas chromatograph (GC) equipped with a splitless injector, a MS detector (MSD), and an ultraperformance capillary column from Agilent, Inc. (MS1, cross-linked 5% Ph−Me silicone, 30 m × 0.20 mm i.d., 0.33 μm film thickness). Before GC analyses, small portions of the TE products were dissolved in liquid hexane without being subjected to any separation/purification methods. Standard solutions of the main FAME components of the BD samples were also prepared and used to confirm the identity of the TE products and to quantify their amounts.

Results and Discussion

Both continuous flow and batch experiments have been executed at the conditions shown in Table 2. Three different oil−alcohol systems were studied: SBO−methanol, SBO−ethanol, and SFO−ethanol. For the continuous flow experiments, the residence time varied from 1 to 8 min, while, for the batch mode, the total heating time was 1 h to slowly heat the reactants from room temperature to SC states.

The solubility of the oil in the SC alcohol phase is a keystone for rapid and complete TE reactions. Liquid–vapor−SC phase transitions for the binary/ternary systems studied have been

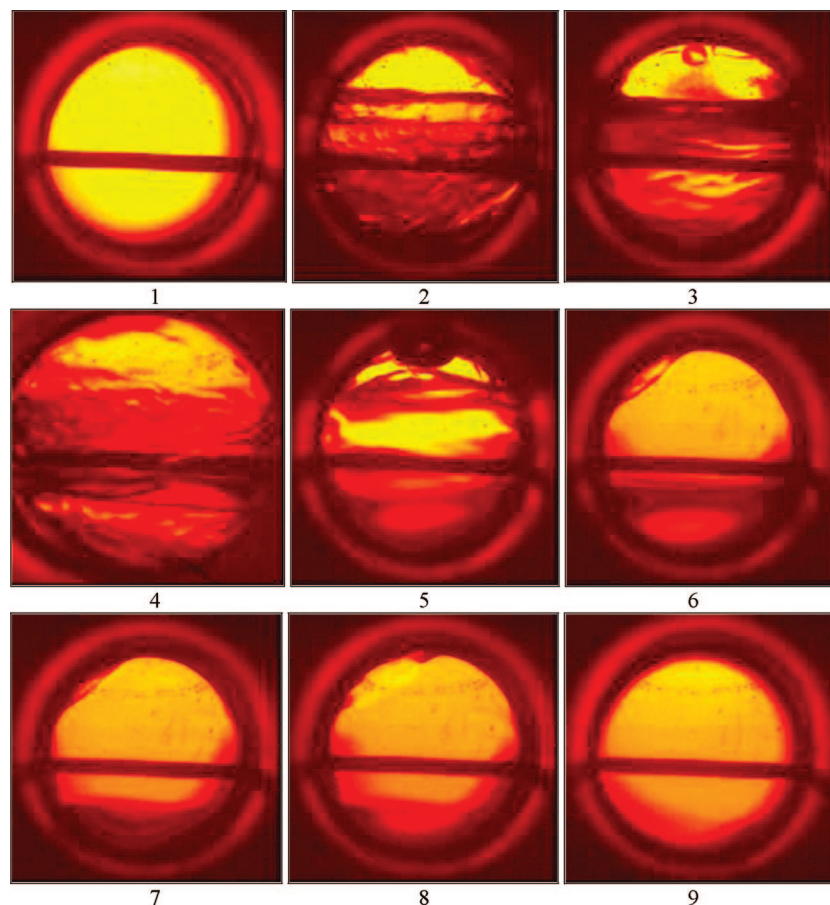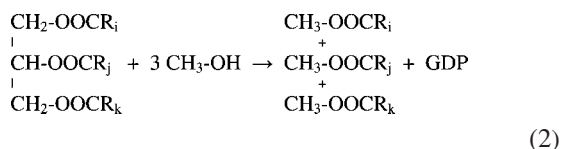(29) Chemcad version 5.6.4; CHEMSTATIONS Inc.: Houston, TX, 2007.

Figure 5. Mixtures of SBO (2 mL/min)−ethanol (0.4 mL/min) (EtOH/SBO molar ratio of 3.4) flowing through a view cell ($V = \sim1$ mL) at 400 °C and 200 bar. Image 1 is for SC EtOH only; images 2–5 are for unsteady states; images 6–8 are for transitions to SC states; and image 9 is for a SC state. The horizontal line in the middle of these images is a 0.2 mm thick wire inserted in the view cell streamline for focusing purposes.

monitored with a view cell attached at the outlet of the reactor. Selected images of the involved phenomena associated with a continuous tubular reactor are shown in Figure 5. Transitions of interest were those from liquid–vapor/SC heterogeneous mixtures to homogeneous SC phases. Additionally, equal volumes of SBO and methanol have been heated in a view cell in a batch mode. Selected photographs of these phase transitions associated with TE reactions between SBO and methanol (1:24 molar ratio) heated from ambient conditions to 420 °C and 120 bar are shown in Figure 6. In this case, SBO, methanol, and reaction products are only partially miscible up to near 350 °C, while, beyond 350 °C and 100 bar, one homogeneous phase has been obtained. Further, SBO and ethanol were also heated in a view cell from room $T-P$ to SC phases (Figure 7). These images show different fluid phase patterns from quasitotal oil−alcohol immiscibility at ambient conditions to homogeneous SC phases.

The SC TE global reaction, used for the process design, was considered for a generic composition of TG and lumped glycerol decomposition products (GDPs):

$$
\begin{array}{c}
\text{CH}_2\text{-OOCR}_i \\
| \\
\text{CH-OOCR}_j \\
| \\
\text{CH}_2\text{-OOCR}_k
\end{array}
\; + \; 3\,\text{CH}_3\text{-OH} \;\rightarrow\;
\begin{array}{c}
\text{CH}_3\text{-OOCR}_i \\
+ \\
\text{CH}_3\text{-OOCR}_j \\
+ \\
\text{CH}_3\text{-OOCR}_k
\end{array}
\; + \; \text{GDP}
$$

$$(2)$$

In this global reaction, R_i, R_j, and R_k are the hydrocarbon chains of the major SBO fatty acids: palmitic, oleic, linoleic, linolenic, and stearic. It is well established that the steps of these TE reactions include TG conversion to diglycerides (DGs), then

to monoglycerides (MGs), and finally to FAME and glycerol.[16] The TE reaction products obtained at the conditions outlined in Table 2 have been analyzed by a GC-MS method and also qualitatively assessed as shown in the last column of this table. In the cases where a clear, nonemulsive phase was observed, there were no immiscible components (e.g., oil, glycerol, and alcohol) in the reaction products, and the reactant conversion was near complete (>98%). Our GC-MSD chromatograms (Figure 8a, c, and d) showed negligible amounts of MG and DG intermediate TE byproducts when compared to a commercial sample (Figure 8b). Although the GDPs were not analyzed in this study, it was estimated that either individual byproducts were in negligible amounts to be captured by GC-MSD or their retention times were positioned in the delay time period of solvent venting.

Parts a and c of Figure 8 are selected chromatograms that show the differences among the reaction products when different alcohols were used in the TE process (e.g., methanol and ethanol, respectively). The small FAME peaks shown in Figure 8c were from intentionally contaminated samples for the purpose of comparison with those of the ethyl esters, when a shift toward the right for the latter was obtained. A comparison between the TE products when different oils were used (e.g., SBO and SFO) is shown in Figure 8a and d. The level of the saturated esters is lower for the SFO products (peaks at 54.0 and 61.0 min in Figure 8d). Also, a comparison between typical TE products obtained with SC methanol and those in a commercial BD sample is shown in Figure 8a and b. It has to be observed the lower level of the saturated esters in our samples (peaks at 51.4/51.6 and 58.7/58.8 min in Figure 8a, b, and c) and more
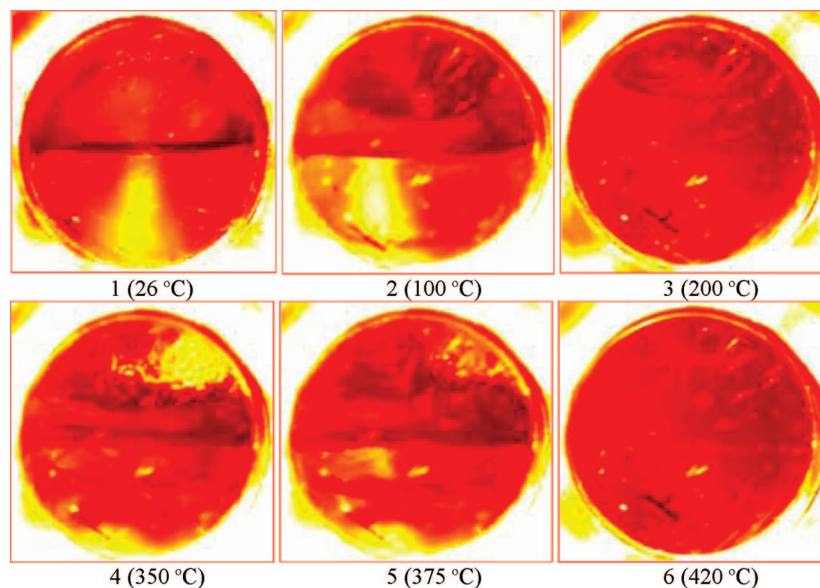
Figure 6. Selected photographs of phase transitions associated with batch TE reactions between SBO and methanol (3 mL each, 1:23 molar ratio), heated from ambient $T-P$ conditions to 420 °C and 120 bar. The images go from (1) SBO(L)−MeOH(L), through (2−3) SBO(L)−MeOH(L)−MeOH(V), (4−5) SBO−BDF−MeOH(LSC), and then (6) BDF−MeOH(SC). The volume of the view cell is ∼6 mL.
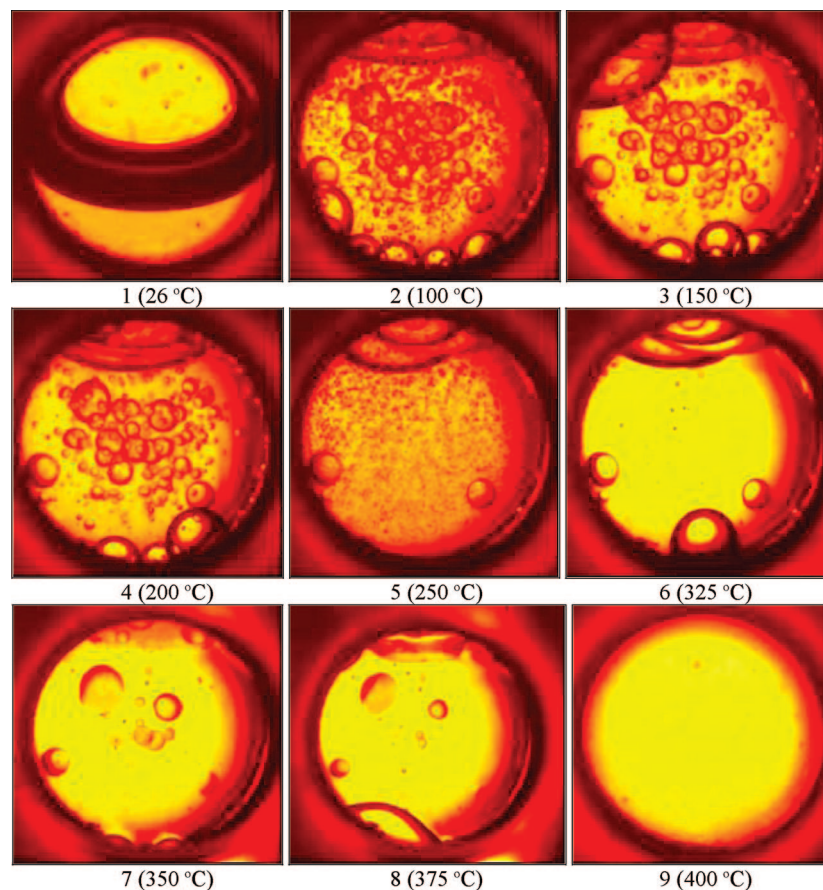

Figure 7. Miscibility of a SBO−EtOH (1:16 molar ratio) mixture being heated from room temperature to 400 °C at 100 bar. The volume of the view cell is ∼1 mL.

byproducts in the commercial sample (peaks at 62–72 min in Figure 8b). From these figures, it is apparent that our BD samples, without any separation, contained less impurities compared to the commercial BD. Unfortunately, the sample size did not permit at this time a comprehensive ASTM analysis, currently performed for BD fuels.

The experiments carried out in our laboratory have shown that nearly complete TG conversions to FAME have been achieved for stoichiometric reactants or a slight excess of alcohol (alcohol/TG molar ratio of 3–5) preheated at 350 °C and then reacted at 350–400 °C and 100–300 bar for 1.6–3.0 min without cosolvent (Table 2, runs 10, 12–14, 17, and 23–25). The effects on conversion of these SC TE conditions are in agreement with studies using pulsed neutron diffraction with isotope substitution, which showed that in the low-density SC methanol (i.e., high-temperature and relatively low-pressure conditions) the large
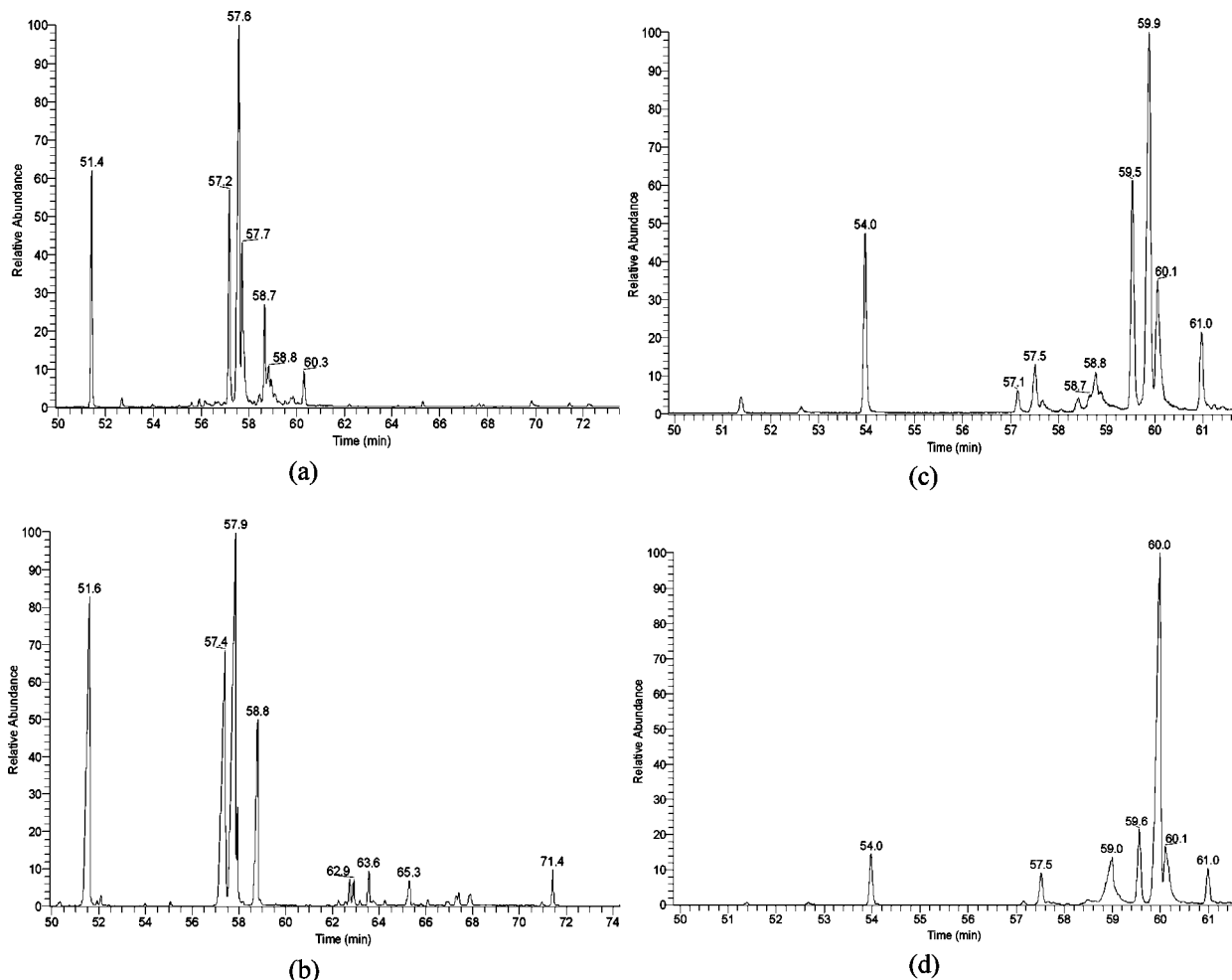
Figure 8. TE products of the following: (a) SBO with methanol (from run 17, Table 2), (b) a commercial sample, (c) SBO with ethanol (from run 8, Table 2), and (d) SFO with ethanol (from run 13, Table 2). The main peaks are palmitic acid methyl ester (51.4/a, 51.6/b), oleic acid methyl ester (57.6/a, 57.9/b), linoleic acid methyl ester (57.2/a, 57.4/b), linolenic acid methyl ester (57.7/a, ~57.9/b), stearic acid methyl ester (58.7/a, 58.8/b), palmitic acid ethyl ester (54.0/b,d), oleic acid ethyl ester (59.9/c, 60.0/d), linoleic acid ethyl ester (59.5/c, 59.6/d), linolenic acid ethyl ester (60.1/c,d), and stearic acid ethyl ester (61.0/c,d).

molecular clusters are broken to generate monomers or small oligomers.[30] These species are readily accessible for TE reactions with the TG in the oil compared to clusters of the H-bonded alcohol. In these particular SC states, in contrast to the BD production at conventional conditions (~1 atm, 60–80 °C, with acid/base catalysts), the reaction rate is about 2 orders of magnitude faster, BD components are formed by using near stoichiometric quantities of alcohol, and negligible glycerol is left in the final reaction products. Instead, a number of other compounds are formed, resulting from the breakdown of the glycerol. A catalytic effect of the reactor walls on this TE performance cannot be, however, excluded.

The conditions at which glycerol decomposed in our reaction system without adversely affecting the FAME compositions have been determined as 350–400 °C and 100–300 bar. The decomposition of glycerol at the temperatures of our experiments has also been reported elsewhere.[6] A near complete decomposition of glycerol in our experiments occurred under the mentioned TE conditions and was based on mass balance evaluations, which indicated that the TE products are obtained in the same amount with the mass of the reactants and only traces of glycerol were present in the final product for the experiments with near complete conversion.

The experiments shown in Table 2 as well as reported data in Table 1 demonstrate that the temperature effect on TG conversion dwarfs that of the pressure for SC TE reactions and shortens the residence time to very attractive ranges for commercial applications. Higher pressures increase the overall density of the reactants but also increase the H-bonded clusters of alcohol molecules as discussed above. These competitive effects render the pressure influence on the FAME yield rather minor when TE reactions are carried out at SC pressures. Under these conditions, an inert cosolvent (e.g., CO_2) used to enhance oil−alcohol miscibility and solubility may also act as a diluent to slow down the FAME thermal decomposition. The cosolvent, however, also may slow TE rates. As shown above, cosolvents should be used to adjust the critical point and phase behavior of the reactive mixture TG−alcohol so that the TE can take place in the convenient SC regions, wherein the FAME yield can be tuned effectively by pressure and temperature.

Although not all of the GDPs have yet been identified, it is expected that they can be directly used as part of the BD fuel. This situation would simplify the BD production process greatly, since the glycerol no longer has to be separated from the BD product and additional fuel could be produced. Further, the presence of small molecular components in BD could positively affect the viscosity and the cloud/pour point of the fuel. For example, at 5 °C, commercial samples of BD are solids while

(30) Yamaguchi, T.; Benmore, C. J.; Soper, A. K. *J. Chem. Phys.* **2000**, *112*, 8976–8987.

ours are still in the liquid state. In addition, because the alcohol can be used only in slight excess of the stoichiometric amounts, essentially all of the alcohol reacts, eliminating the need for its separation and recycling at significant parasitic pumping cost.

We contend that the main difference between our TE conditions and those reported in the literature (Table 1) for near complete TG conversions originates from TG–alcohol miscibility. At similar *P*–*T* conditions, this property is strongly dependent on TG composition and alcohol to TG ratio. Although it is generally claimed that a SC alcohol leads to near complete TG conversions, under stoichiometric or slightly higher alcohol to TG ratios, the reactant system is still biphasic, usually up to ∼350 °C, with bulk TG in a separate liquid phase. A large excess of alcohol is required to bring the system to SC states at the lower temperatures employed in the cited work. The TE reactions occur in the SC alcohol, involving only the dissolved amount of TG in this phase. Further, if glycerol does not decompose, some of the alcohol is dissolved in this phase, being unavailable for TG. On the other hand, if each of the two reactant streams is preheated and the TE occurs in a single homogeneous SC phase (as in most of our experiments), excess alcohol is not needed at the higher TE temperatures we used. Another possibility is that, concurrently, the reaction is catalytically activated by the reactor metal walls.

Technical and Economic Analyses

Process Design. Technical and economic feasibility assessments targeted a system to competitively produce BD from vegetable oils (e.g., SBO) and SC alcohols (e.g., methanol) compared with conventional TE processes[31–33] and current petrodiesel costs.

Plant Capacity Selection. When an optimum plant capacity for BD production integrated with power cogeneration has to be selected, very high capacity and one reactor may not be feasible due to the oversized power generator and pumping hardware. A small/medium capacity plant appears to be the choice for remote locations that are nearby to the source of raw materials and without an available power grid. A plant small enough to be easily built but large enough to overcome the high labor costs seems to be the best choice. However, larger capacity plants can be easily assembled from smaller modules to fit any of the listed capacities by The National Biodiesel Board.[34] Accordingly, three plant capacities for BD production by the proposed SC TE method were chosen to be 0.84, 2.5, and 5.2 million gal/year. The latter was rounded in the following text to 5 million gal/year. These choices also illustrate the influence of scaling-up factors on BD costs.

Process Parameters. On the basis of the laboratory experiments, the optimal conditions for SC TE reactions were determined. Once the flow rates were set, a process flow diagram was assembled in CHEMCAD for process simulation.[29] Such a process flow diagram of a SC TE system, including a source of energy, is shown in Figure 2. Basically, the simple process design consists of pumps and preheaters to transport and preheat the reactants, respectively, and a reactor to produce FAME. The process is unique in that the exhaust gases from a diesel power

generator are used to provide heat for the TE reactions. Also, the reactants were preheated by the hot TE product stream for the effective utilization of the energy.

The thermodynamic properties of SBO and FAME of the three main fatty acid chains of SBO (palmitic, linoleic, and oleic) were estimated from group contribution methods by using CHEMCAD. Vapor–liquid equilibrium compositions were estimated by CHEMCAD using different *K* models such as UNIFAC and SRK EOS. UNIFAC EOS was used for those portions of the flow sheet where the reaction mixture is liquid, and SRK EOS was used for those portions of the flow sheet where at least one of the components of the reaction mixture is above its critical point. The results of the simulation runs were used for the design and sizing of the process equipment. The reactor was sized on the basis of the residence time used in laboratory experiments 23–25 in Table 2. The time was extended to 3.79 min to account for scaling up factors. The diesel engine was sized to provide sufficient heat for the reaction and to use part of the BD (4.53 vol %) as fuel. The electricity produced is consumed locally or is to be sold to the local grid.

Economic Evaluation. The costs of manufacturing (COM) BD (production costs) were calculated with the chemical engineering methods available in the literature.[35–37] The base-case design to be scaled up by factors of ∼3 and ∼6 for plants with higher capacities was the BD production of 0.84 million gal/year with power generation. The plant was assumed to operate 24 h/day for 346 days/year. The capital cost and COM were estimated by using the methods of Turton et al.[35] and Ulrich:[36]

$$COM = 0.2536FCI + 2.2835C_{OL} + 1.0309(C_{UT} + C_{WT} + C_{RM})$$ (3)

where FCI is the fixed capital investment and C_{OL}, C_{UT}, C_{WT}, and C_{RM} are the costs for operating labor, utilities, waste treatment, and raw materials, respectively.

The capital costs for 2.5 and 5 million gal/year of BD production were estimated by scaling up the capital costs for the base-case unit using the six-tenths rule. Most of the total COM comes from the raw materials and labor costs. Although little can be done to reduce the raw materials cost, the COM/gal of product would be significantly reduced for a larger size plant, since the capital cost and the number of operators would not change in direct proportion. The COM for the base-plant capacity were calculated as $4.10 and the processing cost as $1.02, while for 2.5 and 5 million gal/year capacity these costs were calculated to the reduced break even costs of $3.50/gal and $3.34/gal with processing costs of $0.43/gal and $0.26/gal, respectively (Table 3).

For the capacity of 2.5 million gal/year, a comparison of these costs with those reported for BD produced by another SC TE method[26] using waste cooking oil under different process conditions is given in Table 3. Our calculated production cost of $3.50/gal is higher than the $1.80/gal reported. The main reason for this difference is the much lower cost of waste cooking oil. However, our processing cost of $0.43/gal is much

(31) Van Gerpen, J. H. Oilseeds and Biodiesel Workshop, Great Falls, MT, February 15, 2007.

(32) Zhang, Y.; Dube, M. A.; Mclean, D. D.; Kates, M. *Bioresour. Technol.* **2003**, *90*, 229–240.

(33) Hass, M. J.; McAloon, A. J.; Yee, W. C.; Foglia, T. A. *Bioresour. Technol.* **2006**, *97*, 671–678.

(34) http://www.biodiesel.org/buyingbiodiesel/producers_marketers/ProducersMap-Existing.pdf.

(35) Turton, R.; Bailie, R. C.; Whiting, W. B.; Shaeiwitz, J. A. *Analysis, Synthesis, and Design of Chemical Processes*; Prentice Hall International Series: Upper Saddle River, New Jersey, 2003.

(36) Ulrich, G. D. *A Guide to Chemical Engineering Process Design and Economics*; John Wiley & Sons: New York, 1984.

(37) Peters, M. S.; Timmerhaus, K. D. *Plant Design and Economics for Chemical Engineers*; McGraw Hill Chemical Engineering Series: New York, 1991.

(38) http://www.cbot.com/cbot/pub/page/0,3181,1341,00.html.

(39) http://methanex.com/products/methanolprice.html.

Table 3. Comparative Production and Processing Costs ($/gal) of Biodiesel Fuels for Conventional and SC Methods

cost component	840 000 gal/year	2 500 000 gal/year		5 000 000 gal/year	
	SC TE[a]	SC TE[a]	SC TE[26]	SC TE[a]	base TE[31]
oil	2.95[b]	2.95[b]	0.75	2.95[b]	3.23[b]
methanol	0.12[c]	0.12[c]	0.12[c]	0.12[c]	0.13[c]
NaOCH$_3$ catalyst					0.08
neutralizer					0.01
utilities	0.00	0.00	0.10	0.00	0.02
labor	0.40	0.135	0.40	0.066	0.10[d]
depreciation	0.068	0.044	0.073	0.033	0.15
interest	0.052	0.034	0.029[e]	0.025	
administration + overhead	0.327	0.122	0.433	0.064	0.020
maintenance	0.041	0.026	0.148	0.020	0.040
laboratory charges	0.051	0.017	0.063[e]	0.008	0.011[e]
operating supplies	0.006	0.004	0.007[e]	0.003	0.011[e]
local taxes + insurance	0.022	0.014	0.016	0.010	0.040[e]
patents + royalties	0.12	0.10	0.08[e]	0.10	0.12[e]
total production cost	4.16	3.57	2.21	3.41	3.96
net production cost	4.10	3.50	1.80	3.34	3.96
processing cost	1.02	0.43	0.93	0.26	0.51

[a] This study. *[b]* Costs, as per August 2007 for SBO.[38] *[c]* Costs, as per August 2007 for methanol.[39] *[d]* Cost, updated to three shifts/day. *[e]* Additional costs.

lower than that in the above reference of $0.93/gal, due to the different architectures of the two methods and the associated process conditions.

In order to compare these results with those for a conventional method, we selected the reported costs of Van Gerpen[31] (Table 3, the last column) for a 5 million gal/year capacity. Similar costs have been reported to a U.S. Senate Committee by Collins.[2] In refs 26 and 31, some of the COM components have been updated, and others were additionally considered for a same-base comparison. The oil and methanol costs are higher in the reported conventional methods as compared to those of the SC method, since less BD is produced by the conventional method (glycerol is separated out as a byproduct) from the same quantity of raw materials.

The raw material costs for SBO[38] and methanol[39] as well as the diesel fuel cost[40] exhibit timely market fluctuations. SBO at the time of this analysis was available for $2.91/gal[38] and methanol for $0.93/gal,[39] while the price of diesel fuel was ∼$3.00/gal.[40] However, the processing cost is much more stable, such as it can be stated that the BD price is the price of SBO and methanol plus the processing cost of $0.26/gal (for 5 million gal/year plant capacity). It is also important to note that if diesel fuel has to be used for soybean cultivation and SBO production, the BD price will always be above the price of this fuel. Otherwise, this fuel has to be replaced by BD all along these processes.

Conclusions

TE reactions between vegetable oils (e.g., SBO and SFO) and alcohols (e.g., methanol and ethanol) have been conducted

in both tubular and batch laboratory-scale reactors at temperatures up to 425 °C, pressures up to 300 bar, and ratios of alcohol to oil from stoichiometric (i.e., 3:1) to 24:1 values.

Under selected ranges of these conditions (e.g., 350–400 °C, 100 bar, and alcohol to oil ratios slightly higher than the stoichiometric value of 3:1), near complete conversions of oil to BD products have been achieved, and basically all of the glycerol produced has been decomposed to smaller molecular compounds blended within the BD fuel. Upon cooling the TE products generated under the above conditions, one homogeneous liquid phase has been obtained with viscosity, cloud/pour point, and composition superior to commercial BD fuel.

Experimental data showed that the miscibility of oil−alcohol, monitored in this study through a view cell attached at the reactor outlet, plays a key role in the efficiency of the process.

An economic analysis based on a TE process to produce BD in one step under the above conditions has been performed. It was found that the processing cost of the proposed technology could be near half of that of the actual conventional methods. (i.e., $0.26/gal vs $0.51/gal).[2,31] Associated with some other incentives, along with higher diesel fuel prices, this new cost-saving technology is likely to make BD production profitable.

(40) http://tonto.eia.doe.gov/oog/info/gdu/gasdiesel.asp.