

5-2011

# Biodiesel production from waste algae through supercritical methanol and solid catalysts

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## Recommended Citation

Lopez, Alexander, "Biodiesel production from waste algae through supercritical methanol and solid catalysts" (2011). *Chemical Engineering Undergraduate Honors Theses*. 26.  
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Biodiesel Production from Waste Algae through Supercritical Methanol and Solid Catalysts

An Undergraduate Honors College Thesis

in the

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College of Engineering  
University of Arkansas  
Fayetteville, AR

by  
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4/29/2011

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# INTRODUCTION

## Biodiesel as an Energy Source

The need for alternate fuels continues to rise as fossil fuel reserves decline, and the effects of harmful fuel emissions on the environment begin to take its toll. One alternate fuel that has great potential is biodiesel. Biodiesel is a non-petroleum based fuel composed of alkyl esters from feedstocks. Using biodiesel as an alternate fuel source has a variety of advantages over traditional petroleum diesel, including producing no SO<sub>x</sub> emissions and low CO<sub>x</sub> emissions<sup>1</sup>. Another important advantage of biodiesel is that it can be produced from a wide variety of feedstocks. Biodiesel processes using waste cooking oil, animal fats, and other materials have been developed, but the technology to convert indigenous algae into biodiesel possesses great research potential.

Biodiesel also possesses a number of advantages over ethanol. Ethanol contains 26.8 MJ/kg fuel while biodiesel contains 37.47 GJ/kg fuel<sup>2,3</sup>. The higher energy content in biodiesel results in greater transportation mileage. Biodiesel also has a higher octane and cetane number over ethanol. Ethanol production involves a costly distillation process that removes water from fermented ethanol broth. Both biodiesel and ethanol contain oxygen which aides in the combustion process, resulting in a cleaner burning engine. However, biodiesel does have its limitations. Its higher viscosity and cloud point over petro-diesel has the potential to cause severe engine wear in cold weather if left untreated<sup>4</sup>. In addition biodiesel only contains approximately 80% of the energy content per mass found in petro-diesel.

## Algae as a Feedstock

Algae are a fast-growing feedstock that offers continual harvesting, resulting in lower land requirements than most feedstocks (including ethanol from corn) used today. Algae are one of the most efficient ways of converting sunlight, atmospheric CO<sub>2</sub> and little soil nutrients (nitrogen and phosphorous) into fuel feedstock. Using algae also avoids competing with food production since algae can grow on marginal land unsuitable for crop production. Algae contain carbohydrates and oils capable of being converted into biofuels. Carbohydrates are converted into ethanol or butanol while algae oils are converted into biodiesel.

Algae contain several advantages over other feedstocks such as corn, switch grass and soybeans. The greatest advantage is biodiesel production from algae results in a net decrease in CO<sub>2</sub> in our atmosphere. This means producing biodiesel will help remove greenhouse gases from our air. Algae also possess lower nutrient requirements over many feedstocks in order to grow.

### HOW GREEN ARE BIOFUELS?

Biofuels are getting a bad rap as stories of rising food prices and shortages fill the news. But the environmental, energy and land use impacts of the crops used to make the fuels vary dramatically. Current fuel sources – corn, soybeans and canola – are more harmful than alternatives that are under development.

CROP	USED TO PRODUCE	GREENHOUSE GAS EMISSIONS* Kilograms of carbon dioxide created per mega joule of energy produced	USE OF RESOURCES DURING GROWING, HARVESTING AND REFINING OF FUEL				PERCENT OF EXISTING U.S. CROP LAND NEEDED TO PRODUCE ENOUGH FUEL TO MEET HALF OF U.S. DEMAND	PROS AND CONS
			WATER	FERTILIZER	PESTICIDE	ENERGY		
Corn	Ethanol	81-85	high	high	high	high	157%-262%	Technology ready and relatively cheap, reduces food supply
Sugar cane	Ethanol	4-12	high	high	med	med	46-57	Technology ready, limited as to where will grow
Switch grass	Ethanol	-24	med-low	low	low	low	60-108	Won't compete with food crops, technology not ready
Wood residue	Ethanol, biodiesel	N/A	med	low	low	low	150-250	Uses timber waste and other debris, technology not fully ready
Soybeans	Biodiesel	49	high	low-med	med	med-low	180-240	Technology ready, reduces food supply
Rapeseed, canola	Biodiesel	37	high	med	med	med-low	30	Technology ready, reduces food supply
Algae	Biodiesel	-183	med	low	low	high	1-2	Potential for huge production levels, technology not ready

\* Emissions produced during the growing, harvesting, refining and burning of fuel. Gasoline is 94, diesel is 83.

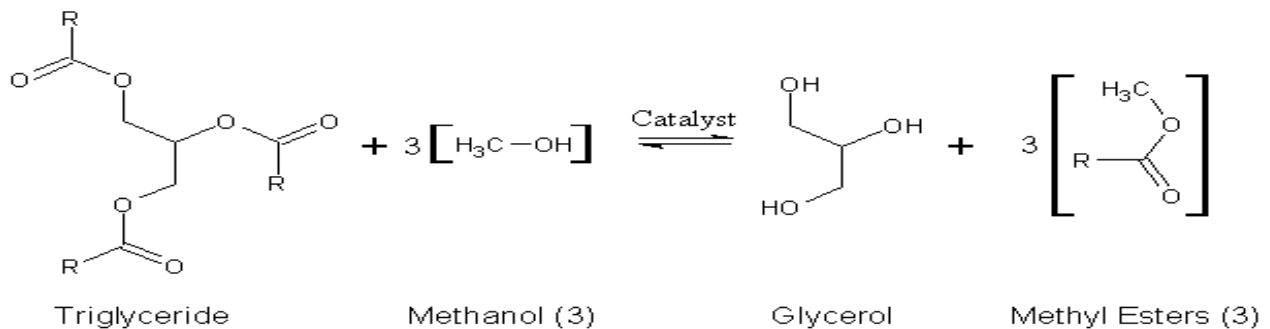
Source: Martha Groom, University of Washington; Elizabeth Gray, The Nature Conservancy; Patricia Townsend, University of Washington; as published in Conservation Biology

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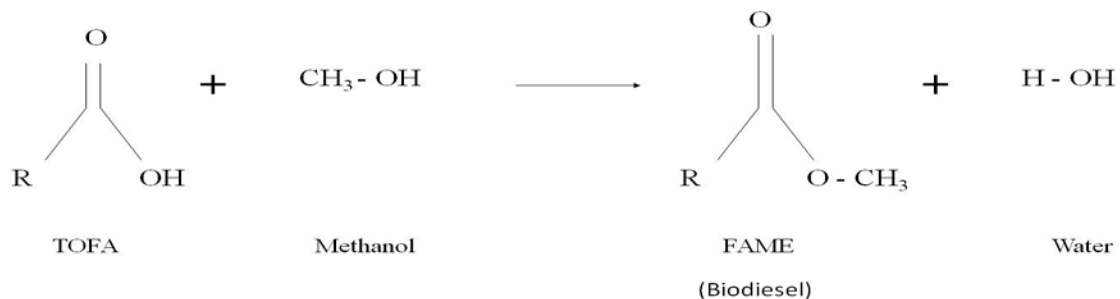
Figure 1. Feedstock comparison for ethanol and biodiesel production.<sup>5</sup>

## Biodiesel Reaction Chemistry

Biodiesel is generally created from two chemical reactions, esterification and transesterification. Other pathways, pyrolysis and micro-emulsions, are economically unfeasible<sup>4</sup>. Esterification occurs when fatty acids found in vegetable oils and animal fats are dehydrated by methanol and heat into fatty acid methyl esters (FAME) with water as a by-product. Transesterification occurs when triglyceride molecules react with methanol under high temperatures and the presence of a base catalyst causing the triglyceride molecules to break down into diglycerides, monoglycerides, and methyl esters. Byproducts of transesterification include unconverted glycerides along with glycerol. Glycerol byproducts can be sold for use in soap and cosmetic production<sup>4,5</sup>. The chemical reaction pathways are shown in figures 2 and 3.



**Figure 2.** Transeserification Reaction Pathway



**Figure 3.** Esterification Reaction Pathway

## **MATERIALS AND METHODS**

Preliminary studies focused on free fatty acid (FFA) conversion from tall oil and triglyceride conversion from vegetable oil. The following procedures were used to conduct algae oil extraction, lipid transesterification to FAME, and FAME analysis. The titration procedure was used when analyzing FAME samples from tall oil FFA's. The overall %FFA conversion was analogous to %FAME production, so this procedure was used until a suitable gas chromatography procedure was developed.

### **Algal Oil Extraction**

Algae was obtained from a local turf-scrubber system and collected periodically to run oil extraction. Samples were weighed placed under a fume hood to dry overnight. Once the samples were sufficiently dry, the sample was weighed and then placed in a blender with approximately 250 mL of hexane. The mixture was blended and allowed to sit for 5 min. then blended again. The resulting mixture was filtered to separate out the residue algae from the hexane and oil. A Turbovap 500 solvent concentrator system was used to distill out the hexane and the residual oil was collected and weighed to determine the percent oil in algae on a dry and wet basis.

### **Supercritical Methanol Reaction**

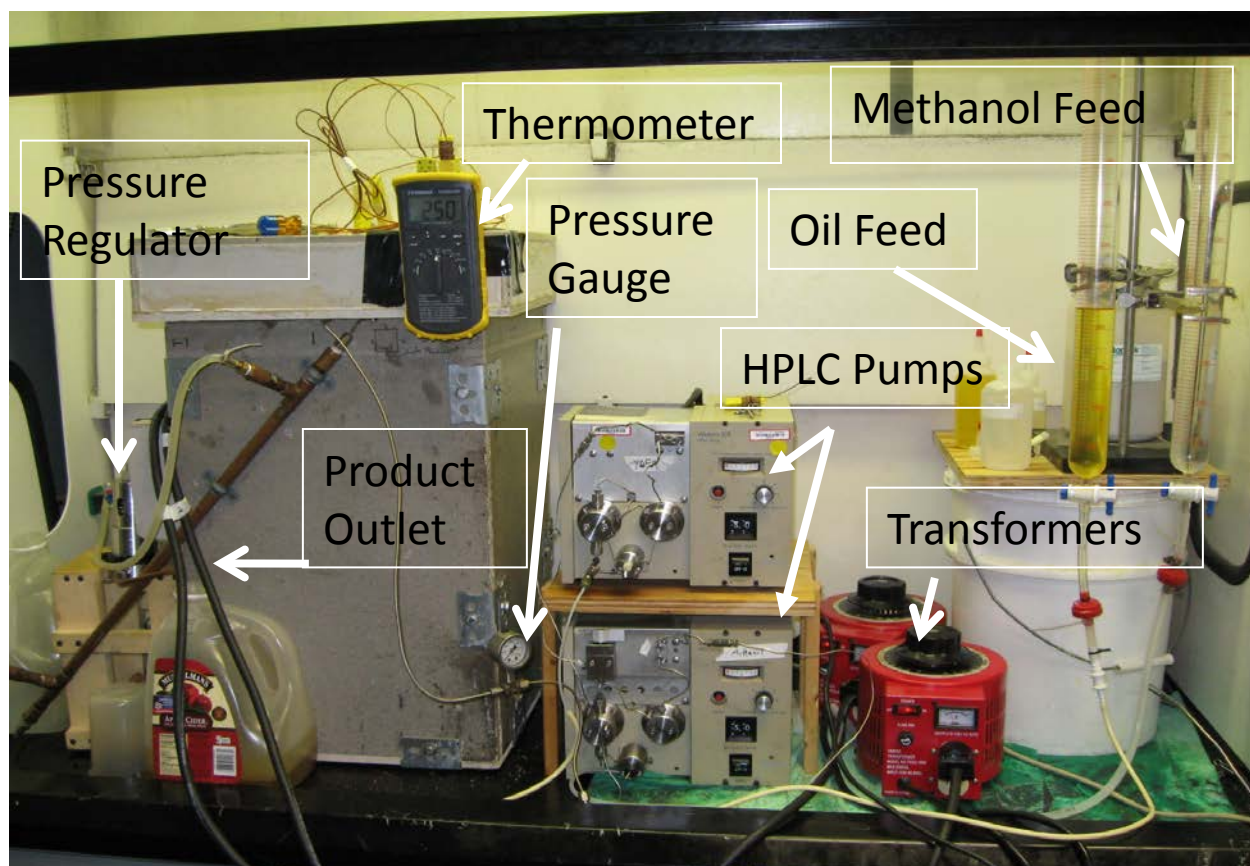
In this study, the continuous production of FAME product was observed through the reaction of algae oils with supercritical methanol. Methanol and oil flow from their respective reservoirs through separate HPLC pumps into a single, coiled plug flow reactor. The fluid reservoirs are 500 mL graduated cylinders so that the volumetric flow rate can be controlled and

recorded via stop watch. The mixture is then heated through a sand bath and vermiculite insulation using four strip heaters connected to two variable voltage transformers. Reactor temperature is monitored using three thermocouples. Two monitor sand temperature at different distances from the strip heaters. The third monitors the reactor exit temperature. The reactor product then flows through a double pipe heat exchanger to quench the mixture to prevent further reaction. A backpressure regulator is affixed to the end of the system to control reactor pressure. Reaction pressure is monitored at the inlet and outlet of the reactor using pressure gauges. Product collection occurs after the backpressure regulator. Table 1 highlights specific pieces of equipment. Figure 4 display this experimental set-up.

**Table 1.** Research Major Equipment List

<b>Equipment Name</b>	<b>Specifications</b>
Back Pressure Regulator	Tescom 26-1723-24-090
HPLC Pumps	Waters 501
Reactor tubing	316 SS, 1/8 in., 0.031 in. wall thickness, 18 mL volume
Methanol	HPLC Grade, JT Baker (obtained from VWR # JT9093-3)
Gas Chromatograph	Hewlett Packard 6890 series with FID
Chromatograph Column	50 m SGE BPX-70 (70% cyanopropyl polysilphenylene-siloxane) capillary column





**Figure 4.** Supercritical Biodiesel Reactor Experimental Apparatus.

The reactor start up consisted of setting the variac transformers to 70 V for one hour as the cooling water valve was opened. Once the thermometer read within 30 °C of the desired temperature set point, the oil and methanol reservoirs were filled. The HPLC feed pumps were set at a low flowrate (< 2mL/min.) and the flowrate was measured using a stop watch to ensure the pumps are working properly. Once the pumps were working the flowrates were increased to the experimental value. The pressure regulator was adjusted to bring the system pressure up to the desired value. The system was allowed to operate until steady state was achieved at the desired experimental temperature, pressure, and feed flowrates.

At steady state, a collection vial was placed in the effluent outlet and the volume of the oil and methanol feeds were recorded. The vial collected 2 reactor volumes (approximately 40 minutes). Once the vial was filled, it was removed and the final volumes of the oil and methanol feeds were recorded. A stop watch was used during the length of the sample collection in order to gain a precise flowrate measurement for both feed pumps. A secondary sample was collected for each experimental condition in order to determine sample precision.

Once experimentation was complete, the heaters were shut off and methanol was flowed through both pumps for at least 1 hour to clean out the pumps and system. Once the system was sufficiently clean, the pressure regulator was slowly loosened to depressurize the system. The pumps were then shut off and the cooling water valve was closed.

### **Gas Chromatography Analysis**

This procedure describes the settings used during gas chromatography. FAME standards and samples used this procedure, and the resulting data was compared using relative peak areas. The Collected FAME samples were analyzed through gas chromatography in concentrations of 0.1 mL of reactor effluent mixed with 4.9 mL of acetone. The samples were injected at 250 °C. The oven began each run at 100 °C and held that temperature for 10 min. This allowed the acetone solvent to separate from the FAME being analyzed. A temperature ramp of 10 °C/min. occurred for 5 min. ending at 150 °C. Next the temperature ramp changed to 5 °C/min. for 20 minutes ending at 250 °C. This temperature was held for 30 min in order to push out any contaminants in the sample. The FID detector was set at 300 °C.

## Titration Analytical Procedure

This titration procedure was used to analyze tall oil samples for remaining % FFA content. This data was compared to gas chromatography analysis to determine which method was more suitable for FAME analysis. Small samples (1-5 g) were weight in an Erlenmeyer flask. 50 mL of 50/50 isopropyl alcohol and acetone were added to the flask. A few drops of phenolphthalein pH indicator were then added. Next 1 N KOH was titrated into the mixture one drop at a time until the mixture began to form a pink color that remained after the solution was sufficiently mixed. The volume of titrant added was then recorded and %FFA was calculated using equation 1. FAME production was determined be % FFA easily due to the tall oil reactant consisted of 100% FFA.

$$\% FFA = \frac{mL \text{ titrant} * KOH \text{ normality} * 28.25}{\text{sample mass (grams)}} \quad (1)$$

## RESULTS AND DISCUSSION

### Vegetable Oil Trials

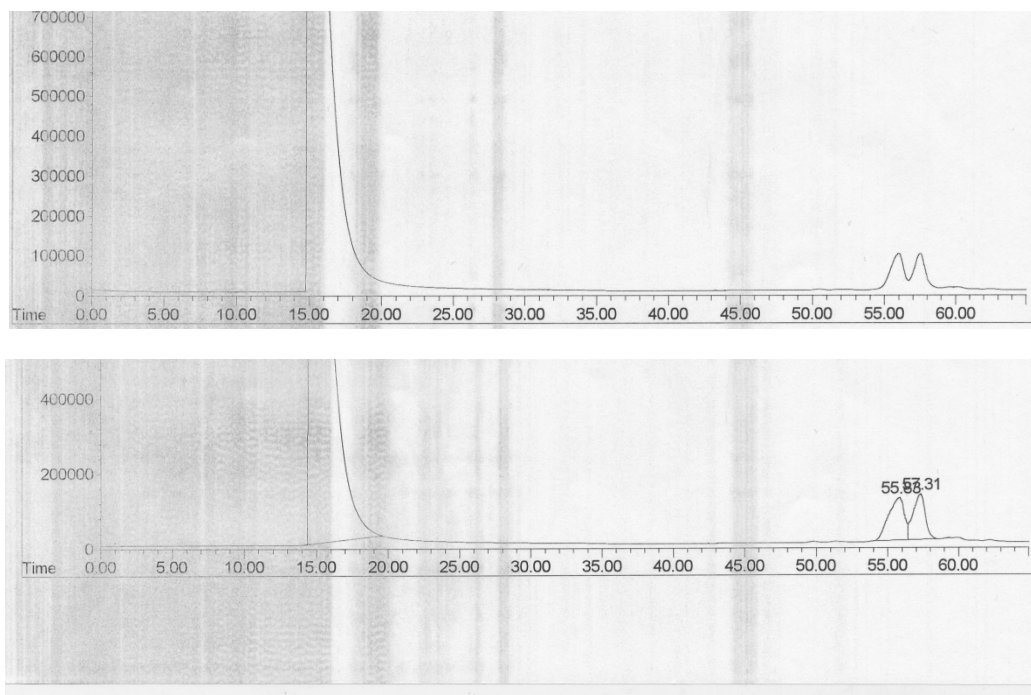
Vegetable oil experimentation with solid catalysts resulted in varied FAME production; however, 86% conversion was achieved in one experimental case. Supercritical methanol experimentation is currently under investigation. Preliminary results show that supercritical methanol reaction pathway is superior to previous work in solid catalysts due to less waste, continual processing, and greater reaction control. Table 2 shows the results from vegetable oil experimentation with solid catalysts. Solid catalysts used were ion exchange resins (acid and base).

**Table 2.** Vegetable Oil Experimental Results

Sample #	Reaction Temperature (°C)	Reaction Pressure (psig)	Reaction Time (min.)	Triglyceride % Conversion to FAME
1	60	0	60	0.34
2	60	0	60	86.17
3	60	0	60	1.12
4	60	0	60	NA*

## Tall Oil Trials

Tall oil experimentation with solid catalysts resulted in low FFA conversion (< 50%). Supercritical methanol experimentation resulted in higher FFA conversion rates (ranging from 60-90%). Also, temperature played a significant role in FAME production with additional experimentation resulting in conversion rates above 90% with temperatures above 300 °C. Figure 5 shows the results from chromatography of FAME samples. The large peak that appeared after 15 minutes is simple the acetone solvent reaching the detector. The two smaller peaks appearing after 55 minutes are two methyl esters produced from experimentation. Sample peak area was compared to peak areas of known FAME standards to determine percent FFA conversion. Table 3 represents sample data comparing solid catalyst experimentation (1 & 2) to supercritical methanol experimentation (3 & 4).



**Figure 5.** GC Results for FFA Esterification.

**Table 3.** Tall Oil Experimental Results

Sample #	Reaction Temperature (°C)	Reaction Pressure (psig)	Reaction Time (min.)	FFA % Conversion to FAME
1	60	0	60	33.25
2	60	0	60	24.27
3	240	1500	20	65.96
4	292	1500	20	86.89

### Algae Oil Trials

The algae oil experimentation is still in progress. Algae oil extraction is proving difficult due to the low concentrations of lipids present in the algae currently supplied. Another algae species containing higher lipid concentrations would be ideal for this experimentation. Results will be presented once experimentation and analysis is complete.

## CONCLUSIONS AND RECOMMENDATIONS

In order to develop a sustainable biofuel that minimizes SO<sub>x</sub>, CO<sub>x</sub>, and NO<sub>x</sub> emissions, research in biodiesel production utilizing research has been conducted to analyze the feasibility of generating biodiesel from algal feedstocks utilizing a supercritical methanol procedure and solid catalysts. Current research has developed a reaction procedure for continuous conversion of algal oil feedstock into biodiesel using supercritical methanol. This reaction procedure is currently in progress of being tested with algae oil. A small scale reactor has been designed and built in order to reduce the amount of reactants used in testing. Methods of algal oil extraction have also been explored. Gas chromatography has been used to analyze reaction samples to determine the production levels of FAME's generated from the biodiesel reactor. Future work will consist of identifying an ideal strain of algae with a high lipid content, design of oil extraction system to maximize oil production, and a scale-up of the supercritical methanol operation to maximize biodiesel production.

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