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Effect of System Conditions for Biodiesel Production via Transesterification Using Carbon Dioxide−Methanol Mixtures in the Presence of a Heterogeneous Catalyst

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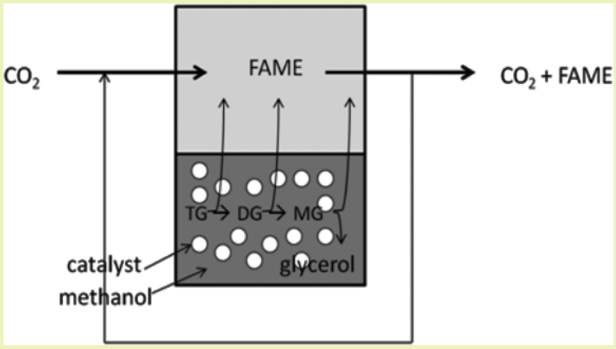
Supporting Information

ABSTRACT: A mixed carbon dioxide (CO_2) and methanol (MeOH) system is shown to successfully transesterify triolein into methyl oleate at moderate pressures and temperatures below 100 °C in the presence of Nafion NR50, a heterogeneous catalyst. An experimental design was developed to explore the effects of mono-, bi-, and tri-phasic CO_2−MeOH−triolein systems through pressure, temperature, and methanol loading, all of which influence the system phase behavior. It was found that one particular set of conditions (>80 °C, 9.5 MPa, 3.6% v/v reactor, ambient MeOH) demonstrated nearly complete yields due to the preferable phase behavior at these conditions. Cloud point curves of the ternary system (MeOH, CO_2, and substrate, including triolein, diolein, monoolein, glycerol, and methyl oleate) are reported to describe this complex system phase behavior. Results indicate that optimized yields (>98% methyl oleate at 95 °C) are achieved when the reaction is carried out in a three-phase system (not including the solid catalyst as a separate phase), which can partially be attributed to increased solubility of triolein in methanol as well as increased mass transfer due to the presence of dissolved CO_2.



KEYWORDS: *Biodiesel, Transesterification, Carbon dioxide expanded liquid, Nafion*

INTRODUCTION

There is an increasing demand to produce transportation fuels from renewable resources as evidenced through the Energy Independence and Security Act of 2007.[1] Biodiesel offers a potentially sustainable and drop-in alternative to traditional fossil-based fuels as it is sourced from a renewable feedstock, with other advantages in that it is cleaner burning than diesel, safer to handle, and promotes longer engine life.[2,3] Efforts to realize a favorable energy balance to sustainably produce biofuel requires lowering the agricultural inputs necessary (fertilizers, pesticides, etc.), producing crops on marginal land, and lowering the energy for extraction and conversion, while developing a reliable stream of value-added coproducts.[4]

Life cycle analyses of the biodiesel production process from various renewable feedstocks[5−11] indicate that significant energy requirements are involved with feedstock growth as well as lipid extraction of triglycerides (TG) and conversion. The preferred reaction for TG conversion to biodiesel is transesterification with an alcohol, commonly methanol yielding fatty acid methyl esters (FAME, biodiesel) and glycerol as a byproduct with monoglycerides (MG) and diglycerides (DG) as intermediates.[12] Biodiesel can be produced by either catalyzed or uncatalyzed transesterification. The former is currently used in commercial biodiesel production, while the latter, which typically involves supercritical conditions, was developed to facilitate processing of lower quality feedstocks and is not currently commercially employed.[12]

In this work, the principles of green chemistry[13] are applied to reduce energy requirements for biodiesel production through the use of carbon dioxide (CO_2) and heterogeneous catalysts, which can lead to lower reaction temperatures and facilitates catalyst recovery and reuse.[14] In addition, sub- and supercritical CO_2 offer several potential system benefits over other supercritical methanol in that CO_2 is nontoxic, highly abundant, nonflammable, and easy to separate from a reaction mixture.[15] CO_2 has previously been shown to be an effective solvent for extraction of TG from algal biomass.[16] Further, the

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selectivity of CO_2 for compounds of varied polarity is of particular relevance for transesterification reactions because the reactants, intermediates, and products all fall within different polarity ranges due to the elimination of alkyl chains as the reaction progresses.

Transesterification at Elevated Pressures. Supercritical transesterification of triglyceride feedstocks has been demonstrated using both methanol and ethanol at significantly elevated temperatures and pressures (typically 250− 400 °C, 19 − 45 MPa),[12,17] as the alcohols and TG do not form a single phase at temperatures below 225 °C.[18−20] The use of cosolvents and/or catalysts, such as CO_2, propane, hexane, and lipase, has been explored to moderate these reaction conditions.[21−23] Both the use of neat methanol and methanol/organic cosolvent gives rise to additional challenges in downstream separations of the reaction products and have inherent hazards associated with toxicity and flammability. CO_2 has also been used as a cosolvent for transesterification using both supercritical ethanol[24] and methanol[25] and was found to be effective at percentages up to 10% CO_2, but temperatures of at least 280 °C were required to reach a 98% yield.[25] Previous studies have used supercritical CO_2 ($scCO_2$) and methanol in a single supercritical phase with both enzyme and heterogeneous catalysts for transesterification.[26,27] Both systems demonstrated high temperature and pressure requirements and suffered from difficulties pertaining to the downstream separation of glycerol from the product. However, monophasic (i.e., supercritical) conditions may not be necessary in order to benefit from using CO_2 (i.e., increased solubility and selectivity, as well as decreased mass transfer resistance). Operating at lower temperatures and pressures in a multi-phase liquid−vapor system may allow for similar benefits without such high energy burdens.[28]

A mixed CO_2 and methanol system operating below the supercritical point leads to the existence of multiple phases. The resulting phase behavior consists primarily of a CO_2-rich phase and methanol-rich phase, which can be considered a CO_2-expanded liquid (CXL). The utilization of a CXL as the reaction medium is potentially advantageous. While much of the functionality of using $scCO_2$ is retained (i.e., lowered viscosity and tunability), CXLs have lower pressure requirements and increased substrate and liquid concentrations with lower mass requirements.[29] Generally, gas-expanded liquids have been shown to be advantageous in a number of catalyzed reactions.[30−33] In terms of esterification, a few studies have successfully esterified fatty acids[29,34−37] or TG[38] (as in this study) into a variety of related components in CXLs.

Design of Current Study. The work presented here uniquely considers CXL methanol for the transesterification of a representative TG, triolein, using a heterogeneous catalyst (Nafion NR50) yielding FAME conversion >98% at temperatures <100 °C at relatively short reaction times (≤2 h). Nafion NR50 was chosen because it is a superacid catalyst that has demonstrated efficacy and stability in CO_2 systems,[38] which tend to be acidic. The specific comparison and optimization of CO_2-mediated transesterification in mono- and multi-phase systems has not been systematically performed previously especially when considering the high yields achieved here. This work undertakes a fundamental approach to provide a comprehensive study of this complex system consisting of CO_2, methanol, substrate, and catalyst used to produce favorable reaction conditions and optimization. Novel contributions of this work include (1) establishing the conditions for a mixed CO_2, methanol, and heterogeneous acid catalyst transesterification at the lowest temperatures for heterogeneous chemical catalysis known to the authors, (2) establishing the solubilities of each reaction substrate using cloud point measurements of the ternary substrate (TG, diglyceride (DG), monoglyceride (MG), glycerol, FAME)−methanol−CO_2 system using a variable-volume view cell (VVVC), and (3) forming a CXL using CO_2 and methanol with significant advantages over a monophasic supercritical system.

■ MATERIALS AND METHODS

Substrate and Solvent Materials. All substrates, including triolein, diolein, monoolein, methyl oleate, and glycerol, were purchased from Sigma-Aldrich of at least 99% purity. Methanol and ethyl acetate were obtained from J.T. Baker. Bone dry CO_2 with a siphon tube and nitrogen gas was supplied by Airgas, Inc. Liquid chromatography solvents, Chromasolv heptane and isopropanol, were obtained from Sigma-Aldrich and American Bioanalytical, Inc. respectively.

Catalyst Materials. Nafion NR50 was purchased from Ion Power, Inc. and stored in a desiccator. An equivalent meq H+ value was determined for Nafion NR50 using the expected 0.037 meq H+/g Nafion NR50 based on chemisorption estimations as reported by Lopez et al.[39] For all of the experiments reported, the catalyst loading was 0.0185 mmol H+ as Nafion NR50.

Reactor and Reaction Conditions. All reactions were performed in a stainless steel 50 mL reactor equipped with a blade stirrer (Parr Instrument Co.) and sapphire windows as seen in Adamsky and Beckman.[40] For each reaction, the catalyst and substrates were added directly into the reactor that was then sealed and heated to the desired temperature using four heating irons controlled by a temperature controller monitored by an in situ probe thermocouple. Once the desired temperature was achieved, methanol was injected through a two-way valve system. The reactor was then pressurized with CO_2 and stirred at 300 rpm. Preliminary experiments indicate that this mixing speed is sufficient to minimize mass transfer limitations within the reactor (Figure S1, Supporting Information). The conditions were maintained for 2 h when CO_2 was vented through heated restrictor and flow control valves.

The venting CO_2 was slowly sparged through isopropanol for collection. The isopropanol was then poured into the reactor and collected in order to get a fair representation of all reaction substrates. The sample was then diluted and analyzed on LC-MS. All reactions were monitored using methyl nonadecanoate as an internal standard for methanol introduction and methyl palmitate as an internal standard for reactor yield recovery. All reactions were performed in at least duplicate with an initial substrate loading of 100 mg.

Cloud Point Measurement. Cloud point measurements were performed in a high pressure VVVC with details found in Miller et al.[41] Briefly, the cell consists of a quartz tube housing a floating piston. The sample was loaded directly onto the surface of the piston, and the mass was determined. Once the apparatus was assembled, methanol was added, and the vessel was sealed. CO_2 was then introduced into the cell and the system temperature set. The pressure was then increased isothermally by compression of the well-mixed system until the system reached a single (supercritical) phase. Once equilibrium is reached, the pressure was slowly decreased by expansion of the vessel volume until a "cloud" of liquid droplets appears, making the vessel opaque. The pressure at this "cloud point" was measured in triplicate and marks the transition between a single-phase (SC) and two-phase (vapor−liquid, VL) system (i.e., when methanol and/or oleate substrate is no longer completely soluble). If the volume is further increased, another transition pressure from two to three phases (VL-VLL) is measured.

Analysis. FAME, TG, DG, and MG were measured using liquid chromatography−mass spectrometry (Varian 500-MS, 212-LC pumps) with a Waters normal phase Atlantis HILIC silica column (2.1 mm × 150 mm, 3 μm pore size) with in-line guard column, a

Prostar autosampler (20 μL sample loop), and atmospheric pressure chemical ionization. The isocratic elution used 9:1 heptane:isopropanol both modified with 0.1% glacial acetic acid at a flow rate of 250 μL/min. APCI was done in positive ion mode with capillary voltage (CV) of 75 V, RF loading at 85% with a corona current of ±5 A, and spray shield voltage of ±400 V. Quantitative ions were $[M - H]^+$. The method was run for 8 min with the following retention times: Triolein 1.6 min; methyl oleate 1.8 min, diolein 2.1 min; and monoolein 5.9 min. Mass was estimated by linear regression of standard curve slopes from known standards.

■ RESULTS AND DISCUSSION

This study, simplifies the highly complex system by using a single TG starting material to assess the fundamental role of phase behavior on the system. That the substrate is continually changing as the reaction proceeds influences the solubility of the system components according to the exact conditions (i.e., temperature, pressure, reagent ratios, etc.) at any singular time. Triolein and related oleate species (diolein and monoolein) were selected as representative substrates due to the prevalence of triolein in many biofuel feedstocks and appropriateness for use as a biodiesel precursor.[42] Initial conditions were chosen to include relatively low concentrations of substrate minimizing the effect of complex interactions from TG, DG, MG, and products (i.e., FAME and glycerol) on the system phase behavior, enabling the assumption that the methanol−CO_2 binary interaction dominates the bulk phase behavior of the system.

Phase Transition Measurements. The phase transition pressures between single phase (SC) and two phase (VL) at 40 °C (Figure 1) with varied MeOH loadings were determined using a VVVC for the ternary system, which consisted of individual substrates, specifically triolein, diolein, monoolein, methyl oleate, and glycerol, in mixtures of CO_2 and methanol (data provided in Table S2, Supporting Information). Note that during the reaction, methanol will decrease at a faster rate than triglyceride due to the 3:1 stoichiometric ratio potentially causing a depressed methanol to CO_2 ratio with significant impact on phase behavior during the course of the reaction. Therefore two mole ratios of methanol were tested—9:1 (3× molar excess) and 90:1 methanol:substrate—as seen in previous studies .[43] These conditions test the effect of methanol on the solubility of the substrates in the ternary system while providing a relatively stable methanol availability and phase behavior during the reaction.

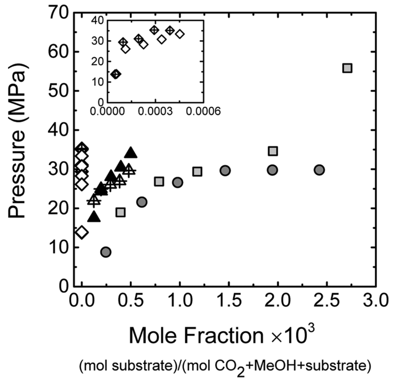


Figure 1. Single-phase (SC) to dual-phase (VL) transition pressures for transesterification substrates at 40 °C. Substrates at 9:1 methanol:substrate ratios are represented as ◊ glycerol, □ monoolein, ○ diolein, and Δ triolein. The 90:1 methanol:substrate ratios for ♦ glycerol and ▲ triolein are also represented. Inset represents low mole fractions in order to depict differences in glycerol solubility. (Tabular data with standard deviations are reported in Table S1 of the Supporting Information).

The addition of a large excess of methanol at 40 °C does not appreciably impact the SC−VL transition pressures for TG or glycerol. That is at both methanol concentrations, the pressure (P) needed to achieve a single phase at a given mole fraction of substrate (x) does not change significantly. Hence, starting with a 90:1 excess of methanol:TG should not significantly impact phase behavior as methanol is depleted during the reaction.

Considering diolein and monolein, we note that the SC−VL transitions lie at significantly lower pressures than those of equal composition for the triolein and 9:1 MeOH:substrate loading (Figure 1). The position of their P−x curves will depend upon both molecular weight (MW) and polarity (and thus associated parameters such as vapor pressure and boiling point), where higher MW and polarity tend to decrease volatility and increase boiling point with the net result of increasing cloud point pressures. Clearly, MW and polarity combine in a complex fashion; converting triolein to diolein lowers MW yet increases polarity with a net result of dropping the cloud point pressures. Progressing to monoolein drops MW still further, but apparently the heightened increase in polarity shifts the cloud point pressures oppositely. Previous works showing similar trends[44−47] suggest that MW (rather than polarity) dominates the phase behavior for the various glycerides found during biodiesel generation.

For the reaction products, FAME and glycerol, the respective solubilites are highly disparate, as expected from the large difference in polarity between the molecules. Methyl oleate solubility is more than two orders of magnitude greater than glycerol. It is important to note that the solubility of glycerol at a given pressure remains more than an order of magnitude less than TG even at the higher methanol loading, and as shown by previous research.[18,48,49] The presence of glycerol will rapidly lead to formation of a separate phase regardless of the phase behavior of the starting materials.

The data indicates that there are tractable conditions (pressure, temperature, and composition) where a single phase of methanol, CO_2, and TG exists. However, we can also see that, at lower pressures, below the VL transition and above the VVL transition, a two-phase system will occur, where the "vapor" phase will be dilute in both methanol and TG while the other liquid phase exhibits significant concentrations of all three components including CO_2 and thus forming a CXL. Previous literature has shown that in two-phase regimes there is significant swelling of the oil phase by the CO_2/alcohol mixture.[50,51] As such, we might find that operating at lower pressures, and hence in a multiphase system, provides superior results. Song et al.,[52] for example, added CO_2 to a methanolysis of glycerol monostearate (H+ as catalyst, 60−70 °C) and found an increase in reaction rate, despite the presence of two- or three-phase behavior during the reaction, suggesting that added CO_2 enhances transport across the various phase boundaries. Galia and colleagues[38] examined methanolysis of rapeseed oil in a CO_2−methanol mixture at 100−140 °C using a solid catalyst. While the solubility of the oil in CO_2 was found to be quite low (as expected), CO_2 swells the oil-rich phase by up to 40% at 20 MPa, which helps to both solubilize methanol in this phase and reduce transport limitations across the interface.

Experimental Optimization of Pressure, Temperature, and Methanol Loading. An experimental design was

Table 1. Mass Percentage Yields with Standard Errors for Each Matrix Reaction Condition[a]

System condition #	Pressure (MPa)	Temp. (˚C)	Vol. MeOH (mL)	A) Mass percentage yields (mg) starting from Triolein			
				Methyl Oleate	Triolein	Diolein	Monoolein
1	9.5	40	0.35	13.2 ± 2.9	64.3 ± 22.2	n.d.	22.5 ± 19.2
2	9.5	40	1.8	22.1 ± 8.8	67.2 ± 14.5	n.d.	10.7 ± 6.5
3	9.5	80	0.35	10.7 ± 3.1	86.3 ± 5.2	n.d.	3.1 ± 2.1
4	9.5	80	1.8	89.4 ± 2.6	9.2 ± 3.7	1.3 ± 1.3	n.d.
5	17.5	40	0.35	9.9 ± 2.6	85.4 ± 4.6	0.0 ± 0.0	4.7 ± 2.0
6	17.5	40	1.8	1.6 ± 0.4	92.3 ± 6.5	6.0 ± 6.0	n.d.
7	17.5	80	0.35	2.7 ± 1.2	91.7 ± 6.9	5.6 ± 5.6	n.d.
8	17.5	80	1.8	4.6 ± 1.2	88.7 ± 7.9	6.7 ± 6.7	n.d.

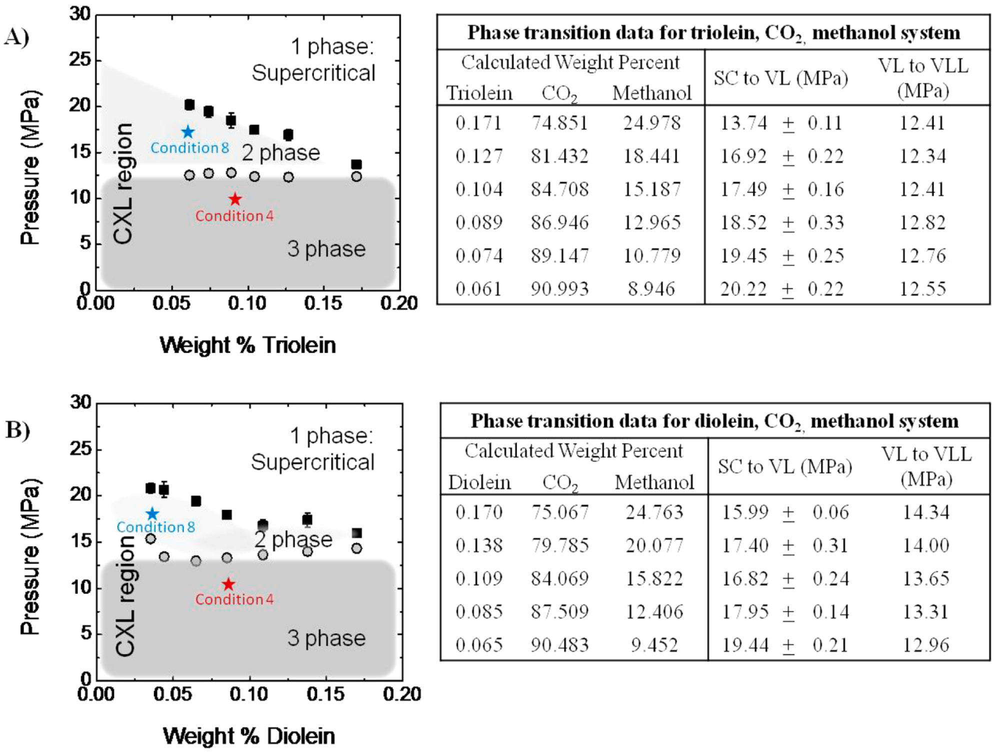
System condition #	Pressure (MPa)	Temp. (˚C)	Vol. MeOH (mL)	B) Mass percentage yields (mg) starting from Diolein			
				Methyl Oleate	Triolein	Diolein	Monoolein
1	9.5	40	0.35	4.3 ± 2.2	8.8 ± 5.7	86.9 ± 7.9	n.d.
2	9.5	40	1.8	7.9 ± 3.6	0.9 ± 0.7	88.2 ± 3.5	3.0 ± 0.5
3	9.5	80	0.35	5.5 ± 2.6	2.5 ± 2.0	92.0 ± 4.6	n.d.
4	9.5	80	1.8	54.0 ± 10.9	4.8 ± 4.8	41.1 ± 6.0	n.d.
5	17.5	40	0.35	4.9 ± 1.7	1.0 ± 0.5	94.1 ± 2.2	n.d.
6	17.5	40	1.8	4.9 ± 1.9	1.9 ± 0.4	93.2 ± 1.6	n.d.
7	17.5	80	0.35	15.0 ± 4.3	5.4 ± 5.4	79.6 ± 1.1	n.d.
8	17.5	80	1.8	43.6 ± 10.6	1.4 ± 0.3	55.0 ± 10.9	n.d.

System condition #	Pressure (MPa)	Temp. (˚C)	Vol. MeOH (mL)	C) Mass percentage yields (mg) starting from Monoolein			
				Methyl Oleate	Monoolein	Diolein	Monoolein
1	9.5	40	0.35	45.2 ± 9.5	11.4 ± 11.4	12.4 ± 12.4	30.9 ± 14.3
2	9.5	40	1.8	31.8 ± 3.1	0.8 ± 0.8	1.0 ± 1.0	66.4 ± 1.4
3	9.5	80	0.35	67.4 ± 18.6	4.0 ± 4.0	12.8 ± 12.8	15.8 ± 1.7
4	9.5	80	1.8	93.1 ± 3.9	1.5 ± 1.5	n.d.	1.5 ± 5.4
5	17.5	40	0.35	43.8 ± 19.8	0.5 ± 0.2	16.6 ± 12.5	39.1 ± 7.5
6	17.5	40	1.8	24.1 ± 5.9	0.4 ± 0.1	4.4 ± 3.3	71.1 ± 2.7
7	17.5	80	0.35	56.9 ± 19.5	0.3 ± 0.1	32.5 ± 29.8	10.2 ± 10.2
8	17.5	80	1.8	78.5 ± 3.6	10.9 ± 10.8	1.7 ± 0.7	8.8 ± 6.5

[a]Starting material is highlighted in gray; methyl oleate is highlighted in green.

developed with high and low values for pressure, temperature, and methanol loading to evaluate the impact of each parameter on phase behavior and reaction yield (Table 1). The 40 °C temperature is just above the critical temperature of neat CO_2 but not necessarily above the critical point for the CO_2 and methanol mixture. The 80 °C temperature is high enough for significant catalytic reaction at ambient conditions to occur, yet still allows for the determination of increased or decreased reactivity in the system. At 9.5 MPa, neither temperature enables the formation of a single phase (SC) in the ternary system. However, this pressure has been indicated to have enhanced transesterification reaction yields due to local composition enhancements.[53] The higher pressure, 17.5 MPa, was chosen to provide a single fluid phase at both temperatures and reflects successful supercritical alcohol transesterifications reported previously.[27] Methanol loadings were also selected to reflect literature values shown to have favorable outcomes in terms of solubility and yield for reactions in $scCO_2$.[53,54] In this system, there is a fixed reactor volume, so by adding the same amount of methanol at each system test condition while at ambient pressure, the methanol to carbon dioxide ratio as well as the system density changes significantly as pressure and temperature are varied (exact calculated substrate, methanol, and CO_2 weight percentages provided in Table S2, Supporting Information). On the basis of these conditions, the system phase behavior may be predicted to exhibit a single supercritical phase or multiple phases (VL or VLL). In the case of VL or VLL, there would exist a CXL where the solute is either soluble (two phase) or phase separates (three phase).[55]

The results of the experimental matrix using Nafion NR50 as the reaction catalyst (0.0185 mmol H+ as Nafion NR50) for triolein can be seen in Table 1a. The catalyst loading for 10 mg triolein (0.011 mmol) was 54%, calculated as 0.0185 mmol H+ per 0.034 mmol ester (as triolein must react three times for each ester moiety with H+ to form FAME). The optimal point of the transesterification of triolein consisted of using the high temperature and methanol loading, but low pressure (Table 1; condition 4) yielding ~93% (wt/wt) methyl oleate. Compared to the other conditions, this yield is significantly higher and occurs where CO_2 and methanol are expected to exist in two phases: CXL MeOH and MeOH-rich CO_2. While there is also a higher methanol loading when normalized to the weight of the other reactor components, there is unlikely to be increasing yield as methanol is supplied in excess (pseudo-first order conditions) making the reaction independent of methanol concentration. The intermediates (DG and MG) of the transesterification reaction were also tested as initial substrates providing insight into the limiting steps of the reaction as well as role of solubility and phase behavior in reaction yields (Tables 1b and c). Again DG and MG were added at 10 mg or 0.032 mmol of ester and 0.028 mmol ester, respectively. Normalizing this to the 0.0185 mmol H+ as Nafion NR50 in the system leads to a catalyst loading of 57% and 65%, respectively. The yields of the methyl ester starting with the



Phase transition data for triolein, CO_2, methanol system

Calculated Weight Percent			SC to VL (MPa)	VL to VLL (MPa)
Triolein	CO_2	Methanol		
0.171	74.851	24.978	13.74 ± 0.11	12.41
0.127	81.432	18.441	16.92 ± 0.22	12.34
0.104	84.708	15.187	17.49 ± 0.16	12.41
0.089	86.946	12.965	18.52 ± 0.33	12.82
0.074	89.147	10.779	19.45 ± 0.25	12.76
0.061	90.993	8.946	20.22 ± 0.22	12.55

Phase transition data for diolein, CO_2, methanol system

Calculated Weight Percent			SC to VL (MPa)	VL to VLL (MPa)
Diolein	CO_2	Methanol		
0.170	75.067	24.763	15.99 ± 0.06	14.34
0.138	79.785	20.077	17.40 ± 0.31	14.00
0.109	84.069	15.822	16.82 ± 0.24	13.65
0.085	87.509	12.406	17.95 ± 0.14	13.31
0.065	90.483	9.452	19.44 ± 0.21	12.96

Figure 2. SC-VL (black square) and VL-VLL (gray circle) transition pressures for triolein (A) and diolein (B) at 80 °C with methanol to substrate ratios replicating experimental conditions. The points correlating with substrate compositions as in Table 1, system condition 4 (red star, 9.5 MPa, 80 °C, 1.8 mL methanol) and 8 (blue star, 17.5 MPa, 80 °C, 1.8 mL methanol) are marked, respectively Note: Solid phase from catalyst is not included but exists as an additional separate phase. Exact values describing system conditions are provided to the right of the graphs.

diolein (specifically a mixture of 75% of 1,3-dioleoylglycerol and 25% of 1,2-dioleoylglycerol) are significantly less than those resulting from triglyceride at the same system conditions (Table 1b; condition 4) even with the slightly increased catalyst loading. This suggests that perhaps under these system conditions, the rate-limiting step is the diglyceride to monoglyceride. Theoretical calculations of activation energy show that the energy barrier for transesterification of 1,2-DG is much greater than that of the TG to DG, but the 1,3-DG transesterification energy is slightly less than that of TG.[56] Thus, because the diolein mixture is only 25% 1,2-DG, a 25% reduction in yield may be expected based solely on activation energy. The actual yield decrease is closer to 40%, and thus, the difference may be due to some other additional factors, particularly phase behavior and solubility because increased catalyst loading does not lead to concomitant increases in FAME yield. It should be noted that there are small amounts of triolein, indicating the reverse reaction. The maximum yields of methyl oleate from diolein were seen with high methanol loading at 80 °C and were less dependent on pressure than the reaction yields where triolein is the initial substrate.

Starting with monoolein, overall yields of methyl oleate are the highest as compared to TG and DG (Table 1c). From an activation energy perspective, the MG should have more of a thermodynamic barrier for transesterification than the TG,[56] but the results from this pressure system with CO_2 do not reflect this trend. The high yields of FAME starting with monoolein may thus potentially be attributed to favorable phase behavior and/or solubility, achieving improved access of the MG to methanol and catalyst. The optimal yield for monoolein was similar to that of triolein at condition 4, but high yields are also seen for condition 8 at the high-pressure conditions with the same temperature and methanol loadings as condition 4, similar to the trend as seen with diolein.

Phase Behavior at Optimal Points. The use of the VVVC allowed us to visually examine the phase behavior of the initial mixture as a function of pressure and composition. The phase transition pressures between SC–VL and VL–VLL for the ternary glyceride–MeOH–CO_2 system have been evaluated for conditions surrounding the optimal reaction point (Figure 2). The results of these observations allow for the determination of the reaction conditions and subsequent yields in SC, VL, or VLL phase conditions. Above the SC–VL transition, the system is a supercritical fluid, while below exists a two-phase VL system. Below the VL–VLL transition, three phases exists. The SC–VL transition pressure changes over the range of substrate composition (x). Generally, starting with pure CO_2 (x = 0), and increasing x, there will be a sharp increase in SC–VL transition pressures until the maximum is reached. After this maximum, increasing x results in a decrease in these transition pressures. It should be noted that Figure 1 reports data from the region before the pressure maximum (small values of x), while the data from Figure 2 is in the region after this maximum when considering the total amount of substrate as both TG and methanol (data have been plotted comparatively in Figure S2, Supporting Information). While the TG mole fractions for Figure 1 and the experimental matrix (Figure 2) are comparable, the amount of methanol used is greater for Figure 2, thus increasing the total substrate composition consisting of both methanol and glycerides. The experimental optimal point occurs in the region after the maximum but below the VL–VLL transition in the three-phase region.

As shown in Figure 2, single (SC)-, two (VL)-, and three-phase (VLL) regimes exist as pressure is decreased at constant composition. If we examine the reaction results (Table 1) in the context of Figure 2, we see some interesting trends. In each case, condition 4 (low pressure, highest MeOH concentration) provided the highest yield of FAME product. Clearly, a pressure of 9.5 MPa produces a three-phase system at 80 °C, and thus, the interaction of the reaction substrates, which is dictated by the system phase behavior and physical properties, is critical for a successful yield.

The known solubilities of the model reactants and products in neat methanol are quite disparate, as expected from the varied polarities. For example, Čerče et al.[20] noted that at temperatures below 100 °C, the methanol–triglyceride binary forms two phases where one phase is nearly pure methanol while the other contains the bulk of the oil swollen by ~10% with methanol. Tang and colleagues[19] showed that the two-phase region dominates the T–x space for the triolein/methanol binary; they found no single-phase region up to 480 °C. On the other hand, during transesterification, each alkyl chain is exchanged for a hydroxyl group, thus increasing the molecule's polarity (such that polarity of TG < DG < MG < glycerol) and subsequent solubility in the methanol. Interestingly, Sawankeaw and colleagues,[17] report high yields, and selectivity can be achieved while operating in a SC, VL, or VLL regime when using methanol as both solvent and reactant (at sub- and super critical conditions). This result is also noted by Hegel et al.[57] who postulate that within a VL system "the oil transesterification possibly occurs mainly in the light supercritical phase, where the oil and the monoglycerides and diglycerides are partially soluble and the concentration of methanol is high. Moreover, the light phase transport properties favor a higher reaction rate." In the system mentioned here, CO_2 offers the same advantages of the light phase for the MeOH-only system mentioned by Hegel[57] in that CO_2 acts as a cosolvent for MeOH and oil allowing for increased transport rates at much lower temperatures than needed for the MeOH-only system. Naturally, glycerol is formed during the transesterification reactions and even in cases where the reaction begins in a single-phase system, generation of even small amounts of glycerol typically leads to phase separation.

Negi et al.[48] and Oliveira et al.[49] examined the phase behavior of glycerol–methanol–methyl oleate and glycerol–monoolein–methyl oleate ternaries and found, not surprisingly, that methanol and glycerol are miscible over a large range, while the presence of the less polar methyl oleate creates a two-phase regime that spans the entire phase diagram at 60 °C. This behavior also holds for the ternary system including monoolein, but a small one-phase regime appears at 135 °C. The obvious conclusion is that the presence of the reaction product, glycerol, creates a second phase and reduces the amount of methanol in the working phase. A report by Hegel et al.[18] on FAME–glycerol–methanol ternaries confirms this finding, although one can grow the size of the single-phase regime by increasing temperature above 150 °C and by employing a large methanol fraction. They also note that FAME and glycerol exhibit significant mutual insolubility at temperatures below 200 °C.

In general, carbon dioxide has proven to be a rather weak solvent.[58] Hence, in order to achieve sufficient substrate solubility in CO_2, a cosolvent is required to render the reaction tractable. By contrast, in the present system, CO_2 acts as a cosolvent, in that it is completely miscible with methanol (above certain very accessible pressures[55]) and has been shown to solubilize TGs and FAMEs.[16,44] Glycerol and CO_2 are generally mutually insoluble (owing to the significant polarity mismatch), and as such, the production of glycerol during the reaction will prompt formation of a second phase, thus pulling methanol with it.[59,60]

Here, we postulate that for the VLL system, the vapor phase is primarily CO_2 with methanol as the minority component, whereas for the two liquid phases one is glyceride-rich and the other is glyceride-poor in equilibrium. We hypothesize that the concentration of methanol in the oil-rich phase may be significantly higher than what would be found if no CO_2 were present in the system.[38] As such, the rate of transesterification should be expectantly higher with CO_2 present. Next, as hypothesized by Song et al.,[52] methanol transport across the interface (between oil-poor and oil-rich phases) will be enhanced by the presence of CO_2 (via its ability to lower interfacial tension;[61] such lowering of transport resistance can entirely outweigh the potential advantages of a single phase system. Finally, the reduced viscosity and enhanced diffusivity in the oil-rich phase owing to swelling by CO_2 will also reduce transport resistance to (and within) the solid catalyst, further enhancing the overall rate.[62] These effects combine to produce a high rate of transesterification despite the presence of multiple phases.

Galia et al.[38] also transesterified rapeseed oil in a mixed CO_2 and methanol over sulfonated polymer matrices with a maximal yield of 62.4% yield. However, they did not report a significant difference between operating in a single- or multi-phase system,[38] a factor that strongly influenced yield here as well for many reactions carried out at elevated pressures.[30,34,35,63–66]

We note differences between the outcomes of the reaction depending upon whether triolein, diolein, or monoolein is employed as the starting material; nevertheless, the overall trend suggesting condition 4 as optimal is maintained. For both the monoglycerides and diglycerides, operation at system conditions reported for condition 8 (17.5 MPa, 80 °C, and higher methanol concentration) produces yields not significantly different from condition 4. For both conditions, the temperature was set to 80 °C, and the pressure and methanol concentrations chosen so as to produce a multi-phase system.

Specific Role of CO_2. To evaluate whether CO_2 offers a unique benefit to system performance and that the increased yields are not simply due to the increased pressure and temperature enhancing reaction rate, a control experiment was performed in the absence CO_2 (Figure 3). Nitrogen gas was used to replace the CO_2 in the reactor at conditions replicating the identified optimal reaction point (condition 4) at the same triolein and catalyst loading.

The duplicated results had a reaction yield of less than 5%, indicating that CO_2 has an important function in the reaction and that elevated pressure and temperature alone are not sufficient to drive the reaction to the observed yields. Preliminary experiments have also indicated that increasing mixing speed, thus decreasing resistance to mass transfer, increases reaction yields in the nitrogen control although not to the levels observed for a mixed CO_2 system (Figure S3, Supporting Information). CO_2 therefore may be (1) enhancing the availability of triolein to methanol by changing either the solubility or interfacial tension between triolein and methanol, (2) changing the phase behavior, and/or (3) affecting mass transfer to/within the catalyst.

To further explore the role of CO_2 in the system, another control experiment was conducted using nitrogen to impart pressure and ethyl acetate as a cosolvent with the same

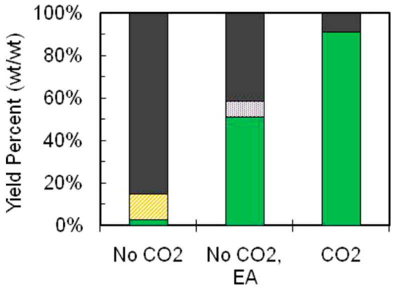


Figure 3. Results of pressure control experiments with nitrogen imparting reactor pressure (No CO_2 conditions) with and without ethyl acetate (EA) as a cosolvent. Reactions were at 9.5 MPa, 80 °C, 1.8 mL methanol loading; 0.033 mmol of ester as triolein to 0. 0.0185 mmol H+ as Nafion NR50). Pictured values are the average of duplicate samples (green bar, methyl oleate; yellow-dotted bar, monoolein; gray dotted bar, diolein; and black bar, triolein].

temperature, pressure, and loadings of methanol and triolein used for point 4 (Table 1; Figure 2) with methyl oleate yield of 50%. If the increased yield were simply a solubility effect where the triolein solubility in methanol is increased sufficiently to promote reaction, then the presence of an alternative cosolvent to CO_2 should produce comparable yields. While the introduction of a cosolvent to promote the solubility of substrate in the reagent increased yields, it does not fully explain the heightened outcome observed for the CO_2−MeOH system at 80 °C, 9.5 MPa, and 3.6% (v/v) methanol loading. As with carbon dioxide, ethyl acetate to some extent facilitates methanol and triolein interaction within the system. The yield in CO_2−methanol though is still far greater than the ethyl acetate−nitrogen−methanol control, thus CO_2 contributions are unique to the properties of this cosolvent. The increased yields may be due to the presence of dissolved CO_2 in the liquid phase, decreasing mass transfer resistance within the liquid phase and/or to the solid catalyst where the reaction rate will be a function of contact with and transport to the catalyst surface. Other factors could also be in play such as local composition effects of methanol surrounding the substrate[53] or preferential catalyst swelling.[38]

Surface Optimization Model. In order to further optimize the reaction yields, a surface optimization model was generated for the system. The experimental results were fit to a two-level factorial design. Effects associated with interactions were estimated considering the total yield at the high and low values for each factor.[67] From these calculated effect parameters, a regression model was calculated with $n = 7$ variables associated with each of the three factors and four interactions. The model had an R^2 value of 0.75 and is helpful in informing future experimental conditions.

The model suggests that the factor with the largest impact on FAME yield is pressure but that all of the factors and interactions had a significant effect. The significant contribution of all parameters and interactions is not surprising as they all contribute to system density and phase behavior that are closely related and difficult to separate. The results shown in Figure 4 represents the yield of methyl oleate from the transesterification of triolein varying pressure and temperature, while keeping methanol volume constant at the previously optimized level of 3.6% (volume/total reactor volume at ambient conditions).

The surface model indicates that a slight increase in temperature will be able to increase the reaction yield to close to 100%. To validate the model and this finding in particular, the same pressure and methanol loading as the previously identified optimal point was evaluated but with an increased temperature of 95 °C. The resultant yield was 98.3% verifying that the model may inform system yields. This high yield is sufficient to compete with other transesterification techniques and can be used to compare the energy needed for processing in this newly reported system versus previously established supercritical systems employing neat methanol.

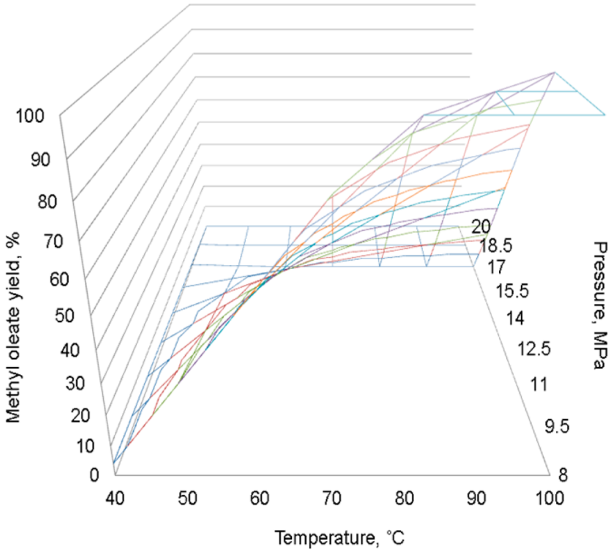


Figure 4. Surface optimization model results for the transesterification of triolein in supercritical carbon dioxide and methanol (high methanol loading condition, 1.8 mL in 50 mL reaction vessel).

■ CONCLUSION

This study provides the groundwork for an efficient process for the transesterification of triglycerides using CO_2, methanol, and a Nafion heterogeneous catalyst at moderate temperatures and pressures. A fundamental approach was taken to understand this system by first ascertaining the fluid phase behavior of the pseudoternary system consisting of a reaction substrate, methanol, and CO_2 (excluding catalyst). The application of a factorial experimental matrix evaluated the impact of reaction temperature, pressure, and methanol loading and provided outcomes that were used to develop a surface optimization model for ideal reaction yields. Employing these calculated optimizations of 9.5 MPa, 95 °C, and 3.6% methanol loading (volume/total reactor volume at ambient conditions), a 98.3% yield of methyl oleate product was realized. The phase behavior at these optimal system conditions consists of three phases: CO_2-rich vapor; methanol-rich, glyceride-poor liquid; and methanol-poor, glyceride-rich liquid. The role of CO_2 in this ternary phase system is proposed to enhance transport between the two liquid phases by decreasing the interfacial tension and viscosity as well as increasing the diffusivity into the solid-phase catalyst thereby enhancing reaction rate and subsequent yield at the fixed reaction time. Results from diolein and monoolein indicate that transesterification of the diglyceride may be the rate-limiting step for this reaction and that substrate properties (i.e., molecular weight, polarity, volatility, boiling point) have significant impact on the reaction yield.

This research has demonstrated the effective transesterification of a single triglyceride, which may come from a number of different biological feedstocks, under moderate temperature and pressure. The next steps for this work would be to investigate the use of mixed TG such as would be found in lipid-rich biological feedstocks that are promising for biodiesel production, i.e., rapeseed, palm, or algae. The extension of this process is toward a one-pot extraction of triglycerides from lipid-rich feedstocks and conversion into biodiesel. Combining supercritical CO_2 extraction of wet biomass[16] with the transesterification shown in this work may be energetically favorable and thus advance achieving sustainably produced biodiesel as indicated by previous life cycle analyses.[7]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tabulated data for Figures 2 and 4 as well results from control experiments related to the impact of mixing speed and elevated pressure with nitrogen substituted for CO_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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