

**Supporting Information for:**

Effect of system conditions for biodiesel production via transesterification using carbon dioxide-methanol mixtures in the presence of a heterogeneous catalyst

Lindsay Soh, Joshua Curry, Eric J. Beckman, and Julie B. Zimmerman

---

This supporting information contains:

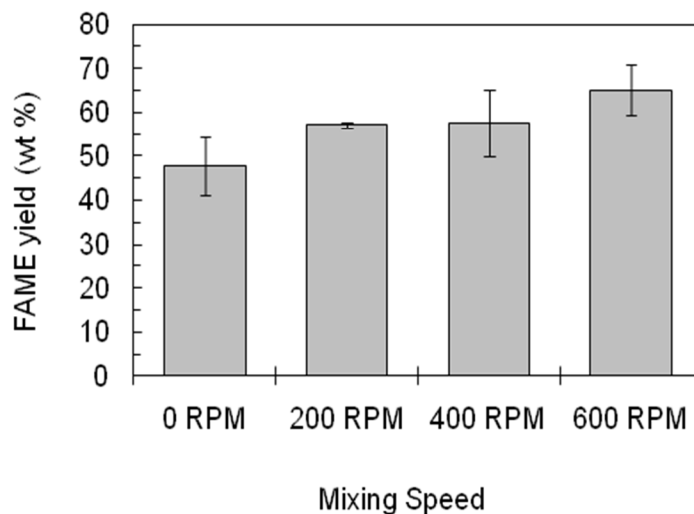
- **Table S1:** Cloud point curve data for oleate species correlating with Figure 2
- **Figure S1:** Effect of stirring speed on FAME yield
- **Table S2:** Data for SC-VL and VL-VLL transition pressure curves for triolein and diolein at 80°C correlating with Figure 4
- **Figure S2:** Triolein-methanol-CO<sub>2</sub> phase behavior
- **Figure S3:** Nitrogen and mixing controls: reaction yield

**Table S1a:** Cloud point curve information correlating with Figure 1 for 9:1 Methanol to Substrate (mol:mol). Error values are based on standard deviation of three measurements.

Weight % Substrate	Cloud Point (MPa)	
Triolein		
0.997	33.90	± 0.87
0.798	30.45	± 0.20
0.599	28.02	± 0.22
0.399	24.36	± 1.05
0.250	17.54	± 1.00
Diolein		
3.335	29.78	± 0.68
2.690	29.76	± 0.69
2.034	29.63	± 0.05
1.367	26.59	± 0.21
0.860	21.58	± 0.25
0.346	8.80	± 0.69
Monoolein		
2.175	55.80	± 0.64
1.570	34.59	± 0.20
0.952	29.37	± 0.25
0.638	26.84	± 0.26
0.321	18.96	± 0.34
Glycerol		
4.00E-02	35.05	± 0.93
3.00E-02	35.28	± 0.54
2.00E-02	31.07	± 0.28
1.50E-02	29.37	± 0.36
1.00E-02	24.45	± 0.38
7.00E-03	20.09	± 1.05

**Table S1b:** Cloud point curve information correlating with Figure 1 for 90:1 Methanol to Substrate (mol:mol). Error values are based on standard deviation of three measurements.

Weight % Substrate	Cloud Point (MPa)	
Triolein		
0.968	29.65	± 0.30
0.779	26.98	± 0.08
0.588	26.06	± 0.25
0.395	24.96	± 0.36
0.248	21.95	± 0.78
0.179	15.97	± 0.53
0.129	11.77	± 0.04
Glycerol		
3.95E-02	33.37	± 0.36
2.97E-02	30.77	± 0.42
1.99E-02	28.29	± 0.11
9.97E-03	26.13	± 0.06
6.98E-03	19.08	± 0.87

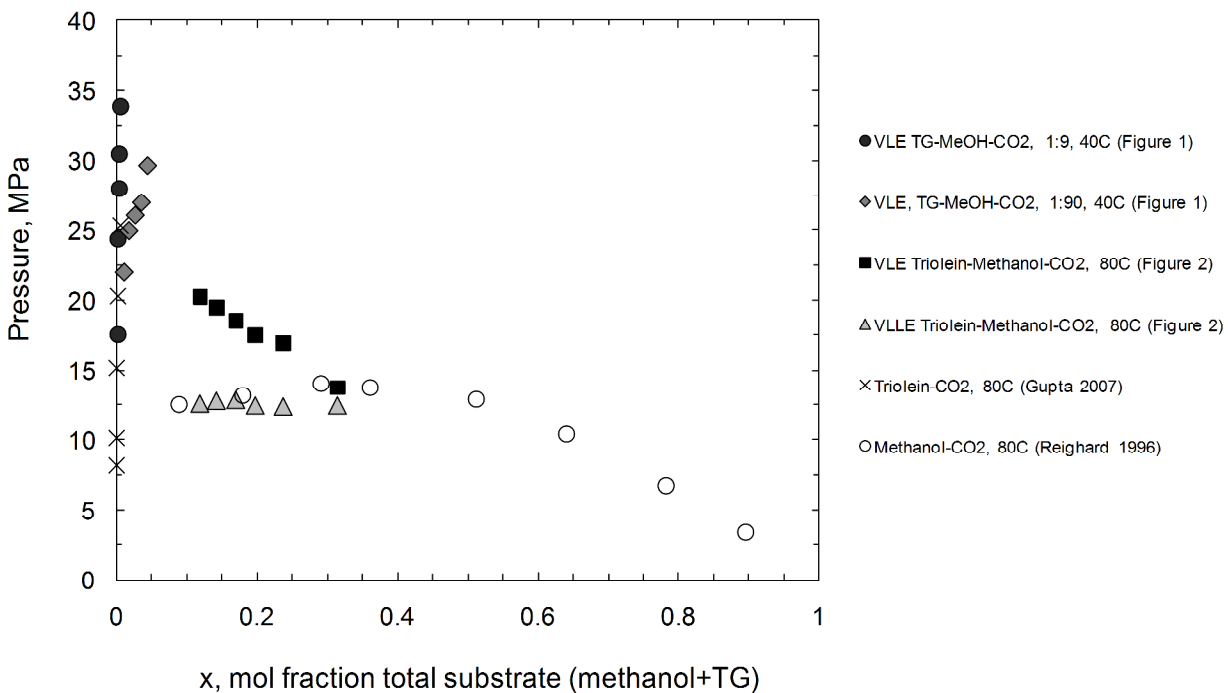


**Figure S1:** Effect of stirring speed on FAME yield using 400 mg triolein, 7.2 mL of methanol, and a catalyst loading of 0.0185 mmol H<sup>+</sup> as Nafion<sup>®</sup>-NR50. Error bars represent the standard error of duplicates.

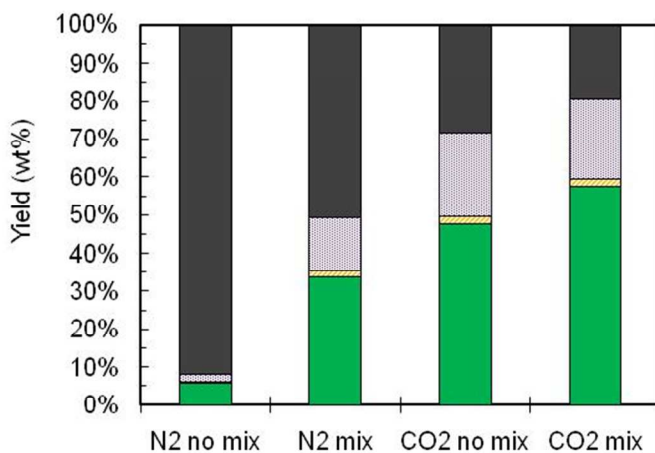
**Table S2:** Data for SC-VL and VL-VLL transition pressures for triolein and diolein at 80°C. (Correlating with Figure 2)

Weight Percent			Cloud Point (MPa)	Bubble Point (MPa)
Triolein	CO <sub>2</sub>	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

Weight Percent			Cloud Point (MPa)	Bubble Point (MPa)
Diolein	CO <sub>2</sub>	Methanol		
0.262	61.475	38.263	16.20 ± n/a	13.79
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
0.262	61.475	38.263	16.20 ± n/a	13.79
0.170	75.067	24.763	15.99 ± 0.06	14.34



**Figure S2:** Triolein-methanol-CO<sub>2</sub> phase behavior (combined data from Figures 1 and 2). Reference data from the binary systems TG-CO<sub>2</sub><sup>1</sup> and Methanol-CO<sub>2</sub><sup>2</sup> has been added as reference for the VLE-VLLE transition pressures.



**Figure S3:** Nitrogen and mixing controls: reaction yield using 400 mg triolein, 7.2 mL of methanol, and a catalyst loading of 0.0185 mmol H<sup>+</sup> as Nafion<sup>®</sup>-NR50. [■ methyl oleate; ▨ monoolein; ▤ diolein; ■ triolein].

## References:

1. Gupta, R.B.S., J.J., *Solubility in Supercritical Carbon Dioxide*. 2007: Taylor & Francis Group, LLC.
2. Reighard, T.S., S.T. Lee, and S.V. Olesik, *Determination of methanol/CO<sub>2</sub> and acetonitrile/CO<sub>2</sub> vapor-liquid phase equilibria using a variable-volume view cell*. *Fluid Phase Equilibria*, 1996. **123**(1-2): p. 215-230.