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Biodiesel Production from Jatropha Curcas, Waste Cooking Oil and Animal Fats under Supercritical Methanol Conditions

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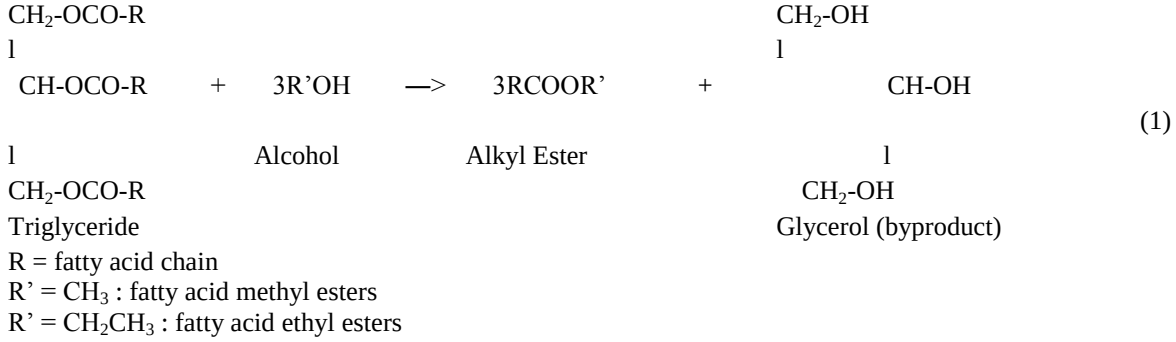
Abstract. In this study, triglycerides of animal fats, Jatropha curcas, and waste cooking oil were used as feedstock for transesterification under supercritical methanol conditions. For waste cooking oil, the fatty acid methyl ester (FAME) yield was >90% at the following reaction conditions: reaction temperature = 300°C and 250 ℃, reaction pressures = 2000 psi, 2500 psi, and 3000 psi, residence time = 18 minutes, and molar ratio of methanol to oil = 40:1. However, when the residence time decreased to 7 minutes, at 250 °C and 2500 psi, the transesterifcation conversion dropped to 86 %. Using a heterogeneous catalyst, ETS-10, the transesterification reaction conditions were lowered to subcritical levels, and a conversion of over 99% was achieved with a residence time of 4 minutes. Because of the short residence times, reduced waste, and high triglyceride conversions, a biodiesel process employing supercritical methanol with a heterogeneous catalyst may present significant economic advantages over the conventional process.

Keywords: Continuous process, supercritical methanol, transesterification.

1. Introduction

As the availability of petroleum-derived diesel fuel slowly decreases, the interest in alternative fuels grows. Biodiesel refers to a vegetable oil or animal fat based fuel consisting of long-chain fatty acid alkyl esters (FAMEs). It is a renewable alternative fuel and has been successfully derived from lipids (vegetable oil or animal fat) and an alcohol as shown in Equation 1.



(1)

Biodiesel is becoming well-known as an environmentally friendly fuel due to its nontoxic and biodegradable characteristics. It has reduced engine emissions of sulfur oxides, carbon dioxide, particulate matter, and aromatic hydrocarbons compared to conventional diesel fuels. Due to federal legislation to promote energy independence (EISA) and the consequent mandates issued by the EPA (in RFS2) requiring the increased production of transportation biofuels, biodiesel has received considerable attention, it appears to be one of the most promising biofuels for meeting the future production volume.

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Transesterification of oils to alkyl esters in supercritical methanol without a catalyst was developed by Saka and Kusdiana [1]-[3]. Supercritical fluids are fluids above their critical temperature and pressure. The supercritical fluid behaves gas-like considering diffusivities but also liquid-like with respect to viscosities. As shown in Figure 1, the critical temperature and critical pressure of methanol are 240^{o}C and 1140 psia, respectively [4].

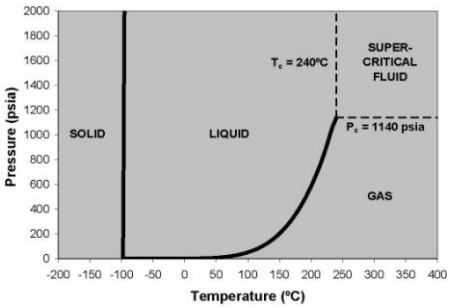

Fig. 1: Supercritical methanol phase diagram.

Nonpolar triglycerides can be well solvated with supercritical methanol to form a single phase oil/alcohol mixture. In addition, the conversion rate of oil into esters increases dramatically in supercritical alcohols, the reaction does not require a catalyst, and it is not affected in the presence of water and free fatty acids.

2. Guide for Author

2.1 Submitting Reactor System

A flowsheet and the continuous transesterification fixed-bed reactor system with supercritical methanol is shown in Fig. 2.

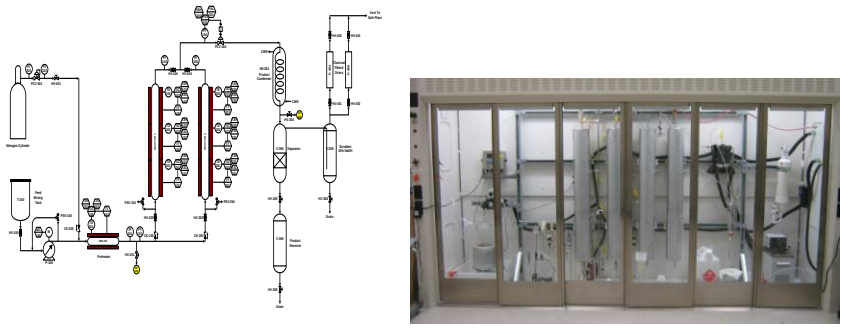

Fig. 2: Process Flow Diagram and the bench unit for biodiesel production with supercritical methanol.

The reactor was constructed from a 3/8" OD x 4' long stainless steel tube with a wall thickness of 0.049 inch, giving a volume of 47.4 mL. The reactor was built with two thermowells welded into the reactor tube and located one third of the way from each end of the reactor. Thermocouples inserted into the thermowells monitored the internal temperature of the chemicals as well as the catalyst temperature. The stainless steel reactor was wrapped with heat tape and insulated inside an aluminum enclosure.

The pressure within the reactor system was recorded with a pressure transducer and regulated with a pressure control valve, both located downstream of the reactor. At the outlet of the pressure controller, the biofuels, the bio-based byproduct, glycerin, and excess methanol were then fed into a condenser and collected in a graduated glass receiver. For safety, pressure relief valves were installed along the reactor and the transfer lines. The process instrumentation was automatically controlled with an i-Fix program. The software allowed for data trending, automatic controls, safety alarms and fail-safe process shutdown.

2.2 Feedstock Preparation

Methanol/waste cooking oil and methanol/Jatropha curcas were prepared in a 40:1 molar ratio, and methanol/pork fat (>200:1 molar ratio). The waste cooking oil (WCO) was filtered first through a 10-micron filter followed by a 0.7-micron filter to remove suspended impurities that could potentially plug the system, particularly the catalyst pores. After combining this filtered WCO with the appropriate amount of methanol based on stoichiometry, the solution was biphasic and thus had to be constantly mixed to maintain a homogeneous consistency while being pumped into the system. The pork fat was in a semisolid state before use, and it therefore had to be heated prior to filtering. The fat was filtered through a 10-micron filter before it was combined with methanol in a 200:1 molar ratio of methanol to pork fat. This molar ratio was increased from the typical 40:1 molar ratio in order to solubilize more of the pork fat in the methanol. The feedstock was biphasic and was mixed constantly.

2.3 Catalysts Preparation Microporous Titanosilicate ETS-10 Catalyst [5]

184.1 g of water and 182.5 g of sodium silicate solution (10.6 wt % Na2O, 26.5 wt % SiO_2) were added to a Teflon beaker and the mixture was stirred. While stirring, 63.2 g NaCl, 12.3 g KF, and 12.3 g TiO_2 were added into the silicate solution producing a translucent thick gel. After the solution was stirred vigorously for 30 minutes at room temperature, the mixture contained in the Teflon beaker was placed into a Parr autoclave and heated to 200 °C for 42 hours. The gel had the composition $5.3SiO_2$:$1.0TiO_2$:$1.6Na_2O$:7.2NaCl:1.0KF or KCl: 110 H_2O, and the pH was around 10.5. The samples obtained were denoted as microporous titanosilicate ETS-10.

Sample ID	Temp.	Pressure,	Flowrate,	Residence	TG (mg/mL)	Triglyceride
	°C	psig	mL/min.	Time, min.	Concentration	Conversion (%)
R8145-8A-033	300	1500	2.78	17.16	33	88.2
R8145-8B-035	300	2500	2.6	18.35	0.34	99.9
R8145-9A-037	250	1500	2.53	18.85	7	97.5
R8145-9B-039	250	2500	2.2	21.68	0.93	99.7
R8145-9C-041	250	3000	2.4	19.88	0.56	99.8
R8145-9D-043	300	3000	2.58	18.49	0.56	99.8
R8145-10A-045	325	1500	2.3	20.74	0.54	99.8
R8145-10B-046	325	2500	2.55	18.71	0.58	99.8
R8145-11A-049	325	1500	2.4	19.88	8.2	97.1
R8145-11B-050	325	2500	2.67	17.87	0.59	99.8
R8145-25A-076	250	2500	4.7	10.15	17	93.9
R8145-25B-077	250	2500	5.57	8.56	26	90.7
R8145-25C-078	250	2500	7	6.81	38	86.4

2.4 Analytical Methods

Direct measurement of triglycerides present in the converted product samples were accomplished using high performance liquid chromatography (HPLC) coupled with an evaporative light scattering detector (ELSD). By analyzing feedstock and product samples, a triglyceride conversion rate was determined. The analytical method was developed on a Waters HPLC system model LC03, utilizing a 600E pump, 717 autosampler and an Alltech 2000 ELSD. A Supleco brand analytical column (part number Supelcosil LC-18-DB, 150 mm x 4.6 mm.) was chosen for the resolution of the triglycerides present in the samples.

2.5 Results and Discussion

2.5.1. Transesterification of WCO under supercritical methanol conditions

The results of transesterification of WCO with SCM (> 240 °C/1140 psig) are tabulated in Table 1. The results show that high conversions of triglyceride into fatty acid methyl esters (FAMEs) with SCM are consistently achievable on a continuous basis with reaction conditions in the supercritical region for

methanol: temperature ranges 250 – 325 °C and pressure ranges 1500 – 3000 psig at a feedstock flow rate of 2.5 mL/min.

However, as shown in figure 4, the conversion dropped to 86.4% when the flow rate increased from 2.2 mL/min (residence time 21.68 min) to 6.81 mL/min (residence time 6.96 min), which indicates that triglyceride conversion is directly dependent on the contact time of the triglyceride with methanol (MeOH).

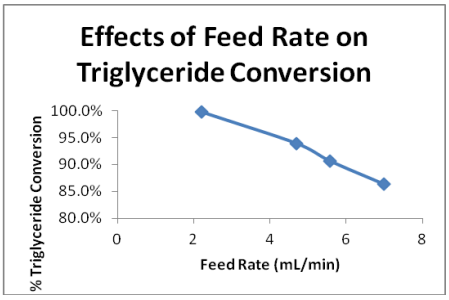

Fig. 4: Effects of feed rate on Triglyceride Conversion

2.6 Transesterification of animal fat under supercritical methanol conditions

Table 2 shows the transesterification results of animal fat with SCM where high conversions were achieved with temperature in the range of 250 °C – 300 °C incorporated with pressure in the range of 2000 psig – 3000 psig. The Eldex pump was not able to perform with higher concentrations of pork fat due to associated plugging problems of the highly viscous feedstock.

Table 2. Pork Fat Biodiesel Conversion with Supercritical Methanol (SCM).

Sample ID	Temp.	Pressure,	Flowrate,	Residence	TG (mg/mL)	% Conversion
	°C	psig	mL/min.	Time, min.	Concentration	
R8145-13A-051	300	2000	2.93	16.28	2	**96.4**
R8145-13B-053	300	2500	2.8	17.04	0.75	**98.6**
R8145-14A-055	300	3000	2.6	18.35	0.05	**99.9**
R8145-14B-056	250	2500	2.87	16.62	0.04	**99.9**
R8145-14C-057	250	3000	2.5	19.08	0.16	**99.7**

2.7 Transesterification of Jatropha curcas under supercritical methanol conditions

Table 3 shows the transesterification results of Jatropha curcas oil with SCM at 250 °C incorporated with pressure in the range of 2000 psig – 2500 psig. The conversions of triglyceride at an initial concentration of 360 mg/mL (98.6% of triglyceride in oil) to FAMEs obtained were >99% and the major FAMEs compounds were methyl esters of palmitic acid, steric acid, oleic acid, and linoleic acid.

Table 3. Jatropha curcas Biodiesel Conversion with Supercritical Methanol (SCM).

Sample ID	Temp.	Pressure,	Flowrate,	Residence	TG (mg/mL)	% Conversion
	°C	psig	mL/min.	Time, min.	Concentration	
R8145-31A	250	2000	3.00	15.00	0.72	**99.8**
R8145-31B	250	2000	3.00	15.00	0.73	**99.8**
R8145-32A	300	2500	3.60	13.17	1.08	**99.7**
R8145-32B	300	2500	3.60	13.17	1.05	**99.7**
R8145-32C	300	2500	3.60	13.17	1.06	**99.7**

2.8 Effect of catalyst at low reaction residence times

At 250 °C/2500 psig/flowrate 6.8 mL/min., the transesterification of WCO into FAMES was low as cited in Table 1 (86.4% conversion). Under the same conditions, 250 °C/2500 psig/flowrate 6.8 mL/min., the transesterification of WCO to FAMEs with SCM dropped in the range of 36.5% -58.6 % in the 12 hour,

nonstop experiment as shown in Figure 5. These reaction parameters were selected to the effect of the presence of a solid catalys by comparing the WCO transesterification activity with SCM/catalyst to SCM without catalyst. The reactor was packed with ETS-10 Catalyst and operated for twenty-four hours with SCM. Figure 5 shows that the conversion efficiency with catalytic remained active throughout 24 hours of experiment, conversion is consistently achieving >99% with a residence time of 4 minutes.

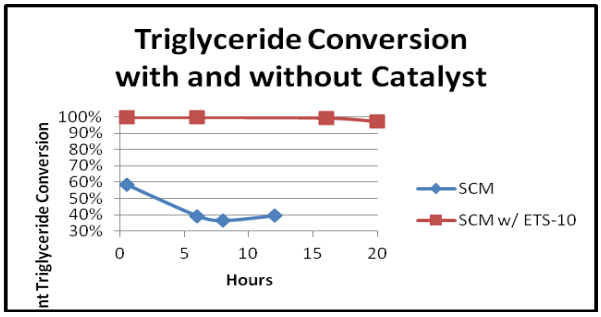

Fig. 5: The effect of a solid catalyst on triglyceride conversion under SCM conditions.

3. Conclusion

Biodiesel production with continuous SCM processing of waste cooking oil and animal fats has been successfully demonstrated in lab scale in our study. Presence of a solid catalyst dramatically improves triglyceride conversion at low reaction residence times. Development of a continuous SCM biodiesel process on a pilot-plant scale is in progress at Southwest Research Institute.

4. Acknowledgement

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5. References

[1] D. Kusdiana, S. Saka, *Effects of water on biodiesel fuel production by supercritical treatment*, Bioresour. Technol., 2004, 91, pp. 289-295.

[2] D. Kusdiana and S. Saka, *Kinetics of transesterification in rapeseed oil to biodiesel fuels as treated in supercritical methanol*, Fuel, 2001, 80a, pp. 693-698.

[3] D. Kusdiana and S. Saka, *Methyl esterification of free fatty acids of rapeseed oil as treated in supercritical methanol*, Chem. Eng. Jpn., 2001, 34 b, pp. 383-387.

[4] R.E. Babcock, E.C. Clausen, M. Popp, W. B. Schulte, *Yield Characteristics of Biodiesel Produced from chicken fat-tall oil blended feedstocks*, http://ww2.mackblakwell.org/web/research/all_research-projects, 2012.

[5] X. Yang, J.-L. Paillaud, H.F.W.J. van Breukelen, H. Kessler, E. Duprey, "*Synthesis of microporous titanisilicate ETS-10 with TiF4 or TiO2,"* Microporous and Mesoporous Materials 2001, **46**, pp. 1-11.