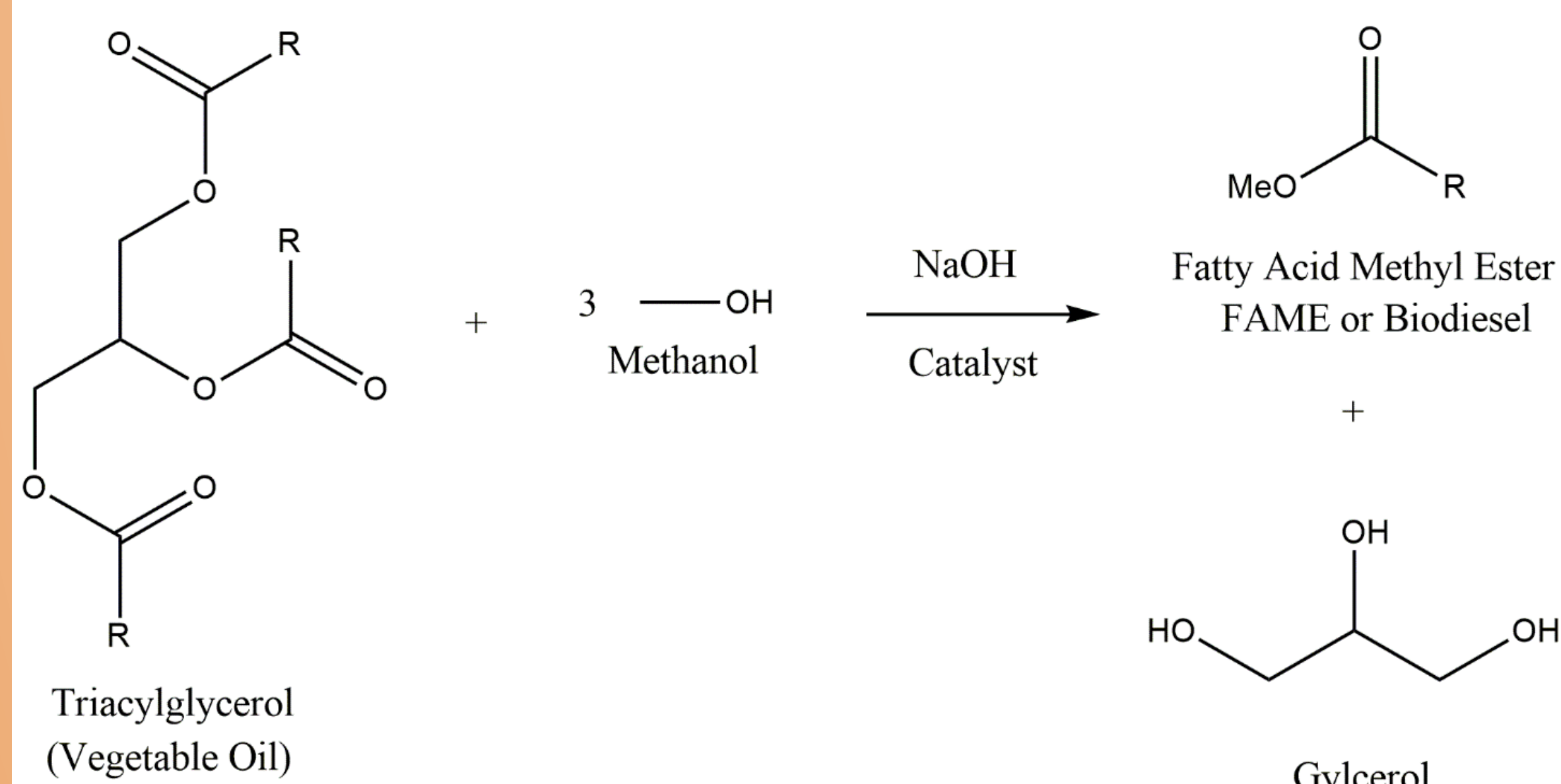


## Introduction

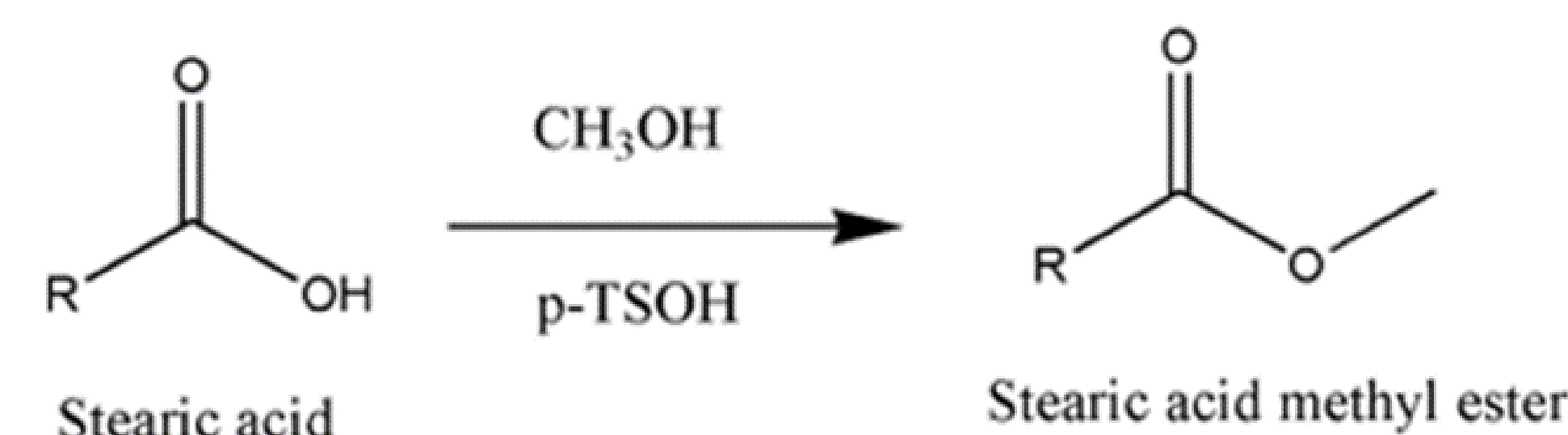
Globally, countries across the world depend on crude oil and its by-products as a result of cracking, to effectively power equipment such as diesel engines in cars, trucks, boats, and trains. Because of environmental concerns and possible political instability across the Middle East region where most of the world's crude oil deposits are located, scientists are looking at other alternative forms of fuel to usurp the production and use of crude oil and its by-products. One search alternative is the use of biodiesel. With the new energy legislation implemented in Europe, the global production of biodiesel has dramatically increased in the last few years. Other countries such as Canada, Australia, U.S.A., and Japan, have also adopted policies that will mean higher biofuels production over the next decade<sup>(3)</sup>. Nicknamed the "Green" fuel, biodiesel is principally derived from biological sources such as vegetable oils and animal fats. For example, most of the biodiesel produced in the United States comes from plant oils such as soybean and corn oil. Some of the advantages associated with the use of biodiesel as an alternative to petroleum diesel include reduced emissions of unburned hydrocarbons and limited emissions of greenhouse gases such as carbon monoxide and nitrous oxide. In addition, biodiesel is considered to be renewable and relatively non-toxic. Biodiesel can be used as a complete replacement (B100) for petrodiesel, or it can be used in blends of biodiesel with petrodiesel (B2 - B80). B2 is a 2% biodiesel and 98% petrodiesel mixture. It is used as an additive to petrodiesel in as low as 1% to improve the lubricity of petrodiesel to acceptable levels<sup>(1)</sup>.

## Formation of Biodiesel



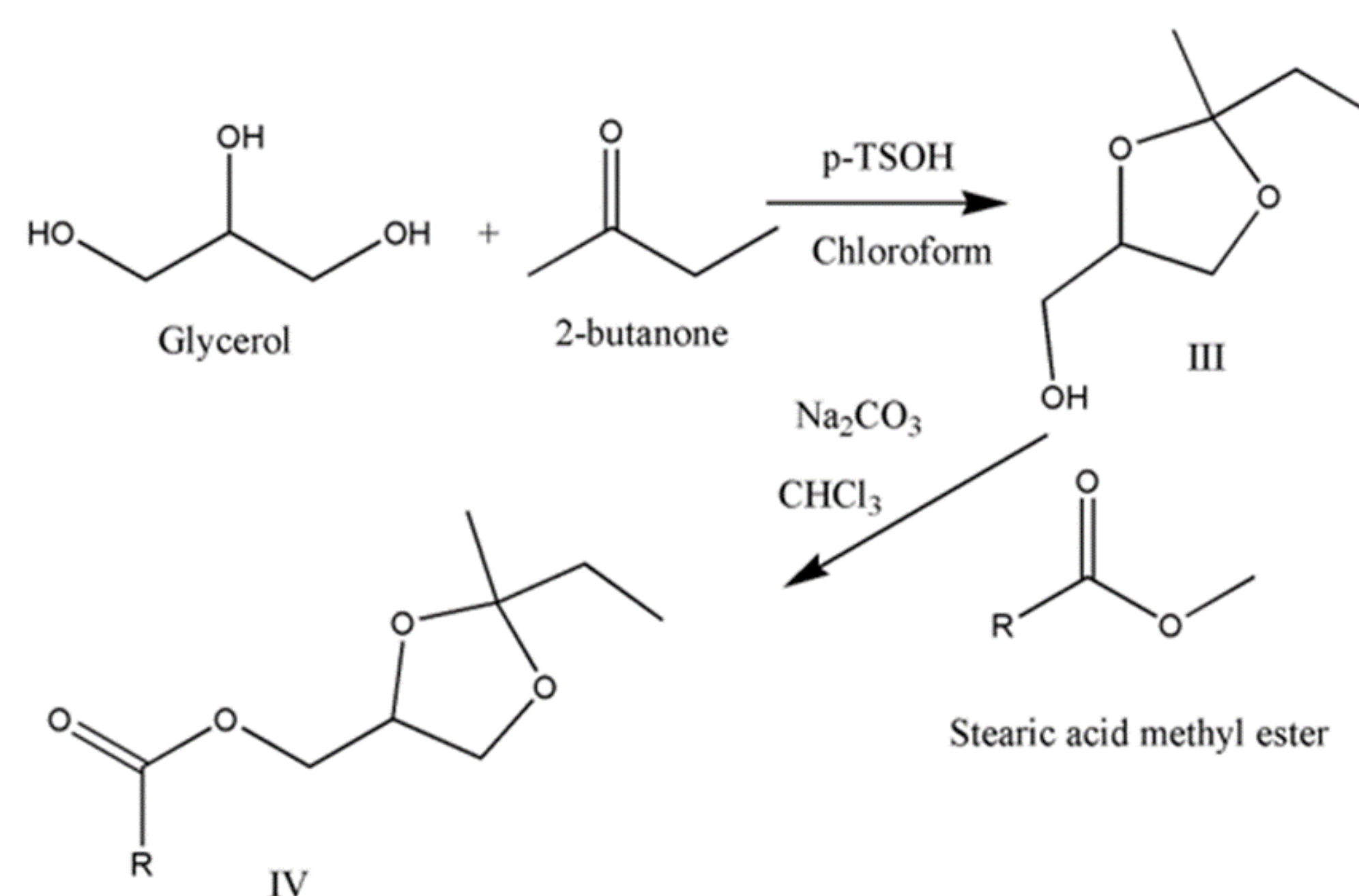
Conversion of vegetable oil such as soybean oil to biodiesel involves a process known as **transesterification**. Transesterification is a reaction that converts one type of ester into another. Vegetable oils and animal fats contain a variety of fatty acid esters which can be converted to methyl esters with methanol in the presence of a base catalyst such as sodium hydroxide or potassium hydroxide. The "R" on the chemical structure represents a hydrocarbon chain containing only carbons and hydrogens. Typically, for triglycerides, the R groups are 10 to 20 carbons long. A major by-product of the transesterification reaction is glycerol. Glycerol (1,2,3-propanetriol) is a viscous and polar substance that has long been known for its useful properties. In the polymer industry, glycerol is added as a stabilizer, plasticizer, and co-solvent in emulsion polymerization. Glycerol is an important raw material for the synthesis of several valuable compounds. It was used as the basis for the first production of alkyd resins while its partial fatty acid esters, the mono and diesters of palmitic and stearic acids, have been widely employed as emulsifiers in processed foods. Besides being the basis for nitroglycerin, which also finds application as a medicinal drug, glycerol is transformed in glycerol carbonate which is an intermediate in chemical synthesis and used as a gelation agent, in polyglycerols which are used in cosmetics and in medical applications<sup>(2)</sup>.

## Project Description



The focus of this research project was three-fold; one, determining the optimal conditions necessary for the synthesis of biodiesel as a result of the transesterification reaction involving vegetable oil, methanol, and NaOH (catalyst) in a series of specific reaction runs (small scale and large scale); secondly, preparation and characterization of ketal esters of glycerol following the reaction between glycerol, a variety of ketones (acetone, butanone, pentanone, and cyclohexanone), p-toluenesulfonic acid (catalyst) and chloroform; thirdly, transesterification reaction involving ketal esters isolated with a mixture of methyl esters derived from a variety of fatty acids including palmitic (hexadecenoic), oleic (9-cis-octadecenoic), and stearic (octadecanoic) acids in the presence of anhydrous sodium carbonate to generate the desired product. Characterization and material properties of the target products involved FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, flash point test, methanol test, mass, volume, and density measurements. Furthermore, the biodiesel formation and testing was incorporated into workshops hosted on UF's campus for STEM middle and high school teachers.

## Formation of Fuel Additive



While production of biodiesel receives more attention, conversion of the waste glycerol into a valuable fuel additive was also explored. This was accomplished by reaction of ketones (e.g., butanone) with p-toluenesulfonic acid. The subsequent ketal (III) was then transesterified with the methyl ester of natural fatty acids to form the target additive (IV).

## Results

Trials	Condition	Time (hrs)	Temperature (°C)	Reactants			Products				
				Veg. Oil (ml)	CH <sub>3</sub> OH (ml)	NaOH (g)	Volume (ml)	Mass (g)	Density (g/ml)	CH <sub>3</sub> OH Test (ml)	% Conversion
1	Run	0.50	40.0	100.00	20.00	0.35	84.00	72.1989	0.8595	0.30	70.00
2	Run	0.25	40.0	100.00	20.00	0.35	83.00	71.6353	0.8631	0.40	60.00
3	Run	24.00	In and out 40	100.00	20.00	0.35	86.00	74.2254	0.8631	0.10	90.00
4	Run	24.00	40.0	100.00	20.00	0.35	84.00	78.6569	0.8368	0.49	51.00
5	Run	48.00	40.0	100.00	20.00	0.35	88.00	75.7671	0.8610	0.05	95.00
6	Run	24.00	50.0	100.00	20.00	0.35	88.00	75.7665	0.8610	0.70	30.00
7	Run	48.00	50.0	100.00	20.00	0.35	93.00	80.1100	0.8614	0.40	60.00
8	Run	24.00	Room temperature	100.00	20.00	0.35	100.00	86.4221	0.8642	0.25	75.00
9	Run	48.00	Room temperature	100.00	20.00	0.35	79.00	66.5195	0.8420	0.40	60.00
10	Run	48.00	Room temperature	100.00	20.00	0.35	70.00	60.6195	0.8660	0.50	50.00
11	Reflux as lit.	3.00	50.0	10.00	100.00	0.10	49.00	71.6353	0.8631	0.10	90.00
12	Reflux	4.00	50.0	10.00	100.00	0.10	1.80	1.3988	0.7771	0.00	100.00
13	Reflux	3.00	50.0	10.00	100.00	0.10	1.30	0.9790	0.7531	0.00	100.00

Note: For the reflux reactions, KOH was the catalyst used.

Table 5: Small Scale Biodiesel Synthesis

Run	Time (hrs)	Temperature (°C)	Reactants			Product				
			Waste Oil (ml)	CH <sub>3</sub> OH (ml)	NaOH (g)	Volume (ml)	Mass (g)	Density (g/ml)	CH <sub>3</sub> OH Test (ml)	% Conversion
1	2	35.0	500.00	100.00	3.339	500.00	438.53	0.8771	0.05	95.00
2	24	40.0	500.00	100.00	3.339	500.00	414.46	0.8289	0.10	90.00
3	24	Room Temperature	1000.00	200.00	6.678	1000.00	879.74	0.8797	0.08	92.00
4	24	Room Temperature	2000.00	400.00	13.356	1850.00	1595.32	0.8623	0.00	100.00

Table 6: Large Scale Biodiesel Synthesis

Glycerol (g)	Ketone (ml)	Reactants		Ketal Products	
		Chloroform (ml)	p-TSOH (Catalyst, mol% glycerol)	Mass (g)	% Yield
21.9047	Acetone (60.00)	0.00	0.1	8.0545	25.65
10.0000	2-Butanone (25.00)	100.00	0.1	8.2640	52.49
10.0000	2-Pentanone (25.00)	100.00	0.1	13.7487	79.64

Table 7: Preparation of Ketal Esters of Glycerol

## Biodiesel Trials

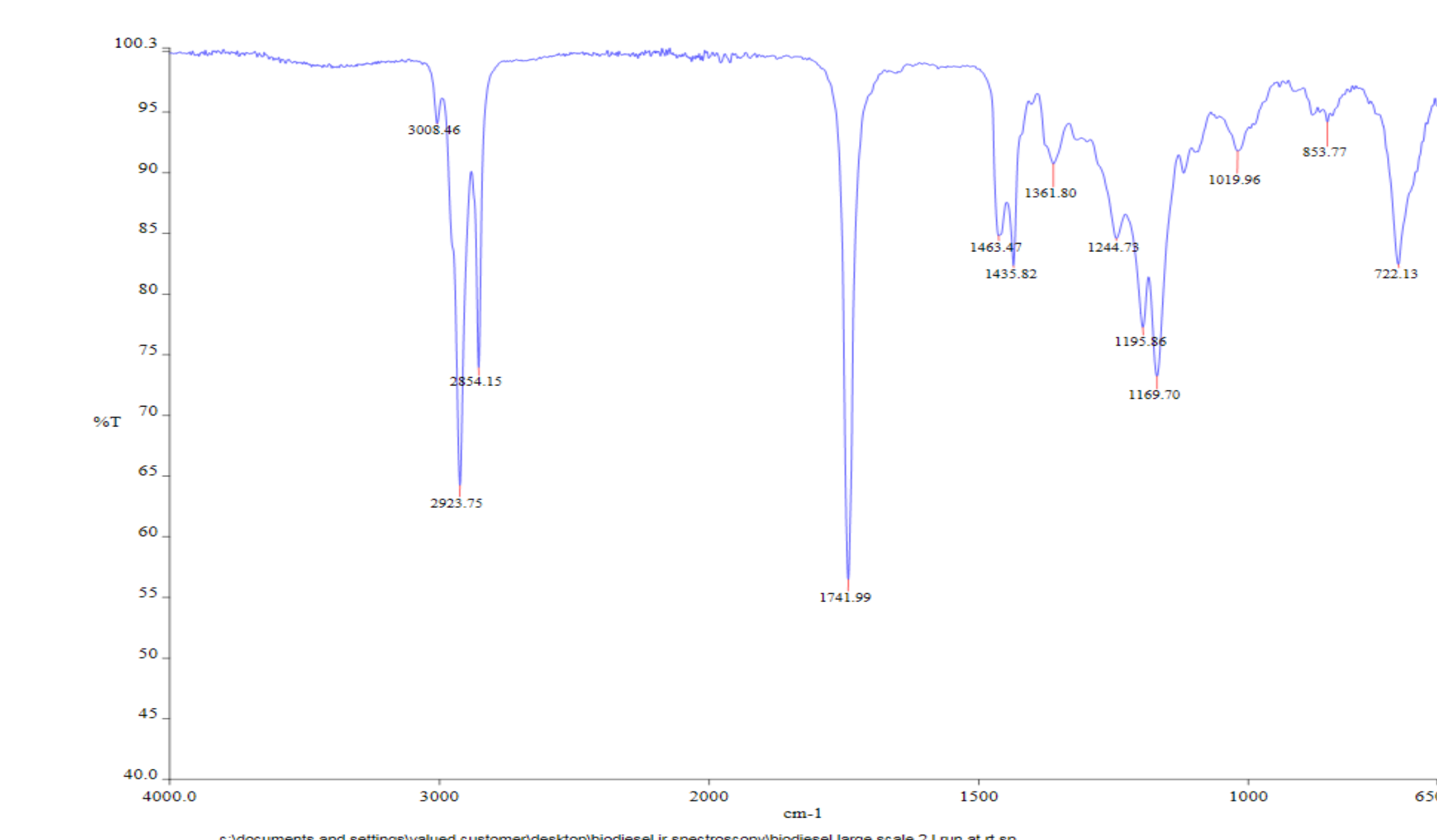


Figure 4: 2 L Large scale biodiesel overnight run at room temperature

IR spectroscopy confirmed the formation of biodiesel. The major peaks of interest for biodiesel synthesis in both the large scale and small scale conversions were the 1400 cm<sup>-1</sup>, 1100 cm<sup>-1</sup>, 1457 cm<sup>-1</sup>, and 1435 cm<sup>-1</sup>. IR spectra of both vegetable and waste oils indicated presence of the 1400 cm<sup>-1</sup> and 1100 cm<sup>-1</sup> peaks. These peaks were absent in synthesized biodiesel as expected. The ratio between the 1457 cm<sup>-1</sup> and 1435 cm<sup>-1</sup> peaks indicated how well the conversion from waste and vegetable oils to biodiesel occurred. For the non-reflux small scale trial runs, the best condition that optimized the biodiesel product yield was the two-day overnight run at 40°C based on the results of the methanol test (95% conversion).

## Future Work

Following the conclusion of this portion of the project, the next step will be to test how well the biodiesel synthesized can power equipment in a small scale such as running a small portable diesel generator. Additional tests such as flash point testing will be conducted to evaluate the purity and efficiency of the biodiesel synthesized. With regards to the ketalation trials, our goal is to further optimize the yields from the glycerol ketals formed. Additionally, use other fatty acids namely oleic and palmitic acids for the transesterification of the precursor glycerol ketals synthesized to form final fuel additive product.



## References

- (1) Adewuyi, G.Y., Mahamuni, N.N. (2009). Fourier Transform Infrared Spectroscopy (FTIR) Method to Monitor Soy Biodiesel and Soybean Oil in Transesterification Reactions, Petrodiesel - Biodiesel Blends, and Blend Adulteration with Soy Oil. *Journal of Energy and Fuels*. 23, Pg. 3773 - 3782.
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- (3) Garcia, E., Garrido, A., Laca, M., Perez, E., Peinado, J. (2008). New Class of Acetal Derived from Glycerin as a Biodiesel Fuel Component. *Journal of Energy and Fuels*. 22, Pg. 4274 - 4280.