# CATALYTIC DEHYDRATION AND ETHERIFICATION OF ALCOHOL AND GLYCEROL TO PRODUCE BIODIESEL COMPATIBLE FUEL ADDITIVES

A Thesis

by

HUSAM AHMED MOHAMMED ALMASHHADANI

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|---|---|
| Chair of Committee, | Sandun Fernando |
| Co-Chair of Committee, | Sergio Capareda |
| Committee Member, | Waruna Kulatilaka |
| Head of Department, | Stephen Searcy |

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# ABSTRACT

Global glycerol supplies have been increasing steadily due to the continual expansion of biodiesel production. This glut has resulted in lower demand for glycerol, price deflation and even environmental concerns. Crude glycerol produced from biodiesel transesterification is not of high quality due to catalyst and alcohol contamination and transportation and disposal issues—all of which have added further constraints to this industry. In light of this, a product that could utilize glycerol, excess alcohol and the catalyst could enhance the value proposition for the biodiesel industry. Here, we show that glycerol can be reacted with methanol and tert-butanol in the presence of common transesterification catalysts to produce an ether-rich mixture that is miscible with biodiesel. Initially, the bimolecular dehydration of two alcohols, n-propanol and methanol, with catalysts that are used in transesterification was investigated. Experiments were carried out to evaluate the feasibility of promoting the etherification reaction using methanol and n-propanol as model alcohols. When methanol and n-propanol are reacted together, three types of ethers can be produced: dimethyl ether, methyl-propyl ether (also referred to as methoxypropane), and di-propyl ether. The latter two ethers are of more fuel interest due to their ability to stay in the liquid phase at room temperature; however, the ability of catalysts to selectively produce liquid ethers is not established.

Initial studies were conducted to discern the effect of sulfuric acid, amberlyst-36 and titanium isopropoxide—catalysts that are known to be effective for transesterification—on the substrate conversion, ether yield, and selectivity using n-propanol at four levels of temperature. Subsequent studies with n-propanol and methanol looked at the impact of select catalyst concentrations and reaction conditions. Studies indicate that liquid mixtures of 1-methoxypropane and di-propyl ethers could be formed by reacting n-propanol and methanol in the presence of sulfuric acid or Amberlyst 36. Higher concentrations of sulfuric acid (5% w/w) coupled with higher temperatures ($>140^{o}$C) favored substrate conversion and ether yields. However, it was revealed that the selectivity toward specific ethers (i.e. coupling of the two larger alcohols to produce di-propyl ether) could be controlled by appropriate selection of the catalyst. It is anticipated that the results would be a starting point for a simple technique to produce specific ethers using a mixture of alcohols. This technique could be applied for applications such as transesterification byproduct utilization. Subsequent studies where glycerol was used as one of the primary alcohols looked at the impact of type and concentration of catalysts, molar ratio of reactants, temperature, and reaction time on alcohol conversion, product yield, selectivity and select fuel properties. Results show that both NaOH and $H_2SO_4$ are active for producing etherified blends from glycerol that are miscible with biodiesel. These results could be a starting point for the development of an effective fuel additive to reuse the byproduct glycerol and excess alcohol resulting from biodiesel production.

# DEDICATION

This work is dedicated to my family, Mom, Dad, brother, and sister, who are always with me and supporting me from overseas. I also dedicate this work to whomever thinks that it is possible to achieve something remarkable in this world.

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# CHAPTER I

# INTRODUCTION AND OBJECTIVES

## 1.1 Background

Renewable energy demand has been in a consistent increase locally and internationally. Several factors cause that demand to increase such as global warming, pollution presence worldwide, economic recession, oil price fluctuation, and the non-perpetual source of energy, oil. Therefore, swift actions were undertaken to meet the demand of energy by providing an equally efficient, perpetual, cleaner for the environment, and more economical source of energy compared to the traditional source such as biofuels. Biofuels are major part of renewable energy revolution in the current times. They are derived from renewable sources, which makes them cleaner, cheaper, perpetual, and environmentally friendly. They are targeted towards gasoline engines and diesel engines. Ethanol and other alcohols are used and blended with gasoline for gasoline engines and biodiesel is used and blended with diesel for diesel engines. They are in the process of being more efficient and economical compared to fossil fuels. One of the advanced technologies introduced to biofuels are biofuel additives. This work elaborates the biofuel additives concept in order to achieve the highest efficiency output.

## 1.2 Objectives

**a)** To produce a biofuel additive that is compatible with biodiesel through dehydration of alcohol using model compounds.

**b)** To optimize the process and conditions developed by the first objective and to investigate the characteristics of the product produced using the first objective.

# CHAPTER II

# PROPERTIES, PERFORMANCE, AND APPLICATIONS OF BIOFUEL BLENDS: A REVIEW

## 2.1 Introduction

Biofuels are fuels derived from living plant or animal matter. Biofuels such as ethanol and biodiesel could be used directly in their neat form as fuels in internal combustion engines; however, blends of these fuels mixed with fossil fuel in different ratios have gained more popularity due to technical as well as economic advantages. The purpose of this review is to analyze different forms of biofuel blends that are under research and development comparing their utility and performance in the two primary classes of engines, i.e., spark ignition and compression ignition engines. The fuel properties, performance and emissions characteristics, advantages and disadvantages of numerous fuel blends are discussed.

## 2.2 Biodiesel Blends

Biodiesel is a type of renewable fuel produced from biological resources [4, 5] that conforms to ASTM D6751 standard (also comparable in general to European standard EN 14214 and the National Standard of Canada CAN/CGSB-3.524). Biodiesel is biodegradable, non-toxic, and has low toxic emissions compared to fossil fuel [6]. Utlu and Kocak reported that about $CO_2$ emissions were decreased by 14%, and CO emissions were decreased by 17.1% [7]. Biodiesel is produced from triglycerides that may be found in different sources, such as vegetable oils, animal fats [8], and algae [9]. In the United States, the most common source of feedstock for biodiesel is soybean oil [10]. Other types of oils also can be used including palm oil which is predominantly used in Asia, and canola oil which is predominantly used in Europe [6, 11, 12]. The fast-paced evolution of biodiesel and other types of biofuels is due to many reasons: including the ability to utilize renewable resources (unlike fossil fuels); price stability compared to crude oil; eco-friendliness and help reduce dependence on foreign oil. Biodiesel is produced through a process called transesterification, which produces fatty acid alkyl esters via breakage of ester linkages in triglyceride in the presence of acid ($H_2SO_4$) or base (NaOH or KOH) catalysts and common alcohols (such as methanol or ethanol). This process results in biodiesel and glycerol as a byproduct [5].

**Table 2.1:** Biodiesel specifications summarized, adapted from (ASTM D 6751 [13])

| **Property** | **Measuring Unit** | **Test Method** | **Grade no.1-B S15** | **Grade no.2-B S15** |
|---|---|---|---|---|
| Flash Point | °C, min | D93 | 130 | 130 |
| Cetane number | -------- | D613 | 47 | 47 |
| Cloud Point | °C | D2500 | Reported | Reported |
| Kinematic Viscosity | $mm^2/s$ @ 40 °C | D445 | 1.9-6.0 | 1.9-6.0 |
| Acid Number | mg KOH /g max | D664 | 0.5 | 0.5 |
| Sulfated ash | % mass, max | D874 | 0.02 | 0.02 |
| Carbon residue | % mass, max | D4530 | 0.05 | 0.05 |
| Copper strip corrosion | ______ | D130 | No.3 | No.3 |
| Total Glycerin | % mass, max | D6584 | 0.24 | 0.24 |
| Sulfur | % mass (ppm), max | D5453 | 0.0015 | 0.0015 |
| Phosphorous content | % mass, max | D4951 | 0.001 | 0.001 |
| Sodium and potassium | ppm max | EN14538 | 5 | 5 |
| Water and Sediment | % volume, max | D2709 | 0.05 | 0.05 |
| Methanol content | % mass, max | EN14110 | 0.2 | 0.2 |
| Distillation temperature | °C, max | D1160 | 360 | 360 |
| Monoglycerides | % mass, max | D6584 | 0.4 | _______ |
| Oxidative stability | hrs, min | EN15751 | 3 | 3 |
| Cold soak filterability | s, max | D7501 | 200 | 360 |
| Calcium and Magnesium | ppm | EN14538 | 5 | 5 |

Biodiesel can be mixed or used as 100% “neat” form in diesel engines to generate power [14]; however, cannot be used in gasoline engines because the fuel’s flash point is higher than gasoline and high cetane index (or low octane index). Thus, it will not ignite as fast as gasoline within the combustion chamber. When mixed, the ratio of mixing or blending biofuel depends on the purpose of the blend. There are different types of blends with fossil fuel such as B-20, where B is biodiesel and the number represents the blending proportion. For example, a B-20 blend would possess 20% biodiesel and the remainder being fossil diesel [14].

Neat (B100) biodiesel could only be used in modified engines that has compatible parts. Since biodiesel esters have good solvent capability, parts made of rubber and plastic are known to dissolve in biodiesel [15].

### 2.2.1 Properties of B-100

Select properties of biodiesel fuel blends are depicted in Table 2.2. Comparison of some critical parameters are also depicted in Figure 2.1.

**Table 2.2:** Biodiesel blends properties compared to diesel

| Properties | Fossil Diesel | Biodiesel B-100 | B-20 Blend | B-5 Blend | Remarks | Ref. |
|---|---|---|---|---|---|---|
| Viscosity $mm^2/s$ | 2.8271 | 4.2691 | ------ | ------ | Fossil Diesel is (no.2), biodiesel is from soybean. | [16] |
| | 3.53 | 4.89 | 3.75 | 3.56 | | [17] |
| | 3.06 | 5.75 | ------ | 4.45 | *FAME | [18] |
| | 4.3* | 11* | ------ | ------ | 40 °C/70 °C, | [19] |
| | 2.71 | 6.17 | 3.21 | 2.92 | At 40 °C | [20] |
| | 2.4 | 4.92 | 2.74 | 2.48 | At 40 °C | [21] |
| Flash point °C | 69 | 120 | 82 | 74 | | [17] |
| | 53 | 168* | ------ | 57 | *FAME | [18] |
| | 71.5 | ------ | ------ | ------ | | [6] |
| | 59 | 111 | 67 | 64 | | [21] |
| Cetane number min | 42.6 | 51.5 | ------ | ------ | Fossil diesel is no.2, | [16] |
| | 50.9 | 56* | 52.2-52.3* | 51.5* | *FAME | [18] |
| | 46 | ----- | ----- | ----- | | [22] |
| Cloud point °C | 0 | 3 | 0 | 0 | | [17] |
| | 2 | ------ | ------ | ------ | | [6] |
| | ------ | ------ | ------ | (-24,-28) | Range | [23] |
| Pour point °C | <-12* | 0 | -9 | -12 | * Less than | [17] |
| | 1 | ------ | ------ | ------ | | [6] |
| | ------ | ------ | ------ | (-36, -39) | Range | [23] |
| Calorific value MJ/Kg | ----------- | ----------- | 44.41 | 45.37 | | [17] |
| | 43.35 | 39.76 | ------- | ------- | | [19] |
| | 46.35 | 39.87 | 44.98 | 46.00 | At 40 °C, | [20] |
| | 45.38 | ------ | ------ | ------ | At 20 °C | [6] |
| | 43.15 | 39.95 | 42.01 | 42.19 | | [21] |
| Sulfur Content | 15-500 | ------ | ------- | ------- | mg/Kg | [24] |
| | 300 | ------ | ------- | ------- | ppm | [22] |
| | 3.59-12.29 | 10.94-11.69 | ------- | ------- | µg/g | [25] |
| | ------- | ------ | 0.07 | ------- | (6.6 mg/Kg sulfur) in fuel | [26] |
| Lubricity | 0.83 | 0.72 | ------- | ------- | (groove diameter mm) | [27] |
| Acid Number | -------- | 0.275 | 0.057 | 0.008 | mg KOH/g | [28] |

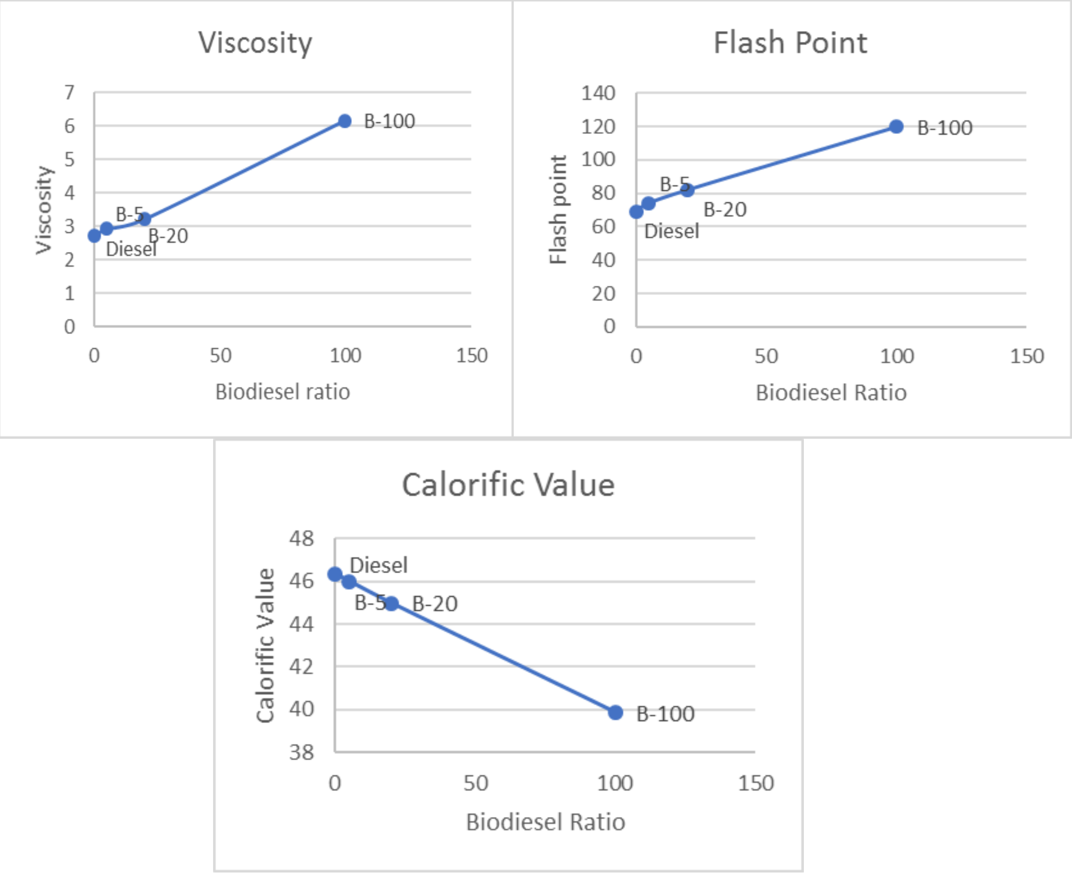

**Figure 2.1:** Comparison of select key properties of biodiesel blends and fossil diesel.

### 2.2.1.1 Kinematic Viscosity

Kinematic viscosity is the liquid's resistance to flow, which basically measures how thick the fuel would be. High viscosity would clog the fuel injection system, and low viscosity may not facilitate complete combustion. However, viscosity might vary depending on the feedstock and the method of measurement. The American Society for Testing and Materials (ASTM), had determined the viscosity in a range of (1.9 – 6.0

mm$^2$/s) by ASTM D445 (Test of Kinematic Viscosity for Transparent and Opaque Liquids) for pure biodiesel from the various feedstock. It has been reported that the viscosity of biodiesel is close to its value in fossil diesel. The viscosity of biodiesel decreases drastically after the alkaline-catalyzed transesterification. Generally, increasing the number of double bonds in the carbon chains causes the biodiesel to be more viscous [6]. Values of viscosity for diesel and biodiesel blends are compared in table 2.

#### 2.2.1.2 Flash Point

Flash point is defined as the temperature at which the fuel ignites when it is exposed to a flame or spark. It varies from one fuel to another and from one blend to another. The higher the flash point is the higher temperature would be required to ignite the fuel. On one hand, it is better to lower the flash point for combustion purposes. On the other hand, the higher flash point means the fuel is safer to transport. Usually, biodiesel flash point is higher than the conventional diesel. In biodiesel, the flash point is around 110-180$^o$ C, whereas in the conventional diesel it is around 55-60$^o$ C. The reason for the high flash point is due to a long chain of unsaturated carbon C 18:1 and longer. The proposed empirical model for flash point estimation made by Catoire and Naudet clarifies the reason for the high flash point for longer carbon chain compounds [29, 30]:

$$FP = 1.477\ T_b^{0.74686} * \Delta H^{o\,0.16845}_{vap} * C^{0.05948}$$

Where:

FP: is the Flash Point (K)

$T_b$: is the boiling point of the compound (K)

$\Delta H^{\circ}_{vap}$: is the standard enthalpy of vaporization of the compound at 298.15 K, expressed in KJ/mol

C: is the number of carbon atoms in the fuel molecule

#### 2.2.1.3 Cetane Number (CN)

CN is the measure of the ignition quality of the fuel after it is introduced to a diesel engine which is measured by ASTM D613 (Standard Test Method for Cetane Number of Diesel Fuel Oil). It measures the ignition timing, or ignition delay, in the combustion chamber of a diesel engine [31]. The higher the CN is, the better and faster the fuel would be combusted or ignited. This means that the fuel will need less time to ignite if CN is higher. Usually, longer and saturated carbon chains have a higher CN. That concept is applicable for biodiesel as well as the conventional diesel. Thus, a higher content of hydrocarbons in the feedstock will have a higher CN. For example, biodiesel derived from animal fat would have higher CN than other feedstock [32].

**Table 2.3:** Cetane number of different feedstock

| feedstock | Biodiesel B-100 | Soybean oil | Biodiesel [33] from Soybean | Diesel no.2 [34] |
|---|---|---|---|---|
| CN | 47 | 37.9 | 49 | 55 |

### 2.2.1.4 Cloud point and pour point

Two of the important physical properties of biodiesel fuel are cloud point and pour point. Cloud point is defined as the temperature at which the fuel will become cloudy, due to wax crystals [14]. Crystallization occurs when the fuel is cooled. Cloud point is measured by ASTM D2500 (Test Method for Cloud Point of Petroleum Products), D5771, D5772, or D5773 [14]. On the other hand, pour point is the temperature at which the liquid will start to lose its fluidity, and begins to turn into a solid [14]. Pour point is measured by ASTM D97 (Standard Test Method for Pour Point of Petroleum Products), D5950 or D5949 [14]. Cloud and pour points are related to the amount of saturated fatty acids. In general, higher amounts of saturated fatty acids increase cloud and pour points. Generally, biodiesel has higher cloud and pour points than conventional diesel. The values of cloud and pour points for B-100 ranges from -15 to 16 $^{o}$C [35]. A recent study showed that cloud point is 3 $^{o}$C whereas the value varied between 1 and 2 $^{o}$C in conventional fuel *[17]*. This increase in cloud and pour points could be as a result of natural occurrence of saturated fatty acids in biodiesel as compared to none in petroleum diesel.

### 2.2.1.5 Calorific Value (CV)

CV is also referred to as Heating Value in literature and is measured by ASTM D240 (Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter). It is known as the amount of energy released when a known volume is of the fuel is fully combusted - an indication of the energy content of the fuel. Generally, biodiesel has a lower heating value than conventional diesel because of the higher oxygen content. The maximum heating value reported for biodiesel has a minimum limit of 35 MJ/ kg, whereas the conventional fuel has a higher limit of 45 MJ/Kg [6].

### 2.2.1.6 Lubricity

Lubricity is a key property biodiesel is known to enhance as compared to fossil diesel is lubricity. Lubricity is referred to as the lubrication ability of a substance. In fact, since fossil diesel have relatively poor lubricity characteristics, sulfur is added [36]; however, due to toxicity concerns, sulfur is not permitted to be added to fuels anymore. And thus, the superior lubricity characteristics makes biodiesel a renewable and an environmentally friendly additive to be used in diesel fuels. Lubricity can be determined through an important parameter which is viscosity [37, 38]. The idea is to have a thin film of a viscous liquid that will protect from severe corrosion between two metal surfaces [37, 38]. This is the basis on which the lubricity evaluation methods will depend. The most common methods for lubricity evaluation are high frequency reciprocating rig test (HFRR), ball on cylinder lubricity evaluator test (BOCLE), and four-ball wear test which was developed in 1933 [27]. The standards for the wear test are ASTM D2266 for greases and ASTM D4172 B for lubricants. Fernando [27] had explained and conducted the four-ball wear test based on ASTM D4172 standard for biodiesel B-100 and diesel fuels from different feedstock. To sum it up, the four metal balls will be forced to move on a metal surface under a specific load, which will cause a groove on the metal’s surface. The diameter of the groove will be measured and compared to a standard measurement. Apparently, the greater the diameter of the groove the lower lubrication efficiency the liquid has. Results are shown in table 2.2

#### 2.2.1.7 Acid Number

Acid number is known as the amount of KOH in mg required to neutralize the acids in 1 g of the sample [39]. In biodiesel area, it is a measurement of the extent of hydrolysis and oxidation for biodiesel [40]. It is measured according to ASTM D6751 and EN 14214; both of which have emphasized the acid number for biodiesel should not exceed 0.5 mg KOH/g for B-100 due to the formation of free fatty acids during the production process [41]. Apparently, acid number is affected by the storage and the age of the biodiesel which will become more acidic as it gets old [41]. Baig [28] had determined the acid number of biodiesel B-100 using the titration method according to ASTM D974 (using 0.02 M KOH in 10 ml titration solvent). The results are shown in table 2.2

#### 2.2.1.8 Sulfur Content

Sulfur is one important property in biodiesel, which has a great impact on the engines performance and emissions. The presence of sulfur increases the particulate matter emissions in the exhaust causing more pollution [26, 42]. The excess amounts of sulfur in the fuel will cause corrosion inside the engine cylinder [26]. The excess amount of sulfur will be oxidized during combustion into $SO_2$. Sulfur dioxide will then be further oxidized into $SO_3$ forming sulfuric acid eventually after reacting with water. Furthermore, sulfuric acid will condensate on the metal parts in the engine, which will cause corrosion, damage, and failure to the engine parts [43]. There are also other effects in the exhaust emissions from sulfur on the environment and health. The exposure to sulfur gaseous emissions will create breathing problems, and longtime exposure will cause heart diseases and eventually death [26]. Therefore, the less sulfur content in the fuel the better the fuel properties would be. Results were collected from different sources and shown in table 2.2

### 2.2.2 Emissions

Emissions measurements including smoke concentration, CO content, $CO_2$ content, NOx, and sulfur emissions of biodiesel combustion, have been compared with conventional diesel such as smoke concentration/particulate matter, CO content, and $CO_2$ content. Biodiesel produces less smoke, and CO emissions are reduced as well as $CO_2$ emissions as compared to conventional diesel. In fact, it has been reported that particles emissions were 33% less than conventional diesel for B-100. Also, levels of CO and $CO_2$ were reduced by 10%, compared to conventional diesel. However, this ratio may vary when using biodiesel blends [44].

**Table 2.4:** Emission comparison of diesel and biodiesel blends

| Emission | Diesel | B-100 | B-20 | B-5 | Remarks | Ref. |
|---|---|---|---|---|---|---|
| $CO_2$ | 12.9%<br>173.6<br>3892.5* | --------<br>172.9<br>-------- | 12.9%<br>--------<br>3664.2* | --------<br>--------<br>3488.7* | <br>g/km<br>*g/kW-h @ 16.3 N.m | [45]<br>[46]<br>[47] |
| CO | 30<br>0.153<br>3.6* | --------<br>0.067<br>-------- | 32<br>--------<br>2.8* | --------<br>--------<br>2.9* | ppm<br>g/km<br>*g/kW-h@ 16.3 N.m | [45]<br>[46]<br>[47] |
| Particulate Matter Concentration (mg/m$^3$) | 12.9 ±0.9<br>14.92 | 8.6±1.3<br>--------- | 12.5±0.9<br>13.38 | --------<br>-------- | | [44]<br>[45] |
| SOx | 96<br>6.8* | -------<br>-------- | 77<br>0.8* | ---------<br>1.4* | $SO_2$, unit is ppm<br>*g/kW-h @ 16.3 N.m | [45]<br>[47] |
| NOx | 104 ppm<br>0.367<br>--------<br>21.5* | -------<br>0.454<br>-------<br>------- | 109 ppm<br>---------<br>---------<br>16.8* | ---------<br>---------<br>571 ppm<br>16.2* | $NO_2$<br>g/km<br>Average<br>*g/kW-h @ 16.3 N.m | [45]<br>[46]<br>[36]<br>[47] |

### 2.2.3 Performance

Generally, biodiesel produced from different oils has about the same performance for the short term as the diesel fuel. For example, A single cylinder engine with various types of vegetable oils (raw sunflower oil, raw soybean oil, and opium poppy oil fuels) operated at 1300 rpm only observed maximum torque differences of about 10% between the diesel reference and peak values of vegetable oil fuels. The maximum power difference between the reference value and peak values of the vegetable oil fuels was about 18% obtained from raw cottonseed oil and raw soybean oil fuels. The minimum torque and power difference was about 3% between reference value and oils [19]. These results may be due to the higher viscosity and lower heating values of vegetable oils.

### 2.2.3.1 Engine Efficiency

One of the effective factors of engines efficiency is Brake Specific Fuel Consumption (BSFC). It is a measure of fuel efficiency that burns and produces rotational motion. BSFC with biodiesel was measured at a full load of engine and 1400 R.P.M. with diesel no.2 as a baseline. It was found that biodiesel had a higher BSFC, almost 13.5% increase, because biodiesel having a 12% lower heating value than diesel no.2 by 12% [16].

### 2.2.3.2 Thermal Efficiency

Another factor that dictates engine performance is thermal efficiency. Thermal efficiency and brake specific fuel consumption are inversely proportional. i.e. BSFC is the inverse of Thermal efficiency. Thermal efficiency of biodiesel is about 0.5% higher as compared to no.2 diesel [16].

**Table 2.5:** Performance efficiency comparison of diesel no.2 and biodiesel

| Fuel type | BSFC (g/kw-hr) | % change in BSFC | Thermal efficiency % | % change in thermal efficiency |
|---|---|---|---|---|
| No.2 Diesel | 228.42 | - | 36.96 | - |
| Soy Methyl Ester | 259.33 | 13.53 | 37.13 | 0.45 |

### 2.2.4 Advantages of B-100

1- Renewable and thus carbon neutral.

2- Less price fluctuations as compared to fossil fuel.

3- Elicits higher thermal efficiency.

4- Provide a higher brake specific fuel consumption compared to fossil fuel.

5- Even though CN is not as high as conventional fuel, it is still relatively close and good as a renewable fuel.

6- Affords a better emissions profile than diesel fuel and thus environmentally friendly.

### 2.2.5 Disadvantages

1- Long-term storage will oxidize and degrade biodiesel impacting the stability/quality of the fuel.

2- High levels of total insoluble materials.

3- Engine must be modified to handle neat biodiesel.

4- Many reports of increased NOx emissions.

## 2.3 Biodiesel Blends

Biodiesel is miscible in diesel fuel at any ratio. However, there are several standardized blends ranging from B2, B6, B10 and B20 (other intermediate blends are also available, but used less frequently). Table 2.6 presents summarized requirements for 6% biodiesel (B6) to 20% biodiesel (B20) as listed in ASTM D7467-13.

**Table 2.6:** Summarized requirements for 6% biodiesel (B6) to 20% biodiesel (B20) as developed from ASTM D7467-13 [13].

| **Property** | **Measuring Unit, level** | **Test Method** | **Grade B6 to B20 S15** |
|---|---|---|---|
| Flash Point | $^{o}$C, min | D93 | 52 |
| Cetane number | --------, min | D613 | 40 |
| Cloud point | $^{o}$C, max | D2500 | ---------- |
| Viscosity | $mm^2/s$ @40 $^{o}$C | D445 | 1.9-4.1 |
| Acid number | Mg KOH/g, max | D664 | 0.3 |
| Sulfur Content | ug/g or ppm | D5453 | 15 |
| Distillation temperature | $^{o}$C, max | D86 | 343 |
| Carbon residue (Rams bottom 10%) | % mass, max | D524 | 0.35 |
| Mass | %, max | D2622 | --------- |
| Mass | %, max | D129 | --------- |
| One Criteria should be met: | | | |
| Cetane index | ----- | D976-80 | 40 |
| Ash content | % mass, max | D482 | 0.01 |
| Biodiesel content | %(v/v) | D7371 | 6, -20 |
| Water and sediment | %vol, max | D2709 | 0.05 |
| Copper corrosion | 3h @ 50 $^{o}$C, max | D130 | No.3 |
| Aromaticity | %vol, max | D1319-03 | 35 |
| Oxidation stability | Hours, min | EN15751 | 6 |
| Lubricity | HFRR @ 60 (micron um), max | D6079 | 520 |

Biodiesel blends are added to fossil diesel in order to improve certain physical properties - such as lubricity, efficiency, cetane number, and oxygen content - of the final blend. Some of these property improvements are attributed to the high degree of oxygenation.

The degree to which fuel properties change depends on the blend composition and the key characteristics of some common biodiesel blends (i.e., B-20 and B-5) are discussed below. Biodiesel and diesel are blended such that the desired properties of both biodiesel and fossil diesel are enhanced.

### 2.3.1 B-20

B-20, mixture 20% of biodiesel and 80% conventional fuel, is a key blend since this is widely considered as the highest amount of biodiesel that could be used in compression ignition engines without engine modification. [6].

#### 2.3.1.1 Properties

Properties of B-20 generally would only be slightly different from that of B-100. A comparison of key properties of B-20 along with B-100 and #2 diesel fuel are depicted in Table 2.

##### 2.3.1.1.1 Viscosity

As can be seen from Table 2, neat and blends of biodiesel have viscosity values that are close to the diesel fuel. In general, the viscosity of diesel fuel is lower as compared to neat biodiesel. Viscosity of B-20 was between neat biodiesel and diesel fuel and ranged from 3.416 $mm^2/s$ [17] to 3.416 $mm^2/s$ at 25 $^oC$ [45].

### 2.3.1.2 Flash Point

It is known that the lower the flash point is for a fuel, the faster and more efficient that fuel would be in terms of combustion [31]. In this case, the flash point of B-20 is 67 $^oC$ which is lower than B-100; however, it is still higher than pure fossil diesel. Therefore, B-20 would combust faster as compared to B-100.

### 2.3.1.3 Cetane Number (CN)

The value of CN for B-20 has not been specifically measured; however, the values of other blends such as B-15 and B-25 have been reported [18]; Thus, the value of B-20 is likely to be ~52.2-52.3. This value is still higher than that of diesel (50.9).

### 2.3.1.4 Cloud and Pour Point

Cloud point of B-20 is reported to be $0^oC$ whereas the pour point is to be at $-9^o$ C by some accounts [17]; however, others [45] reported the values to be $-3.6^o$ C, and $-24^oC$ respectively. Regardless of the variation, it is clear that lower than diesel fuel and neat biodiesel [44]. Studies indicate that B-20 to be superior in its cold flow/start properties as compared to neat biodiesel or diesel fuel.

### 2.3.1.5 Heating Value (Calorific Value)

Since B-100 has a lower calorific value than conventional diesel, blending biodiesel with diesel will definitely increase the calorific value of the blends as compare to using neat biodiesel. The calorific value of B-20 is approximately 44 MJ/kg, which is quite close to that of conventional diesel (45 MJ/Kg). Heating value is related to fuel consumption because a cylinder must be charged with more fuel in order to produce the same power [45]; and in this measure, B-20 outperforms neat biodiesel while impacting least on energy density or fuel consumption basis.

### 2.3.2 Emissions

Generally, blending will decrease the positive effects of neat biodiesel on emissions as blends only contain a fraction of biodiesel that largely contribute to improved emissions; however, blends do improve emissions profile significantly as compared to diesel fuel. For example, B-20 decreased $SO_2$ by 19.7 ± 2.5% as compared to diesel fuel. Also, particle emissions were 15.7 ± 7.5% lower than no.2 diesel [45]. Lower emissions are attributed to lower sulfur content of biodiesel as compared to fossil diesel and the higher oxygen content that facilitates more complete combustion.

### 2.3.3 Performance

Engine performance of B-20 fuel is only slightly different from either B-100 or diesel fuel. Under identical tests, BSFC, which is one indicator of fuel consumption efficiency of the engine (ratio of rate of fuel consumption and power), B-20 resulted in 234.55 (g/kW-hr) which was 2.69% higher than fossil diesel [16]. Nevertheless, B-100 resulted in 259.33 (g/kW-hr) which was even higher. The increase of BSFC could be attributed to higher oxygen content of biodiesel fuel blends. It should be noted that the oxygenation, although increases fuel consumption efficiency, reduces power slightly since the heating value of B-100 is less than diesel fuel. Similarly, thermal efficiency of B-20 is slightly less than the conventional diesel (by 0.16%), which is already less than B-100 [16].

### 2.3.4 Advantages

1. The ability to use B-20 blends without any engine modification.
2. Possess closest energy density to fossil diesel and thus with minimal impact to fuel consumption.
3. Burns cleaner than fossil diesel.
4. B-20 has better cold flow / cold start properties than diesel or neat biodiesel.

### 2.3.5 Disadvantages

1. No significant reduction of toxic and pollutant emissions as compared to neat biodiesel; even though, $SO_2$ is reduced to some extent.
2. The blend still relies on conventional diesel and thus lesser impact on energy security and environment as compared to neat biodiesel.

## 2.4 Biodiesel B-5

B-5 is another biodiesel blend that consists of 5% biodiesel and 95% fossil diesel. It is considered the minimum effective blend of biodiesel/diesel that does not cause any problems for the engine [16]. Minimal biodiesel blends of this sort are only used to enhance certain properties of the conventional diesel fuels that diesel fuel alone cannot provide such as lubricity.

### 2.4.1 Properties

Key properties of B-5 compared with other biodiesel blends and fossil diesel are depicted in Table 2.

#### 2.4.1.1 Kinematic Viscosity

Several studies were conducted to determine the viscosity of B-5 blend. One can predict that the viscosity will be closer to the diesel fuel's viscosity rather than pure biodiesel due to the low biodiesel: diesel blend ratio; and, in fact was confirmed by several studies. The viscosity of B-5 was reported to be between 2.48 – 4.45 $mm^2/s$ to whereas the diesel fuel's viscosity was 2.40-4.3 $mm^2/s$ [21].

#### 2.4.1.2 Flash Point

The flash point of this blend was not close to biodiesel; however, was not as high as fossil diesel either. Overall, the flashpoint, 64°C, was closest to that of B-20 (and higher than diesel fuel which is 55°C) [21]. This implies that addition of even a small amount of biodiesel improves safety of the fuel during storage and handling.

#### 2.4.1.3 Cetane Number

The B-5 biodiesel blend does not show significant variance from B-20 on CN. In fact, the CN of B-5 (53.5) was closer to B-20 (52.2) than pure diesel (42.6-50.9) [48]. This indicates that even a slight addition of biodiesel can improve cetane rating of the fuel enhancing combustion properties under compression ignition.

#### 2.4.1.4 Cloud and Pour Points

The value of cloud point of B-5 was between -24 and -28 $^{o}$C, which is close to that of diesel no.1 (-26) $^{o}$C. Also, pour point of B-5 ranged between -36 and -39 $^{o}$C, which is higher compared to diesel no.1, (-42) $^{o}$C [23]. Cloud point and pour point of B-5 and low biodiesel blends are closer to that of diesel fuel than high biodiesel concentration blends. So, B-5 and almost all low ratio biodiesel/diesel blends tend to behave more like diesel fuel in cold weather. [49].

#### 2.4.1.5 Calorific Value

It was reported that the calorific value of B-5 is closer to diesel fuel than B-20. Since the calorific value of biodiesel is lower than that of fossil diesel, it is expected for the blends to vary the calorific values proportionately. The calorific value of B-5 was 42.19 MJ/kg which lied between that of B-100 (39.95 MJ/kg) and pure diesel (43.15 MJ/Kg) [21].

### 2.4.2 Emissions

As with other properties, the emissions profile also tend to change proportionately with the strength of the blend and in general, B-5 biodiesel blends have better emissions profiles as compared to fossil diesel but not as good compared to neat or B-20 biodiesel as could be seen from Table -4- [20].

### 2.4.3 Performance

The performance of B-5 is not significantly different from that of fossil diesel primarily due to the low blending ratio - which results in domination of diesel fuel performance and properties. For example, BSFC for B-5, from rapeseed oil, was almost the same as the diesel fuel [50]. Experiments on fuel consumption with B-5 in place on diesel fuel has resulted in a consumption increase of 7-8% [51]. The thermal efficiency of B-5 was reported to be slightly higher than diesel fuel [20]. However, this increase cannot be considered as significant compared to that of B-100 which ranged between -0.8 to +5.8% [20].

### 2.4.4 Advantages

1. B-5 blends could be used as lubricity enhancers without changing performance characteristics pertinent to diesel fuel.
2. B-5 improves cetane number of fossil diesel while also enhancing efficiency characteristics.

### 2.4.5 Disadvantages

1. B-5 emissions are closer to that of fossil diesel.
2. B-5 blends are not considered adequate renewable substitutes to diesel fuel and thus the environmental impact is not that significant.

## 2.5 Ethanol and Ethanol Blends

### 2.5.1 Ethanol E-100

Ethanol is an important renewable fuel that is targeted for spark ignition engines [52] and produced primarily via carbohydrate fermentation (primarily corn in the temperate regions and sugarcane in the tropics) and more recently from cellulose [53]. Regardless of source, the backbone for ethanol is glucose sugar [53]. Ethanol can be used in its pure form called E-100 or blended with fossil gasoline at any ratio. Similar to biodiesel, the percentage amount of ethanol in ethanol-gasoline blends are referred by the number that follows the prefix E. The most common blends in the United States are E85 and E10 [54].

#### 2.5.1.1 Properties

Key properties of ethanol and ethanol-gasoline blends are depicted in Table 2.7. And compiled in Figure 2.2

**Table 2.7:** Comparison of key properties of ethanol and ethanol-gasoline blends

| Properties | Gasoline | E-100 | E-85 | E-35 | E-10 | Remarks | Ref. |
|---|---|---|---|---|---|---|---|
| Viscosity $mm^2/s$ | 0.84 | 1.57 | 1.42 | ------ | ------ | @ 20 °C | [55] |
| | 0.48 | ------ | ------ | 0.69 | 0.53 | @ 30 °C | [56] |
| Flash Point °C | -65 | 13 | 5 - 8.5 | (-13.5) - (-15) | -40 | | [57] |
| | ------ | ------ | (-20) - (-28) | ------ | ------ | | [58] |
| | ------ | ------ | ------ | 31 | ------ | | [56] |
| RON °C | 88-100 | 108.6 | ------ | ------ | ------ | Research Octane number | [59] |
| | 91 | 114 | 107-110 | 97-98 | 94 | | [57] |
| | 86.4 | ------ | ------ | ------ | 87.4 | | [60] |
| MON °C | 80-90 | 89.7 | ------ | ------ | ------ | Motor Octane number | [59] |
| | 85 | 112 | 102.5-105 | 89-92 | 86 | | [57] |
| | 98.8 | ------ | ------ | ------ | 99.9 | | [60] |
| Octane number (ON) ° C | 86-94 | 98-100 | 105 | ------ | ------ | The average of RON and MON is ON | [55] |
| | 93.2 | ------ | ------ | 104.1 | 97.1 | | [56] |
| Cloud point °C | ------ | ------ | -30 | ------ | ------ | Not above | [61] |
| | -22 | ------ | ------ | 8* | 8* | *Above | [56] |
| Pour point °C | (-17) - (-19) | ------ | ------ | 0* | 0* | *Above | [56] |
| Calorific value MJ/Kg | 30-33 | 21.1 | ------ | ------ | ------ | Lower Heating Value | [59] |
| | 44.4 | 30 | 30.1-33.8 | 38.5-40.4 | 44.22 | | [57] |
| | 42.5 | 26.9 | 29.2 | ------ | 40.9 | | [62] |
| | 41.9-44.2 | 26.8 | 29.1 | ------ | ------ | Lower Heating value | [55] |
| | 34.84 | ------ | ------ | 30.92 | 33.19 | | [56] |
| | 44 | 26 | ------ | ------ | | Lower heating value | [63] |

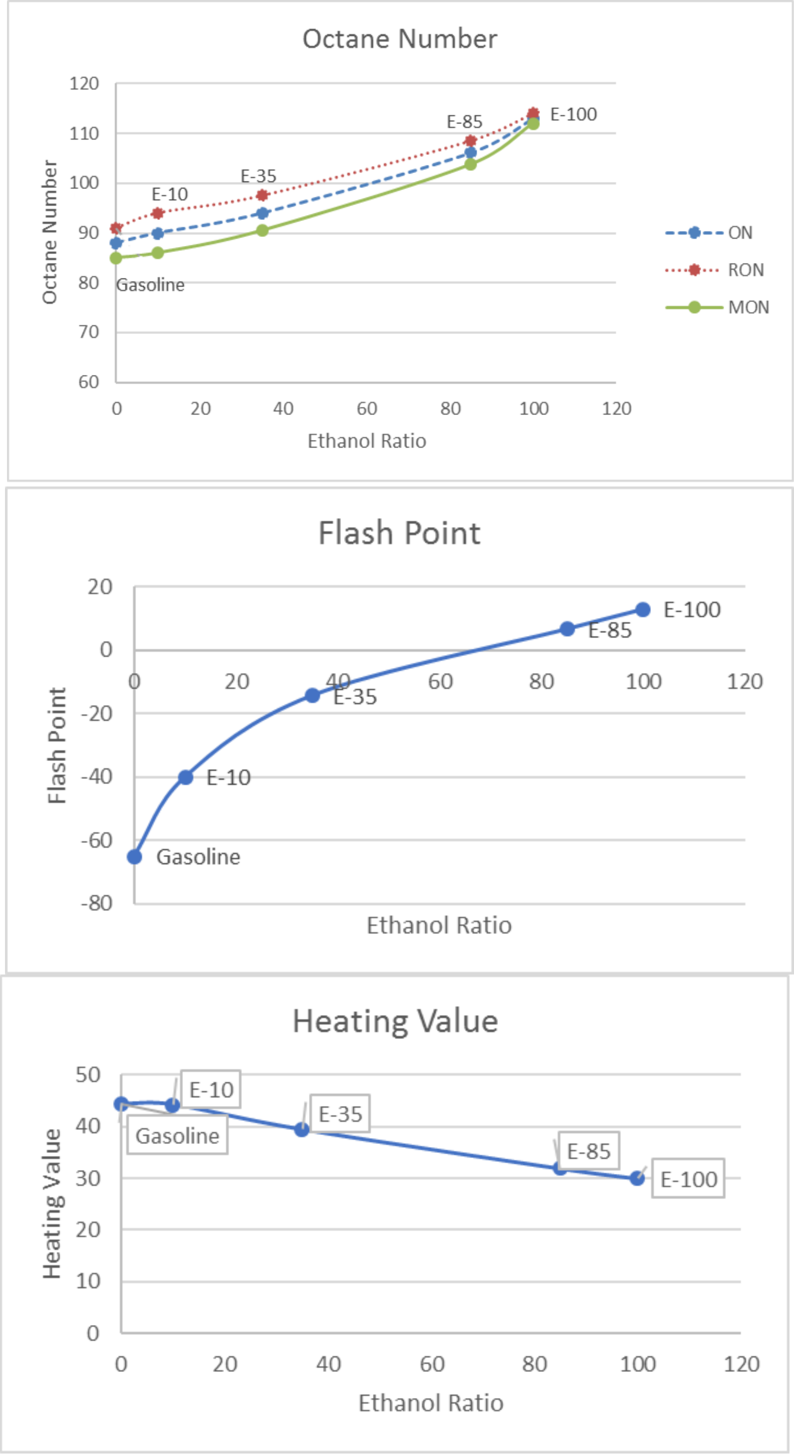

**Figure 2.2:** Comparison of key properties of ethanol and ethanol-gasoline blends

It can be seen from Figure 2 that the octane number increases with the amount of ethanol in the blend while pure ethanol having the highest octane rating [64] suggesting that pure ethanol has the highest antiknock properties of any of the blends or gasoline. Flashpoint of ethanol is also the highest of all the blends considered. It is also clear that the heating value of pure ethanol is lowest primarily due to the high oxygen content. It is also reported that viscosity increases with higher ethanol content with pure ethanol eliciting the highest viscosity [65]. Ethanol also has higher ignition and flashpoints than gasoline and thus is safer during handling and transport.

#### 2.5.1.2 Performance

It should be noted that similar to biodiesel, using pure ethanol warrants engine modifications [64]. Water being miscible with pure ethanol elicit corrosion issues [59]. Nevertheless, research suggests that once blended with gasoline, no engine modifications are necessary [66]. The heating value of ethanol is lower than gasoline; and thus, a higher amount of ethanol is required to achieve the same power output. Nevertheless, the amount of air required to get a full combustion is less for ethanol [66] due to its high oxygen content. Moreover, the latent heat of evaporation for ethanol is higher than gasoline, reducing the temperature of intake pipes of the engine and increasing volumetric efficiency.

#### 2.5.1.2.1 Brake Thermal Efficiency (BTE)

BTE is a function of the input heat to the engine in the form of fuel. It is used as a criterion for engine's efficiency to convert the amount of heat from the fuel to a mechanical energy and motion [67]. It was found that 5% ethanol presence in the fuel increases the BTE by 4-12% [68]. Turner et al. had used the E-85 blends to measure the performance of a high compression ratio, spark ignition engine. The results was an increase in the BTE with an increase in the knock effect due to the higher octane number of ethanol compared to gasoline [69].

#### 2.5.1.2.2 Brake Specific Fuel Consumption (BSFC)

It follows the same definitions in biodiesel blends as well. Calorific value and density of the fuel are important factors in BSFC measurement [67]. Koc et al.[59] found that BSFC values for E-50 and E85 were higher than the gasoline values by 16.1% and 36.4% respectively. This increment is depending on the ratio of ethanol. Because the heating value of ethanol is less than the value of gasoline by 35%, more amounts of ethanol needs to be burned to produce the same power [70]. This is the reason why the BSFC of E-85 was higher than E-50.

### 2.5.1.3 Emissions

Several studies were conducted to see the effect of ethanol blends on the emissions. It was shown that blending ethanol with fuels in especially low concentration ethanol enhances the engine performance and reduces emissions such as CO and NOx [60, 71].

He et al.[72] showed that emissions of CO, HC and NOx were drastically reduced with E-30 at idle and increased acetaldehyde emissions in the meantime. Hsieh et al.[66] concluded a dramatic decrease in CO and HC emissions due to leaning effect for different ratios of ethanol in ethanol-gasoline blends. The results were that CO emissions less than 0.6% when the engine is working at 2000 rpm and compression ratio 10:1. On the other hand, $CO_2$ emissions were increased due to improve in combustion characteristics. He also stated that NOx emissions depend on the operational conditions of the engine and not on the fuel conditions. NOx emissions were around 1000 ppm with the same engine conditions and parameters [66].

### 2.5.2 Ethanol Blend E-85

E-85 is one of the common blends used in the U.S. which consists of 85% ethanol in gasoline. E-85 is typically used in Flex Fuel engines – that have been manufactured to tolerate a range of (ethanol-based) fuel blends [73]. It should be noted that usage of E-85 in a non-flex fuel vehicle can lead to poor acceleration, a substantial increase in maintenance costs, and eventually component failure [73].

#### 2.5.2.1 Properties

Properties of E-85 are primarily dictated by the presence of molecular oxygen.

#### 2.5.2.1.1 Kinematic Viscosity

The viscosity of E85 is higher than gasoline and lower than E-100 and is attributed to the presence of hydrogen bonding [55].

#### 2.5.2.1.2 Flash Point

The flash point of E-85 is slightly above 5$^o$C [57] and is higher than pure gasoline but lower than E-100. However, according to the Renewable Fuel Association (RFA) [58], the flashpoint of E-85 could go significantly lower. The low flashpoint is favorable for engines performance and efficiency while posing some risks for fuel handling and safety.

#### 2.5.2.1.3 Octane Number

Octane number is a measure of gasoline fuel performance in spark ignition engines and provides an indication of the anti-knocking behavior of the fuel. Anti-knocking is an important parameter for gasoline engines [74]. If the fuel ignites before the piston reaches the desired point, i.e., top-dead-center, the combustion will generate a counter-power that will force the piston to move down when it is supposed to move up. This phenomenon is known as a knock, and it occurs when the octane number is low.  There are two common forms of octane ratings, i.e., Research Octane Number (RON), and Motor Octane Number (MON). Both types depend on the composition of the fuel blend. Also, there is what is known as combined octane number, which is the average of both

(RON) and (MON) ((R+M)/2)[75]. Reported octane numbers ranged from 105 [55] to 94-96 [58] and thus E-85 has excellent octane boosting properties.

#### 2.5.2.1.4 Cloud Point and Pour Point

Kheiralla [56] had compared the values of cloud and pour points of both E10 and E35 with pure gasoline. In all cases the cloud and pour points of both blends, E10 and E35, were the same and they were higher than cloud and pour points of gasoline. Results were shown in table 6.

#### 2.5.2.1.5 Calorific Value

For ethanol blends, Lower Heating Value is generally reported; and, the calorific value is slightly lower than normal heating value [76]. The lower heating value of E-85 was reported around 29.1 MJ/kg which is the higher compared to other blends [55]; however, the calorific value is lower than gasoline – again due to the presence of structural oxygen.

### 2.5.2.2 Performance

In general E-85 is reported to yield better engine performance than other lower concentration blends [59]. The performance of ethanol blends is proportional to the blends ratio – and increases as ethanol concentration increases in the blend [64]. E-85 has more different compositions from gasoline than any other ethanol blend [77] .It was shown that Brake Specific Fuel Consumption (BSFC) for E-85 was 36.4% higher as compared to pure gasoline or E-0 at compression ratio 11:1 [64]. Thermal efficiency of E-85 also increased by more than 3 -10% as compared to gasoline.

#### 2.5.2.3 Emissions

Studies report that emissions of NOx reduced when using E85 as opposed to gasoline; however, $CO_2$ emissions were the same [71]. Also, Hydrocarbon emissions were the lowest when using E-85. It was also reported that CO emissions were lowered by significantly when using E-85 as compared to gasoline [59]. Another study conformed reduction of CO, NOx, and non-methane hydro-carbon emissions by 72%, 48%, and 55% respectively when using E-85 [77].

#### 2.5.2.4 Advantages

1- E-85 contains a higher ratio of ethanol than other blends increasing the amount of heat absorbed to spread the fuel for injection. The latent heat of vaporization is 2.5 times higher than gasoline which reduces the temperature of the air charge at the intake. As such, air density increase allows more engine output [78, 79].

2- E-85 elicit higher octane ratings and thus allows higher knock resistance [79, 80].

3- E-85 could be used with higher compression ratio engines resulting in higher thermal efficiencies than gasoline [81].

4- E-85 reduces greenhouse gasses.

5- E-85 yields in better performance due to higher flash point than other blends and gasoline.

#### 2.5.2.5 Disadvantages

1- E-85 has a higher ratio of ethanol than any other blends that allows water solubility; and therefore, is more corrosive warranting engine modifications [79].

2- Handling this E-85 blend is more difficult due to the corrosiveness and higher flash point.

3- Storage problems due to susceptibility to microorganism growth which deteriorates the blend’s quality.

4- E-85 is susceptible to cold start problems.

5- The heating value of E-85 is lower than gasoline. Thus, engines running on E-85 would require higher amounts of fuel as compared to gasoline.

### 2.5.3 Gasohol

Gasohol is a general term used for alcohol-gasoline blends that contains at least 10% ethanol by volume [82]. However, the term also refers to blends of alcohol with a ratios between 10% and E85 ( Flex fuel) [83]. Most of the gasohol blends do not require major engine modifications due to the small ratio of ethanol to gasoline. In fact, Al-Hasan [63] reported the possibility of using up to 20% ethanol on spark ignition engines without any issues; however, Najafi [84] reported that spark ignition engines would not run as usual when the ratio of ethanol exceeds 20%.

### 2.5.3.1 E-35

E-35 is an ethanol-gasoline blend that has 35% ethanol and 65% gasoline. The reason to consider E-35 is because it was found that the highest ratio of ethanol that an engine could handle without any modifications  was this blend [56].

#### 2.5.3.1.1 Properties

##### 2.5.3.1.1.1 Kinematic Viscosity

Generally, the viscosity increased about 0.006 $mm^2/s$ for each 1% increment of ethanol and thus, the viscosity of E-35 was reported to be 41% more than that of gasoline. E-35 is less viscous than E-85 flex fuel.

##### 2.5.3.1.1.2 Flash Point

The flashpoint of E-35 is higher than pure gasoline due to the presence of ethanol. Nuevo [57], reported the flashpoint is between the range of -15 to -13$^{o}$C; however, Kheiralla [56] reported that value was more closer to +/-0$^{o}$C.

##### 2.5.3.1.1.3 Octane Number

The MON and RON of E-35 was reported to be ~10% higher than that of gasoline [56] and was between (89-92) and (97-98) respectively [57].

#### 2.5.3.1.1.4 Cloud and Pour Point

Cloud point of for E-35 was reported to be 8$^{o}$C [56]. It was also reported that cloud point for this blend is about (5-8) $^{o}$C above pour point. Cloud point is more important than pour point for heavy fuels with high boiling points.

#### 2.5.3.1.1.5 Heating Value

The heating value of E-35 was reported in the range of (38-40) MJ/Kg and thus ~11% lower than that of gasoline. It is reported that the heating value decreases by 0.1069 for every 1% increment of ethanol [56].

### 2.5.3.2 E-10

E-10 is the most common blend and is widely adopted in more than 35 countries around the world including USA, Canada, France, and many countries in Asia including Thailand and Philippines [71, 85]. E-10 used commonly in the United States; 21% of the fuel used for transportation is E-10.

#### 2.5.3.2.1 Properties

#### 2.5.3.2.1.1 Viscosity

It has been reported that the viscosity of the blend increases continuously and linearly by 0.006 mm$^2$/s @ 30 $^{o}$C for every 1% increment of ethanol [71]. The viscosity of E-10 was reported to be 0.5383 mm$^2$/s @ 30 $^{o}$C, which is slightly higher than gasoline viscosity

0.4872 $mm^2/s$ @ 30 $^oC$ [86]. However, Kheiralla also reported in another work that the viscosity of E-10 was 10.4% higher than gasoline [56].

#### 2.5.3.2.1.2 Flash Point

Nwufo [57] reported that the flash point of E-10 was higher than pure gasoline, and it increases as the ethanol ratio increases. Kheiralla [56] was not able to determine the flash point of E-10 as the fuel starts to ignite before its flash point can be determined due to the differences of the flash points between ethanol and gasoline. Consequently, the flash point of E-10 and other blends would depend on and would be dictated by the flashpoint of the more volatile substance.

#### 2.5.3.2.1.3 Octane Number

The octane number of E-10 was found to be 93.2 which was 4% higher than that of gasoline. However, E-10 has the lowest octane number among ethanol blends. The octane number was found to be increased by 0.29 for every 1% increment of ethanol [56, 57].

#### 2.5.3.2.1.4 Cloud and Pour Point

According to Kheiralla [56], E-10 will have the same values of cloud and pour points as E-35; which are ~8, and 5-8 $^oC$ respectively. However, the cloud point of E-10 is still higher than that of gasoline [71].

###### 2.5.3.2.1.5 Calorific Value

The heating value of ethanol is 1.6 times lower than that of gasoline and as a result, there will be a need for 1.5-1.8 times more ethanol to elicit the same energy output. The heating value for E-10 is around 9511 cal/g [66].

##### 2.5.3.2.2 Performance

The fuel economy of E-10 is the same as gasoline, but offers better environmental benefits [87]. It was found as the optimum blend that can work under different compression ratios [66]. Generally, ethanol blends improve engine performance [64] with an increase of power produced by 5% [88, 89]. Ethanol affects the intake temperature due to its almost 3x higher latent heat of vaporization than gasoline decreasing the intake manifold’s temperature; and thereby increasing the engine efficiency [63, 90]. However, BSFC of E-10 is lower than E-85; however, is still slightly higher than pure gasoline – and BSFC be improved by increasing the compression ratio [72].

##### 2.5.3.2.3 Emissions

It was reported that E-10 could reduce CO emissions by up to 30% [91]. In fact, the addition of ethanol up to 20% would help decrease CO and HC emissions, however, would be increased if the ratio of ethanol goes higher. In contrast, $CO_2$ elicits an opposite behavior - this is because ethanol increases the engine’s efficiency by allowing more complete combustion – increasing $CO_2$ emission eventually [63]. It was also reported that NOx emissions are decreased with the increase of ethanol content [92]. Also, NOx was lower for E-10 compared with gasoline [92]. However, it was higher than other blends like E-30 [72].

#### 2.5.3.2.4 Advantages of Gasohol

1- Gasohol blends can be used without any major engine modifications.
2- Increased flashpoint enhances combustion properties.
3- Gasohol blends efficiently reduce exhaust emissions such as CO (up to 15%) and NOx [82].
4- Gasohol increases the overall efficiency of engines.
5- Improves power [92].
6- Fuel economy does not change compared to gasoline [87].

#### 2.5.3.2.5 Disadvantages

1- Ethanol is miscible in water, which could promote corrosion of engine/fuel system metal parts.
2- Not that effective for displacing fossil fuels due to the low concentration blends.
3- The high flash point raises safety concerns during handling, storage and transportation.

## 2.6 Ethanol-Diesel Blends (E-Diesel)

Ethanol-Diesel also referred to as E-Diesel is another fuel blend that uses ethanol in diesel targeted for compression ignition engines. Initial work started with methanol (M-

100) as a substitute for diesel fuel [93, 94]; however, as methanol prices started to increase, ethanol was tested as a substitute due to its cheap price [94]. Anhydrous ethanol is miscible with diesel fuel making stable solutions. However, ethanol-diesel blends are reported to be less stable than ethanol- gasoline and other blends. In fact, the blends would separate below 10$^{o}$C when 20% ethanol is blended with diesel [94]. Two approaches can be used to maintain the stability of the blend: adding emulsifiers that produce stable emulsions or adding co-solvents that produce stable solutions. Nonetheless, the current approach is to prepare ethanol-diesel blends with less than 20% ethanol. E-diesel has been a successful replacement for M-100 and succesfully demonstrated in transit buses.

### 2.6.1 Properties

Table 2.8 presents properties of a common blend E-Diesel blend with 10% ethanol. It could be seen that viscosity of E-Diesel is lower than diesel. The flashpoint and pour points of E-diesel are 65% and (from 10$^{o}$ to 20$^{o}$ C) lower than that of diesel fuel. Interestingly, the cloud points of both fuels remained the same. The heating value of E-diesel was 90% of that of diesel [85].

**Table 2.8**: Select properties of E-diesel 10 and diesel

| Type of fuel | Viscosity mm$^2$/s @ 20 C | Flash Point C | Cloud Point C | Pour Point C | Heating Value MJ/Kg | Ref. |
|---|---|---|---|---|---|---|
| Diesel | 5.61 | 74 | 5 | 5 | 44.51 | [85] |
| E-D 10* | 5.46 | 25 | 5 | -10 | 43.19 | [85] |

*ethanol-diesel blend with 10% ethanol

### 2.6.2 Performance

It is reported that usage of E-Diesel generally in diesel engines presents some concerns; primarily, the risk fire or explosion due to the lower flash point of ethanol as compared to diesel [95]. The engine performance is also adversely affected due to lower heating values of the blend that leads to higher fuel consumption as compared to diesel. Also, the efficiency is also reported to be lowered as a result of decreased cetane number of the diesel blend (as ethanol is an octane enhancer which is the antitheses to cetane). Moreover, using alcohol in high ratios will have corrosion effects which can causes engine deterioration [96].

Nevertheless, some of these drawbacks could be addressed: First, using low ratios of alcohol would help eliminate issues associated with corrosion and compatibility. Second, performance can possibly be improved by using fuel pumps with higher capacity. Additionally, the cetane number could be improved by using cetane enhancers as additives to the blend [96].

### 2.6.3 Advantages

1- Ability to use renewable ethanol as an additive in compression ignition engines.

2- Oxygenation that assists combustion.

### 2.6.4 Disadvantages

1- Cannot eliminate the reliance on fossil fuels completely since only minor quantities of ethanol could be blended.

2- Fire and explosion hazard.

3- Adverse impact on engine performance due to lowering of cetane number.

4- Lower energy content compels higher fuel consumption.

### 2.6.5 Ethanol-Biodiesel (E-Biodiesel)

Generally, blending ethanol to biodiesel is meant to improve oxygenation properties of biodiesel. These blends follow the common nomenclature with the number following prefix E depicting the percentage of ethanol and that following prefix B representing the percentage of biodiesel. The most common E-Biodiesel blends are E5B95, E10B90, and E15B85 representing 5%, 10%, and 15% of ethanol blended with 95%, 90%, and 85% biodiesel respectively.

The purpose of blending ethanol is to improve most important fuel properties related to the injection process, i.e., flash point, pour point, cloud point, and viscosity. It was found that adding 3% ethanol to biodiesel reduces the flash point of the blend almost to ethanol’s flash point. Also, when the ratio of ethanol increases, kinematic viscosity decreases because ethanol’s viscosity is lower than that of biodiesel. The pour point of the blend follows the same behavior as ethanol’s pour point is significantly low compared to that of biodiesel. However, pour point improvements are not notable beyond E10B90 - when the pour point decreased only by less than 3°C with ethanol addition. As ethanol has a better behavior in low temperatures than biodiesel, ethanol addition improved cold-flow properties such as cloud point, pour point and cold filter plugging point [97].

Properties related to performance also improved as a result of ethanol addition. Viscosity has a direct effect on atomization of the fuel in the combustion chamber and atomization affects the combustion process thereby impacting the overall efficiency. In general increased viscosity negatively affects fuel atomization and thus efficiency [98]. By adding ethanol to biodiesel, viscosity is decreased enhancing efficiency. Consequently, combustion is improved and in turn reducing the formation of engine deposits [97]. The most recommended blend among E-Biodiesel blends is E15B85. This is because E15B85 results in the most improved engine performance and emissions profile. Some drawbacks include lowering of lubricity compared to other blending ratios, and the low flashpoint that causes safety concerns. Nevertheless, these issues could be addressed by using additives that help increase flashpoint and lubricity to acceptable limits [97].

### 2.6.6 Other Blends

There are several less common renewable fuel and fossil fuel blends that are still under research. Some of these blends are binary while others are ternary.

### 2.6.6.1 Binary Blends

#### 2.6.6.1.1 Bio-Oil /Biodiesel Blends

Bio-oil is derived from thermal depolymerization of biomass under pyrolytic conditions in the absence of oxygen. The resulting product consists of two phases, an oily phase termed bio-oil and an aqueous phase [99].

Bio-oil was found to be compatible with biodiesel; however, using bio-oil in its neat form in diesel engines might not be effective due to significant variability of properties resulting from complex structure and composition. Nevertheless, the use of bio-oil as an additive has been investigated. The oily phase is more soluble than the aqueous phase in biodiesel due to the low water content [99]. The aqueous phase once processed to be compatible with biodiesel is called as polar oil. It has been demonstrated that modified diesel engines can successfully run on bio-oil [100].

Properties of the two phases were studied separately, obtained from and compared to the properties of biodiesel. The properties studied were viscosity and heating value.
Table 2.9 shows properties of bio-oil obtained by pine chips and pine pellets pyrolysis. It could be seen that the viscosity of the oily bottom phase is higher than polar oil for both feedstock, and viscosity of the oily phase of pine chip is the highest. This indicates that only a small quantity of bio-oil could be used as an additive without adversely affecting fuel properties of the blend. It could also be seen that the heating value of the oily bottom phase is higher than polar oil for both feedstock; however, the heating value for

biodiesel is the highest [99]. The likely reason for low heating values of bio-oil is the significant presence of structural oxygen and presence of some moisture.

**Table 2.9:** Properties of bio-oil and biodiesel

| Properties | Pine Chips | | Pine Pellets | | Biodiesel |
|---|---|---|---|---|---|
| | Polar oil | Oily bottom | Polar oil | Oily bottom | |
| Viscosity mm$^2$/s @ 25ºC | 125.6 | 140.2 | 44.8 | 76.8 | 6.4 |
| Heating Value MJ/Kg | 17.9 | 23.8 | 19.5 | 24.8 | 39 |

### 2.6.6.1.2 Methanol-Gasoline

Methanol in gasoline, also commonly referred to as gasohol is another blend targeted for spark ignition engines [83] . The most common methanol-gasoline blends are M10 and M20.

#### 2.6.6.1.2.1 Properties

Methanol has high octane number (108.7). It has been reported that high octane number and oxygen content leads to more efficient combustion and thus higher efficiency [83]. As such, Zaid [101] has suggested that methanol-gasoline blends can be used as an alternative to engines with higher compression ratio due to superior performance of the fuel blend. Due to oxygenation, the emissions profile is also improved [102, 103].

### 2.6.6.1.2.2 Performance

Using methanol with gasoline is reported to result in better engine performance. Methanol addition improved brake thermal efficiency (BTE) as compared to other alcohol-gasoline blends. Methanol has about 50% more oxygen per mass basis than other common alcohols, which leads to improved combustion quality and higher BTE [83]. Also, latent heat of vaporization of methanol (1103 KJ/Kg) is higher than other alcohols and gasoline (305 KJ/Kg) [104-106] leading to a decrease in the intake manifold's temperature (as methanol absorbing more heat). As a result, the density of the incoming charge increases and thereby increasing the efficiency. It has been concluded by Agarwal [83] that BTE for M20 was higher than M10. On the other hand, Bardaie and Janius [107] reported that the engine's power decreased by 4-5% when pure methanol was used. BSFC of methanol blend was also reported to be higher under some engine operation conditions compared to gasoline [105, 106].

### 2.6.6.1.2.3 Emissions

It was reported that methanol addition results in better emissions profiles as compared to other alcohols or gasoline due to higher oxygen content allowing more complete combustion. Arapatsakos' [108] work with M10, M20 and M30 found that by increasing methanol ratios, fuel consumption increased and CO and HC emissions decreased. However, HC emissions significantly increased using pure M100 methanol [109]. Also, HC emissions from this blend were higher than gasoline at low engine speeds. Therefore, HC emissions differ depending on engine operational conditions. Yanju [106] reported that CO and NOx emissions decreased with the increase of methanol/gasoline ratio. In particular, M85 reduced CO and NOx by 25% and 80% respectively.

#### 2.6.6.1.2.4 Advantages

- Methanol can be used for light to mid-duty engines due to presence of structural oxygen that improves octane number of the fuel and thus efficiency.
- Improved emissions profile.

#### 2.6.6.1.2.5 Disadvantages

- Methanol is corrosive and is not safe unless the engine modifications are done.

### 2.6.6.2 Ternary Blends

#### 2.6.6.2.1 Gasoline-Ethanol-Methanol (GEM)

Tertiary blends combine two renewable additives such as alcohols or esters to with fossil fuels; and in the case, ethanol and methanol are added to gasoline. The letters stand for respective components, i.e., G for gasoline, E for Ethanol, and M for Methanol. The number next prefixes represent the percentage of each component in the blend. EM 10, for example, is the most common blend which means ethanol and methanol are 10% of the GEM blend and so on. This specific blend combines ethanol and methanol with gasoline in order to have an iso-stoichiometry of air: fuel which is geared toward generating a balanced and reduced amount of emissions [104].

#### 2.6.6.2.1.1 Performance

It was mentioned earlier that the latent heat of vaporization of ethanol is almost 3 times that of gasoline; apparently, methanol has a latent heat of vaporization 3.5 times higher than of gasoline. The higher latent heat of vaporization reduces intake manifold temperature increases the volumetric efficiency leading to better combustion and an increase in the output torque, especially, at a high engine speeds. Since methanol has a latent heat of vaporization even higher than that of ethanol, engine performance is even better. Elfasakhany [104] reported that brake power, torque, and efficiency were higher for GEM than gasoline especially at high speeds; nevertheless, the increase was non-significant at low engine speeds.

#### 2.6.6.2.1.2 Emissions

Turner [110] studied the effects of GEM blends on emissions, NOx and $CO_2$, and showed that these blends can reduce emissions moderately compared to pure gasoline. Slieghem [111] studied the effects of GEM blends on emissions of NOx and CO and found that these blends produce fewer emissions than pure gasoline, but more emissions than pure methanol. Elfasakhany [104] found that EM10 gives lower CO and NOx emissions than ethanol, but higher than methanol. GEM blends also resulted in moderate performance compared to M or E blends. It was also reported that emissions and performance of GEM blends depend on the engine’s speed and load.

The higher latent heat of vaporization leads to complete combustion of incoming fuel leading to fewer emissions. Therefore, methanol produces the lowest CO and HC emissions due to the lean-effect, which refers to the burning of the fuel with an excess amount of air. This is because of the high (50%) oxygen content in methanol. The oxygen ratio in ethanol is around 34.8% which is also helpful in improving the lean-effect. Generally, GEM 10 reduces emissions moderately at all engine speeds.

#### 2.6.6.2.1.3 Advantages

1- Emissions profile from the GEM blends are better than pure gasoline.

2- The engine performance (efficiency, torque and power) is improved especially at higher speeds.

#### 2.6.6.2.1.4 Disadvantages

1- Only lower (renewable) blend ratios are effective (up to 20%); thus, cannot displace significant amounts of fossil fuels.

2- Emissions and performance are not as good as when using pure alcohol-based fuels.

#### 2.6.6.2.2 Ethanol-Biodiesel-Diesel (EB-Diesel)

This is another ternary blend targeted for compression ignition engines. The diesel engine cannot run properly on E-diesel without modifications due to immiscibility issues of ethanol in diesel [112] and the cetane lowering effect of ethanol [113]. Nevertheless, ethanol can improve cold start properties once mixed with diesel. Also, ethanol has relatively high oxygen content which is known to improve emissions profile. To rectify issues with ethanol, addition of biodiesel has been attempted and the fuel blend EB-Diesel is proposed that consists of ethanol, biodiesel and diesel targetting compression ignition engines [15, 112]. It was reported that biodiesel works as an emulsifier with enhancing lubricity properties of the fuel [112, 114]. Some blends of EB-Diesel reported are Fernando D76 E4 B20 [112] and Hulwan [114] D70 E20 B10, D50 E30 B20, and D50 E40 B10.

###### 2.6.6.2.2.1 Properties

Table 2.10 illustrates some key properties of select EB-Diesel. As can be seen EB-Diesel blends significantly improved cold flow properties and oxygenation as compared to diesel fuel. The best results were obtained with D50 E40 B10 with biodiesel derived from Jatropha [114]. It was also reported that the D76 E4 B20 blend has the ability to stay as a stable micro emulsion even in the presence of some moisture [112] while improving lubricity of the fuel.

**Table 2.10:** Properties of EB-Diesel

| Fuel Properties | Diesel D100 | Ethanol E100 | Biodiesel B100 | D70 E20 B10 | D50 E30 B20 | D50 E40 B10 |
|---|---|---|---|---|---|---|
| Viscosity $mm^2/s$ | 2.64 | 1.10 | 4.64 | 2.380 | 2.40 | 2.01 |
| Heating Value MJ/Kg | 44.89 | 28.18 | 38.08 | 39.930 | 38.96 | 36.33 |
| Cetane Number | 54 | 8 | - | 50 | 50 | 41 |
| Flash Point C | 50 | 12 | - | 14 | 12.50 | 12 |
| Pour Point C | 0 | - | 0 | -3 | -9 | -12 |
| Oxygen content %w | 0 | 34.73 | 10.79 | 7.77 | 12.21 | 14.53 |

#### 2.6.6.2.2.2 Performance

EB-Diesel blends display comparable or sometimes better performance as compared to diesel. Studies reported an increase in Break Thermal Efficiency (BTE) at high loads and speeds of 1200 and 1600 rpm with increasing ethanol proportions in the blend. However, this also lead to increase in BSFC requiring more fuel to produce the same power [114-116].

The increased presence of ethanol impacts injection timings which creates an ignition delay. The delay would allow the charge to mix well before it ignites producing more power. The advantage of the ethanol and biodiesel presence is the ability to modulate cetane number of the fuel by changing ratios of the two oxygenates. Oxygen enrichment is also reported to help mixing as well [114, 117].

#### 2.6.6.2.2.3 Emissions

Generally, NOx emissions depend on internal temperature in the cylinder, the oxygen content in the fuel, and residence time of the charge in the combustion chamber. NOx emissions, therefore, will be decreased for the EB-Diesel blends compared to diesel at low load and at both 1200 and 1600 rpm. CO emissions depend on air/fuel ratios in any blend as well as combustion temperature. CO emissions increased drastically at lower loads and decreased at high loads for EB-diesel blends compared to diesel fuel [114].

## 2.7 Summary

This chapter discusses properties, emissions profiles and performance of different biofuel blends that has been attempted for spark-ignition and compression ignition engines. The most common biofuel blends targeted for compression ignition engines are biodiesel-diesel blends while ethanol-gasoline blends are targeted for spark-ignition engines. Less common fuel blends for gasoline engines include methanol-gasoline (M-gasoline) and gasoline-ethanol-methanol (GEM); bio-oil/biodiesel, ethanol-diesel (E-Diesel) and ethanol-biodiesel-diesel (EB-Diesel) are targeted for compression ignition engines.

In general, emissions profile improves with addition of oxygenates (regardless of the engine type). Addition of oxygenates also improves combustion properties leading to increased efficiency and power in general. However, due to increased oxygen content, addition of oxygenated fuels into fossil fuels reduces the energy content also increasing break specific fuel consumption as compared to using fossil fuel counterpart(s) alone.

Addition of biodiesel to diesel fuel improves the cetane number of the final blend while also improving its lubricity properties. Addition of ethanol to diesel in moderation improves the cold-flow properties of the blend; however, also reduces the cetane rating. Addition of biodiesel to ethanol-diesel blends can counter the cetane reduction while also improving the miscibility of ethanol in diesel fuel – enhancing the quality of the final fuel blend.

Addition of alcohols to gasoline increases the octane rating of the final blend. Addition of oxygenated renewable alcohols to gasoline improves the cold-flow properties of the blend.

From this meta-analysis, it is surmised that E-10 to be the most pragmatic fuel blend for unmodified spark-ignition engines and B-20 to be the one for compression ignition engines. GEM seem to have significant promise as spark-ignition alternative blends while EB-diesel (with low ethanol content) for compression ignition engines; however, needs to be thoroughly investigated for engine performance and safety before being adopted for commercial use.

# CHAPTER III

# DEHYDRATION OF N-PROPANOL AND METHANOL TO PRODUCE ETHERIFIED FUEL ADDITIVES [1]

## 3.1 Introduction

Due to the advances of biodiesel industry, a glut of glycerol has been resulted and there is a need for finding alternative uses for methanol contaminated glycerol. Due to the chemical composition of glycerol and methanol, dehydration and rearrangement could result in deoxygenated products that could be used as fuel additives. However, how methanol-containing glycerol could be converted into dehydrated products have not been widely investigated. This work attempts elucidating reaction conditions and performance parameters of an analogous system using methanol and n-propanol as model compounds reactants while using catalysts that have been proven to be effective for transesterification.

Ethers consist of an oxygen atom bonded to two alkyl or aryl groups, or one alkyl and one aryl group [118]. Ethers have properties that might be beneficial as fuel additives to

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[1] Reprinted with permission from “DEHYDRATION OF N-PROPANOL AND METHANOL TO PRODUCE ETHERIFIED FUEL ADDITIVES” by Husam Almashhadani, Nalin Samarasinghe, and Sandun Fernando, 2017. AIMS-Energy (American Institute of Mathematical Sciences) Journal, 2017, 5(2): 149-162.doi; 10.3934/energy.2017.2.149. Copyright [2017] by Husam Almashhadani, Nalin Samarasinghe, and Sandun Fernando.

biodiesel and other biofuels. Ethers have good solubility in hydrophilic and hydrophobic solvents making them compatible with esters such as biodiesel [119].

Ethers can be synthesized through several methods. The most common ones are bimolecular dehydration and Williamson method [118, 120]. In dehydration reaction, alcohol is treated with a strong acid under dehydrating conditions. The general equation for dehydration reaction would be as follows [121]:

$$ROH + R'OH \longleftrightarrow ROR' + ROR + R'OR' + H_2O \quad (3.1)$$

More specifically, above reaction may proceed according to following elementary steps:

$$ROH \longleftrightarrow ROR$$

$$R'OH \longleftrightarrow R'OR'$$

$$ROH + R'OH \longleftrightarrow ROR'$$

In this work, we will use bimolecular dehydration to produce dipropyl ether (DPE) and methyl propyl ether (MPE) from methanol and n-propanol. It is anticipated that when a mixture of two alcohols was reacted through etherification, the result would be a mixture of three types of ethers as given in Scheme (3.1). In this case, three products, i.e., DPE, MPE, and dimethyl ether are anticipated.

DPE and MPE have been of interest in chemical and pharmaceutical industry. DPE, a common oxygenated hydrocarbon, is used widely in industry as a solvent [122, 123]. MPE is an isomer of diethyl ether, and has found many applications such as analgesic reagent [124], anesthetic [125] in the medical industry and a solvent and fuel additive [126] in the chemical industry.

DPE can be prepared from reacting 1-propanol by dehydration [127]. It has been predicted that DPE can be obtained through dehydration reaction from an already separated mixture of DPE and n-propanol using sulfuric acid as a catalyst. The mixture would be separated using extractive distillation and pressure-swing distillation [127]. Another general example is producing diethyl ether from ethanol dehydration. This work was done in the range of temperature of 140-250$^{o}$C with three different catalysts [128]. 1-Butanol has also been used to produce di-butyl ether; in that work, acidic ion-exchange resin Amberlyst 36 was used as the catalyst [129].

MPE has been produced as fraction of biocrude produced using Hydrothermal Upgrading (HTU) process by thermochemical conversion of biomass. This process requires high temperature and pressure, around 350$^{o}$C and 180 bar respectively [130]. However, MPE comprised of only 2.5% of the bio-crude produced. Other work done on methanol-isobutanol, ethanol-isobutanol and, ethanol etherification [128] also followed dehydration principle [131]. Above examples show that dehydration is a feasible method to produce ethers using alcohols.

Work to date on dehydration reveals that the yields are still low. Also, the high temperatures and pressures required makes the process energy intensive and less economical. Additionally, there is little work has been done on strategies to increase the yield, conversion, and selectivity of ethers produced from common alcohols. This present work is geared toward identifying key parameters that impact alcohol conversion and ether yields and selectivity using methanol and 1-propanol with the intention of identify the best combination of parameter that would cost effectively produce dehydrated ethers. The novelty of this work is the study of the impact of three different catalysts that have distinct properties, i.e., sulfuric acid (a homogeneous duel proton donor), Amberlyst 36 (a heterogeneous strongly acidic cation exchanger) and titanium isopropoxide (a condensable base in the isopropoxide form that becomes acidic once condensed to $TiO_2$).

## 3.2 Material and Methods

Initial studies were conducted to establish catalysts and conditions that promote n-propanol etherification to form di-propyl ether. The rationale was that these variables would be a good starting point for MPE synthesis using methanol and n-propanol.

Studies with n-propanol were conducted in the presence of 1% (w/w) sulfuric acid, amberlyst-36, and titanium isopropoxide. The reaction temperatures ranged from 100 - 160$^{o}$C at 20$^{o}$C intervals with a reaction time of 4hrs.

Prices of the catalysts vary depending on the type of the catalyst and the amount of order. Sulfuric acid was priced as an industrial grade in the range of \$200-300/ton for commercial scale bulk orders [132], whereas titanium isopropoxide was priced higher with about \$1-2 /Kg (\$1000-2000/ ton) for bulk orders. Amberlyst 36, on the other hand is not available on a commercial scale and was priced for about \$355/Kg provided from Sigma Aldrich.

Etherification studies on n-propanol methanol mix was conducted with select catalysts identified based on proposal etherification studies under the same conditions. The only exception was that in this case, 1% and 5% (w/w) of catalyst concentrations were tested. In this case, three products, i.e., DPE, MPE, and dimethyl ether (DME) are anticipated. However, we will report DPE and MPE data as a result of DME being a gaseous product and is of less use as a liquid fuel additive.

### 3.2.1 Response Measurements

Primary variables that were calculated include substrate conversion, product yield and selectivity. For the case with n-propanol, aforementioned variables were calculated as follows:

Yield of DPE = $\frac{n_{(DPE)}}{n^{o}_{(n-propanol)}}$ Eq. 3.1

Selectivity Toward DPE = $\frac{n_{(DPE)}}{n^{o}_{(n-propanol)}+n_{(n-propanol)}}$ Eq. 3.2

Eq. 3.3

Propanol Conversion = $\frac{n^{o}_{(n-propanol)}-n_{(n-propanol)}}{n^{o}_{(n-propanol)}}$

Where

n= Final Number of Moles

$n^{o}$= Initial Number of Moles

When a methanol and propanol mixture was used, the variables were calculated as follows:

#### 3.2.1.1 Ether Yields

Yield of DPE = $\frac{n_{(DPE)}}{n^{0}_{(n-propanol)}}$ Eq. 3.5

Yield of MPE = $\frac{n_{(MPE)}}{n^{0}_{(n-propanol)} + n^{0}_{(methanol)}}$

#### 3.2.1.2 Ether Selectivity

Selectivity Toward DPE = $\frac{n_{(DPE)}}{n_{(DPE)}+n_{(MPE)}}$ Eq. 3.6

Selectivity Towards MPE = $\frac{n_{(MPE)}}{n_{(DPE)}+n_{(MPE)}}$ Eq. 3.7

#### 3.2.1.3 Substrate Conversion

Propanol Conversion = $\frac{n^{0}_{(n-propanol)}-n_{(n-propanol)}}{n^{0}_{(n-propanol)}}$ Eq. 3.8

Methanol Conversion = $\frac{n^{0}_{(methanol)}-n_{(methanol)}}{n^{0}_{(methanol)}}$ Eq.3.9

Where

n= Number of Moles

$n^{0}$ = Initial Number of Moles

### 3.2.2 Materials

#### 3.2.2.1 N-propanol Etherification

Three catalysts were used: Sulfuric acid was obtained from J.T. Baker with an assay of 95.9%; Amberlyst 36 was provided from Sigma Aldrich with a water content of (51-57)

% and a total pore volume of 0.2 ml/g, particle size 0.6-0.85 mm, surface area 33 $m^2/g$, >1.95 eq/L exchange capacity; Titanium iso-propoxide (colorless to yellow liquid with a density of 0.96 g/ml at 20 $^oC$, boiling point of 232 $^oC$, and molecular weight of 284.22 g/mol) was provided by Alfa Aesar company with > 97% purity. All the catalysts were used at 5% w/w concentration. Other reactants used were n-propanol and di-propyl ether and were obtained from Sigma Aldrich with a purity > 99%.

#### 3.2.2.2 Methanol and N-propanol Etherification

Methanol (99.8% assay with a maximum of 0.1% water content) was obtained from VWR. Other reactants, n-propanol (99.7% assay), di-propyl ether (> 99% assay) and MPE (97% assay), were obtained from Sigma Aldrich. Methyl-propyl-ether (Methoxypropane) and Di-propyl-ether were used as standards.

### 3.2.3 Equipment

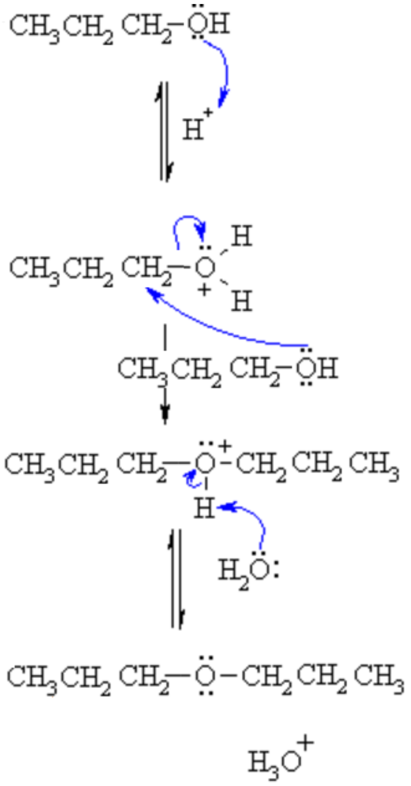
The reactions were carried out under stirring in a 25ml high pressure vessel (Buchiglas USA) rated for 100 bar at 200 $^OC$ with temperature/pressure readout (it should be noted that the pressure in the vessel varied based on reaction temperature, and type and concentration of catalyst. The pressure in general ranged between (5-30) bar for Amberlyst 36, and between (10-40) bar for sulfuric catalyzed reaction). Weight measurements were carried out in a scale (PA 120) (with 0.001mg sensitivity). Quantitative product analyses were carried out in a Gas Chromatograph (Agilent

Technologies Model 6850) and Liquid Chromatograph (Agilent Technologies Model 1120 Compact LC).

### 3.2.4 Reaction Procedure (N-Propanol Etherification)

The reaction between two n-propanol molecules in the presence of acid catalysts is expected to proceed according to Scheme (3.2) as follows:

$$\underset{\text{n-propanol}}{2C_3H_8O_{(l)}} \xleftrightarrow{\text{Catalyst}} \underset{\text{DPE}}{C_6H_{14}O_{(l)}} + H_2O_{(l)}$$



**Scheme 3.2:** Mechanism of acid catalyzed etherification of n-propanol (adopted from [2])

The reaction is exothermic; however, energy input is necessary to overcome kinetic limitations. Therefore, the reaction progresses only with adequate energy input.

In terms of the methods, initially, the empty weight of a 32-ml vial was recorded. Then, reactants were added into the vial in a stepwise manner starting with 4 ml of n-propanol and 5% w/w of catalyst (note: equal catalyst weights were used since catalytic activity comparisons in biodiesel production generally uses mass basis rather than proton concentrations). The weight of the vial after addition of the chemical (s) was recorded. When the catalysts were solid, the weight of the catalysts was recorded separately. The chemicals and the magnetic stir-bar were added to the reactor securely sealed and placed in a stir hotplate (with stirring speed 700-800 rpm) for the reactions to progress. Once the reaction was over, the products were swiftly transferred to collection vials and sent for further analyses (GC, LC or weight/volume measurement) as needed.

### 3.2.5 Reaction Procedure (Methanol and Propanol)

The reaction between methanol and propanol progresses according to Scheme (3.3) as follows:

$$6CH_3OH_{(l)}+2C_3H_8O_{(l)} \xleftrightarrow{\text{Catalyst}} C_4H_{10}O_{(l)}+C_6H_{14}O_{(l)}+C_2H_6O_{(g)}+5H_2O \quad (3.3)$$

Methanol N-propanol MPE DPE DME

More specifically, the reaction(s) would follow elementary pathways as depicted below:

$$2CH_3OH \longleftrightarrow C_2H_6O + H_2O$$

$$2C_3H_8O \longleftrightarrow C_6H_{14}O + H_2O$$

$$CH_3OH + C_3H_8O \longleftrightarrow C_4H_{10}O + H_2O$$

The procedure for methanol and n-propanol etherification was similar to above except that the amounts of the reactants were different, i.e, 2 ml of methanol and 2 ml of n-propanol. The catalysts used in this case were sulfuric acid and Amberlyst-36 at 1% and 5% w/w concentrations.

### 3.2.6 Calibration Standard Preparation

The calibration standard consisted of methanol, n-propanol, methoxypropane, and di-propyl ether. Standard curves were developed by mixing above chemicals in predetermined ratios. When necessary, an internal standard (ISTD) was also used. An ISTD was used to account for any errors associated with sample handling. This was done by incorporating a correction factor as a result of internal standard analyses.

### 3.2.7 Gas Chromatography (GC) Analysis

The top phase of each sample was analyzed via the GC. Each sample consisted of 1 ml total volume. The GC method consisted of following parameters:

- Column Information: Model (J&W 122-703E), Capillary Column with dimensions (30m X 250um X0.25 um)
- Inlet type (EPC split-splitless inlet), and temperature is 220°C

- Outlet Temperature: 240°C
- Oven Temperature: 250°C
- Gas Carrier and flow rate: Helium, 1.0 ml/min
- Detector: Flame Ionized Detector

### 3.2.8 High Performance Liquid Chromatography (HPLC) Analysis

The bottom aqueous phase was analyzed using HPLC. After separation from the top phase, the bottom phase was neutralized and filtered (to remove any solid material) before injecting to the HPLC. Neutralization was performed using NaOH for acid catalyzed reactions. During neutralization, the neutralizing solution (NaOH) was added dropwise while stirring and monitoring pH. The sample was considered neutral when the pH reached 7.0 ± 0.1. Sample filtration was done sequentially using 0.8 um, 0.45 um, and 0.25 um syringe filters respectively. Then, samples were diluted as appropriate to be compatible with HPLC column and injected manually to HPLC. The HPLC method consisted of following parameters:

- Column Information: Supelcogel 610H (30 cm X 7.8 mm).
- Flow rate: 0.5 ml/min.
- Mobile phase: 0.1% phosphoric acid.

### 3.2.9 Statistical Design

The n-propanol etherification (Ancillary Study) was done as a Completely Randomized Design (CRD) that consisted of one replicate and 12 units, whereas methanol and propanol etherification was done as a full factorial design. In this design, all the variables and levels were randomized with three replicates using JMP software (SAS Institute). Results were obtained, organized, and analyzed using JMP software as well.

## 3.3 Results and Discussion

### 3.3.1 Propanol Etherification (Ancillary Study)

Substrate conversion and DPE yields & selectivity information is depicted in Figure 3.1. According to Figure 3.1A, the conversion clearly increased with increasing temperature for all the catalysts tested. Sulfuric acid clearly resulted in higher substrate conversions as compared to the other two catalysts for each temperature. Interestingly, at 140 and 160$^{o}$C, sulfuric acid resulted in complete conversion of di-propyl ether. Titanium isopropoxide performed the least with the highest conversion being only ~20% at 160$^{o}$C.

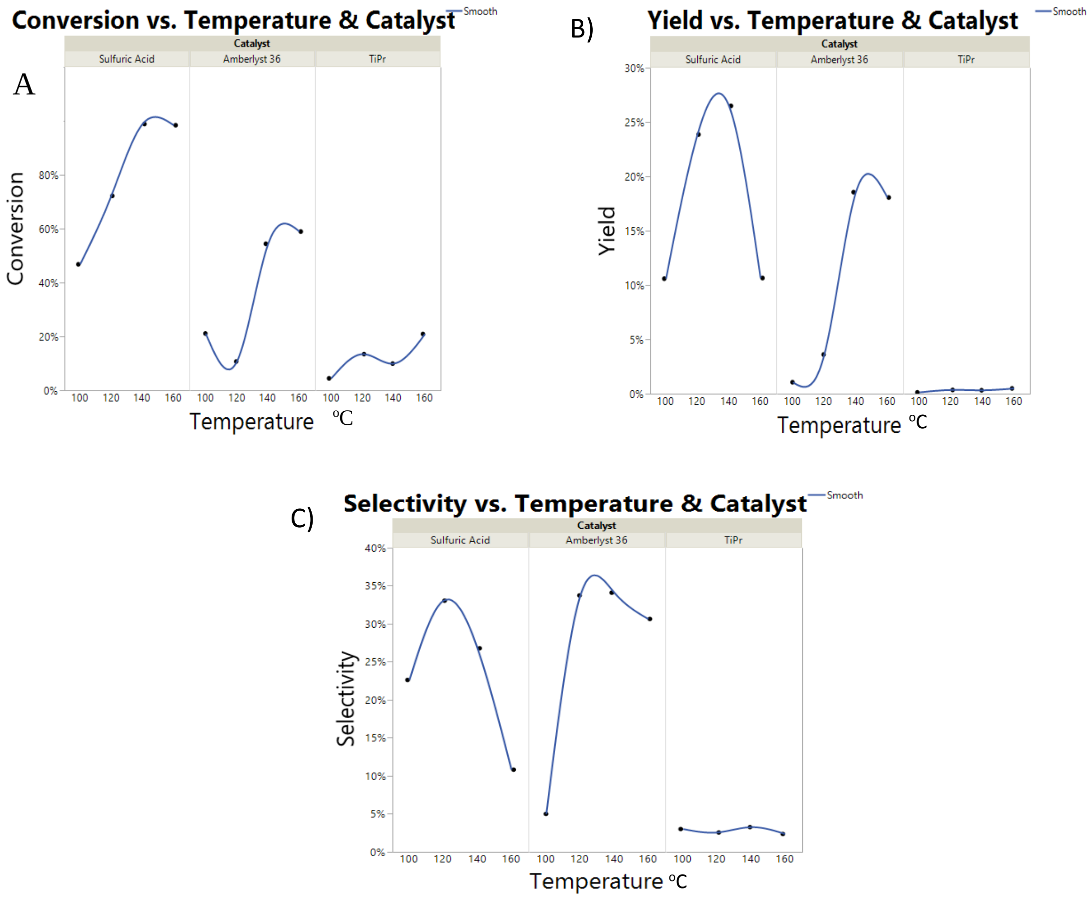


**Figure 3.1:** A) n-propanol conversion; B) di-propyl ether yield; and C) selectivity toward di-propyl ether as a function of temperature and type of catalyst

DPE yields followed a similar trend to propanol conversion (Figure 3.1B). Again, sulfuric acid resulted in the highest DPE yields at 140°C. It was interesting to note that the yields dropped at 160°C, likely due to product disintegration. DPE yields increased with increasing temperature when Amberlyst-36 was used as the catalyst; however, the yields were lower as compared to when sulfuric acid was used. No significant ester yields were observed with titanium isopropoxide.

It should be noted that based on the selectivity equation used, the maximum selectivity obtainable in this situation is 50%. Interestingly, Amberlyst-36 resulted in the best selectivity toward DPE from the three catalysts tested. Sulfuric acid performed similar to Amberlyst-36 but with slightly lower overall selectivity values. It was evident in both cases, i.e., sulfuric acid and Amberlyst-36, that there was an optimum temperature that renders highest product selectivity which was ~120°C for both catalysts. Again, titanium isopropoxide did not show any appreciable selectivity toward etherification. The impact of temperature and type of catalyst on propanol conversion, DPE yield and the selectivity toward DPE are given in Table 3.1.

**Table 3.1.** Analysis of variance (ANOVA) of effect of temperature and type of catalyst on propanol conversion, DPE yield and the selectivity toward DPE

| **Factor** | **Conversion** | **Yield of DPE** | **Selectivity towards DPE** |
|---|---|---|---|
| Temperature °C | P= 0.0502 | P= 0.3526 | P= 0.3785 |
| Type of Catalyst | P= 0.0012 | P= 0.0312 | P= 0.0249 |

ANOVA indicates that temperature alone doesn’t impact the conversion, yield or selectivity; however, the type of catalyst has a significant impact on all of the above responses. How the temperature and type of catalyst impacted propanol conversion, DPE yield and the selectivity toward DPE are depicted in Figure 3.1 A, B and C respectively.

### 3.3.2 Propanol and Methanol Etherification

#### 3.3.2.1 Substrate Conversion

The impact of catalyst type and concentration and temperature on n-propanol and methanol conversion is depicted in Figure 3.2.

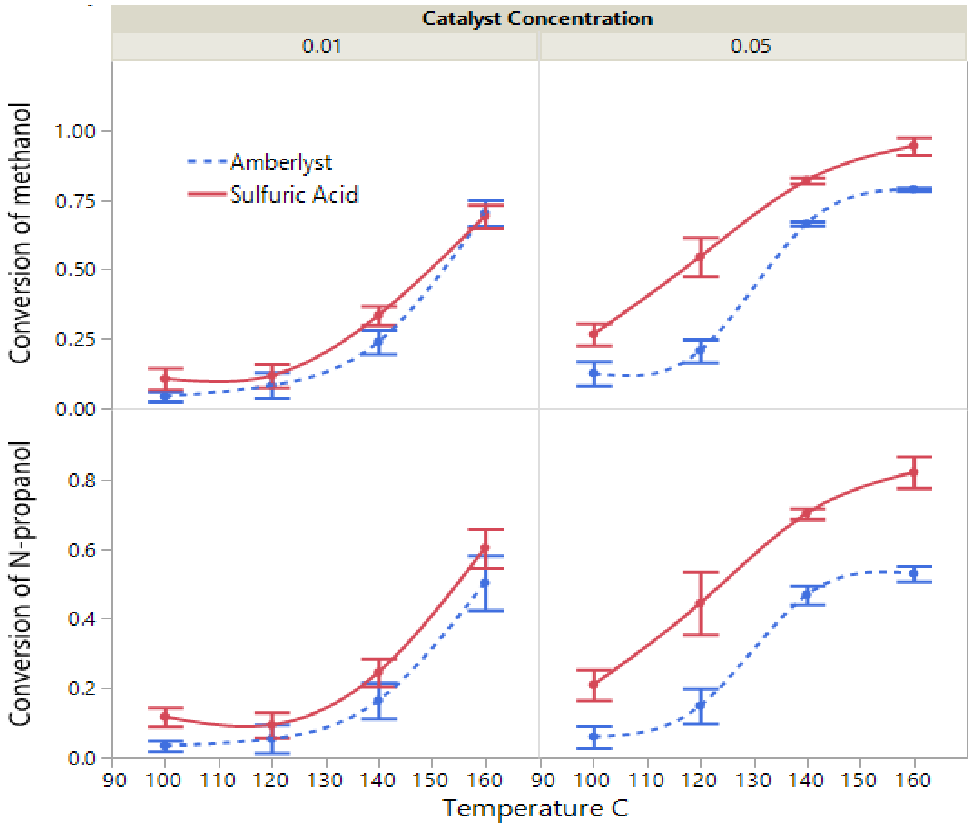


**Figure 3.2:** The impact of catalyst type, catalyst concentration, and temperature on conversion of n-propanol and methanol

It can be noted that sulfuric acid resulted in higher conversions of both n-propanol and methanol as compared to Amberlyst-36 even with the same concentration. This superiority in activity was evident at higher catalyst concentrations. This is likely as a result of the higher proton content in the case of sulfuric acid (twice as much protons) as compared to Amberlyst 36 per unit mass basis. The higher performance of sulfuric acid could also be attributed to the catalyst being homogeneous. Homogeneous catalysts generally perform better than heterogeneous catalysts due to much favorable mass transport characteristics in reactions [133-135]. Clearly, higher temperatures favored conversion of both substrates regardless of the type of catalyst; however, in a non-linear fashion. The better performance at higher temperature could be attributed to better reaction kinetics[136]. It was evident that methanol conversion was higher as compared to n-propanol and this could be attributed to more favorable steric of methanol (being the smaller of the two). Also, it should be noted that since methanol is initially in excess in the reaction medium, the fact that methanol conversion is higher than that of n-propanol implies that most of methanol may have converted in to byproducts such as dimethyl ether.

#### 3.3.2.2 Product Yield

The yields of DPE and MPE as a function of catalyst type and amount for different temperatures are depicted in Figure 3.3.

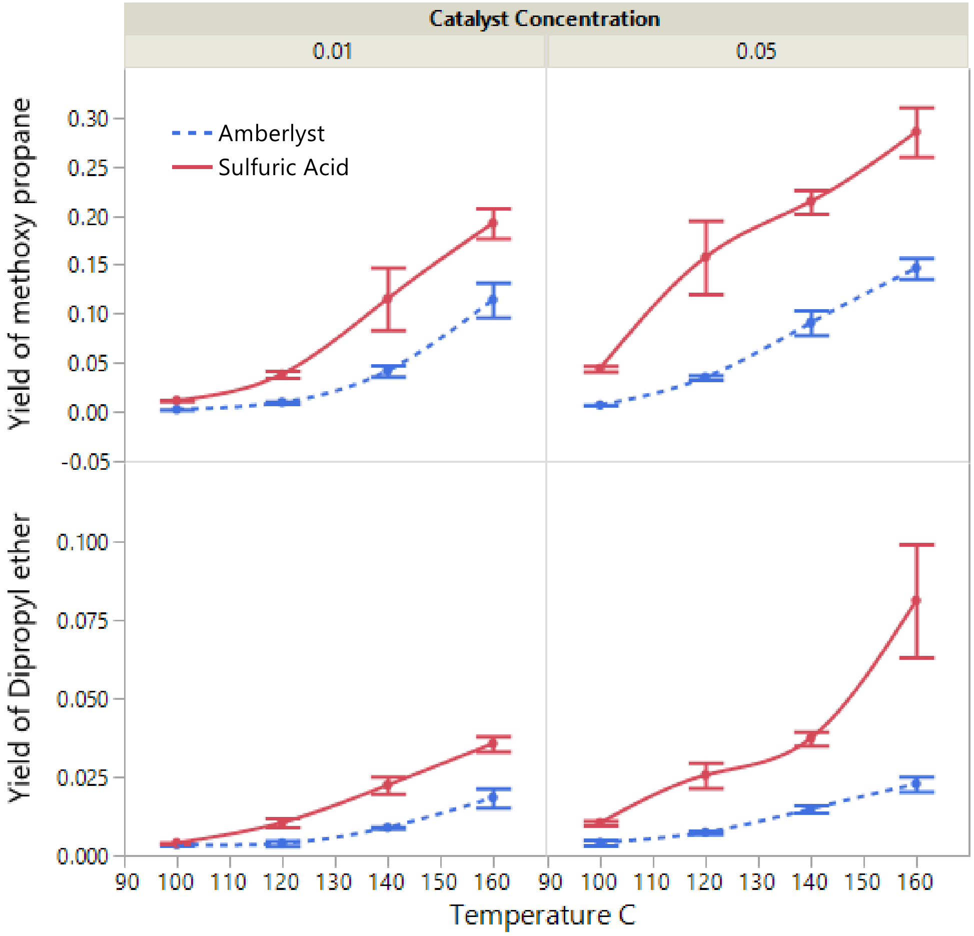


**Figure 3.3:** Impact of type and amount of catalysts on ether yield as a function of temperature.

Overall, sulfuric acid resulted in higher DPE yields as compared to Amberlyst 36 over the temperature range tested. DPE yields increased with increasing temperature for both catalysts. The DPE yield was 7.5% with 5% sulfuric acid catalyst at 160ºC. Although the DPE yields increased as temperature increased with both catalysts, Amberlyst lagged sulfuric acid in all instances. In terms of MPE yields, sulfuric acid resulted in better overall yields at all temperatures and catalyst concentrations as compared to Amberlyst 36. The yields tended to increase linearly with temperature for both catalysts.

#### 3.3.2.3 Selectivity Toward Ether

The selectivity of the two catalysts, i.e., sulfuric acid and Amberlyst 36 toward production of and di-propyl ether are depicted in Figure 3.4.

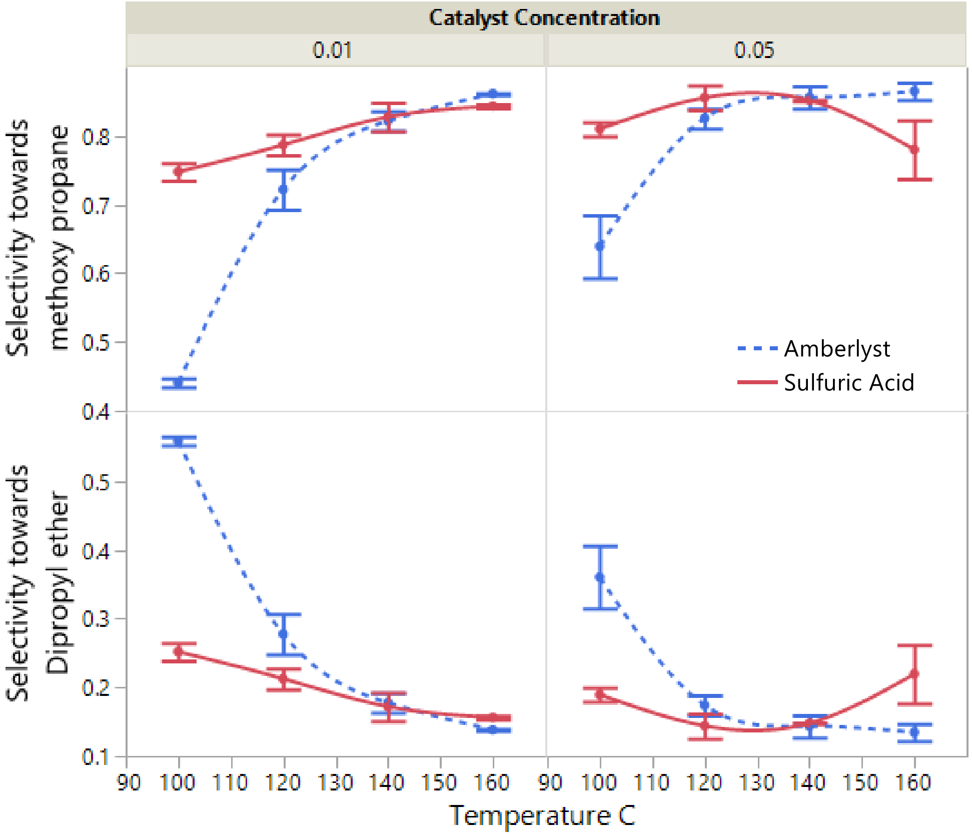


**Figure 3.4:** The impact of catalyst type and concentration on ether selectivity as a function of temperature.

It is interesting to note that the selectivity behavior of the catalysts for di-propyl ether was the antithesis to that of methoxypropane. In general, higher temperatures favored selectivity of both catalysts toward methoxypropane. At low temperatures, sulfuric acid showed markedly higher selectivity toward methoxypropane production as compared to dimethyl ether. However, as temperatures increased, the selectivity of Amberlyst 36 reached the same levels as sulfuric acid (at temperatures around 130°C and even surpassed the values of sulfuric acid at higher temperatures). On the other hand, the selectivity of both catalysts toward di-propyl ether production was highest at low temperature and steadily declined as temperature increased. Amberlyst 36 was comparatively more selective toward di-propyl ether production as compared to production of methoxypropane. Also, both catalysts were comparatively more selective for methoxypropane production as opposed to production of di-propyl ether.

The impact of catalyst type, concentration and temperature on n-propanol and methanol conversion and yield and selectivity toward the products, di-propyl ether (DPE) and methyl-propyl ether (MPE) are presented in Table 3.2.

**Table 3.2:** Analysis of variance of impact of catalyst type, concentration, and temperature on conversion, yield and selectivity

| Responses | | | | | | |
|---|---|---|---|---|---|---|
| Factor | Conversion of Methanol | Conversion of n-propanol | Yield of DPE | Yield of MPE | Selectivity towards DPE | Selectivity toward MPE |
| Temperature, $^{o}$C | P=<0.0001 | P= <0.0001 | P= <0.0001 | P= 0.595 | P= <0.0001 | P= <0.0001 |
| Type of Catalyst | P= 0.0003 | P= <0.0001 | P= <0.0001 | P= 0.9 | P= 0.0181 | P= 0.0181 |
| Catalyst Concentration | P=<0.0001 | P= <0.0001 | P= 0.0010 | P= 0.0295 | P= 0.0295 | P= 0.0295 |
| Catalyst Concentration*Type of Catalyst | P= 0.0181 | P=0.0089 | P= 0.0176 | P= 0.8815 | P= 0.2027 | P= 0.2027 |

*P: Probability value for significance. Green indicates significance

It can be seen that with the exception of catalyst concentration vs type interaction on product selectivity, all other factors significantly impacted the responses. This implies that applying different combinations of levels of the variables matter when it comes to substrate conversion, product yield and to a great extent, selectivity toward ethers.

In general, sulfuric acid resulted in comparatively higher conversions and ether yields. However, Amberlyst 36 gave comparable values of MPE yields and selectivity to sulfuric acid, especially when considering MPE. The high activity of sulfuric acid is likely as a result of the catalyst having a higher number of protons per mass basis. Sulfuric acid has twice number of protons as compared to Amberlyst 36. Also, it is possible that sulfuric acid being homogeneous would explain the higher activity (as opposed to Amberlyst 36 being a heterogeneous catalyst) [137]. Homogeneous catalysts in general have a mass transport advantage in comparison to heterogeneous catalysts [135].

The higher selectivity of Amberlyst 36 for DPE production and surpassing the selectivity toward MPE at higher temperatures is interesting. It has been revealed during recent experiments that Amberlyst 36 has swelling capability [138]. This swelling capability has been associated with Amberlyst's ability to absorb water and polar components [139]. Karl-Fisher titration has revealed that the bottom product phase contains about 67% water. The ability of Amberlyst 36 to help remove the produced more efficiently than sulfuric acid may at least partially explain why Amberlyst 36 performed better under some conditions.

### 3.3.3 Mass Balance

A mass balance was conducted for the reaction that consisted with 1:1 methanol to n-propanol volume ratio (i.e., 0.128 mol (4.08g) of methanol, 0.064 mol (3.83g) of propanol) with 5% sulfuric acid for 4h. The products on average were 0.0215 mol (1.59g) of MPE (~20% w/w) and 0.0048 mol (0.49g) of DPE (~6%). The rest 5.83g (~74%) were distributed among bottom phase (water and unconverted alcohol), and gaseous products.

Based on the above experiments, it is clear that nearly all the variables tested, i.e., catalyst type & concentration and reaction temperature, had some impact on the substrate conversion and product yield & selectivity. All the variables taken together, higher temperatures (i.e., 160 $^{o}$C) seems to favor higher substrate conversion. However, if the objective is to promote coupling of larger alcohols, somewhat milder temperatures seem to favor higher product yield and selectivity. Of the two catalysts, sulfuric acid consistently produced higher conversion and DPE yield and selectivity. However, amberlyst 36 gave higher product yields, and selectivity for MPE.

# CHAPTER IV

# CATALYTIC ETHERIFICATION OF GLYCEROL FOR PRODUCING BIODIESEL-COMPATIBLE BIOFUEL BLENDS

## 4.1 Introduction

Glycerol is a polyol byproduct resulting from the transesterification process that produces biodiesel [140]. Glycerol comprises ~10% of transesterified product with a purity of only 50-55% [141]. Crude glycerol resulting from transesterification is of low quality due to contamination with water, organic and non-organic salts, catalysts and alcohol left from transesterification [142, 143]. The continued growth of biodiesel industry has resulted in a glut of crude glycerol [144] that has led to lower prices and even disposal concerns. A product that could utilize glycerol, excess alcohol and catalyst from transesterification that is also miscible and thus blendable with biodiesel as a fuel additive could significantly benefit the biodiesel industry.

Ethers are oxygenated hydrocarbons that are generally miscible with fuels such as biodiesel that are formed by reacting two alcohols. Fortuitously, the bottom phase that results from biodiesel transesterification process is rich in alcohols – glycerol and methanol. This research was conducted to ascertain if this alcohol-rich stream could be converted to ethers that could eventually be blended with biodiesel.

Several attempts have been made to produce ethers from glycerol. Noureddini [145] produced ether from glycerol with isobutylene in a 3:1 isobutylene to glycerol molar ratio. The products were mono-, di-, and tri-ethers. Da Silva and Pico [146, 147] also have reported etherification of glycerol with benzyl alcohol using different catalysts. Pico reported glycerol etherification with benzyl alcohol with 3:1 and 1:3, benzyl alcohol/glycerol reactants molar ratios. Ether obtained were mono ethers and di-ethers. On the other hand, Da Silva obtained primarily mono-benzyl-ether using different catalysts and reactant molar ratios. Jaworski also reported their success in glycerol etherification with benzyl alcohol using sulfated zirconia catalysts [148]. Several other attempts of using tert-butanol are reported. Klepacova [149] carried out etherification of glycerol with tert-butanol using catex catalyst (Amberlyst 15 zeolite) with a molar ratio of 4:1 tert-butanol-glycerol. The product primarily comprised of mono-tert butyl glycerol ether. Frusteri [150] on the other hand reported a mixture of four different alkyl glycerol ethers in his attempts on  etherification of glycerol with tertbutyl alcohol using two types of ion-exchange resins. All this work had focused on utilizing external alcohols to couple with glycerol; however, none had attempted utilizing excess methanol that is already present in the byproduct mix. Our work focused on maximum utilization of all the ingredients that are output from a biodiesel transesterification operation.

## 4.2 Materials and Methods

Preliminary studies were conducted elucidating the reaction conditions with model compounds (i.e., model alcohols) such as n-propanol, methanol with catalysts including

NaOH, $H_2SO_4$ and Amberlyst-36 [151]. Subsequent studies with glycerol and methanol indicated that although ethers were formed, the mixtures were not miscible with biodiesel. Accordingly, based on preliminary investigations and previous work by others, an alcohol triad, glycerol, methanol, and tert-butanol was used as the ingredient mix.

Prices of the catalysts were dependent on the catalyst types and the amounts purchased. Sulfuric acid was priced in the range of \$200-300/ton for commercial scale orders [132]. This is a bulk price for industrial grade. However, sodium hydroxide was priced higher for the same industrial grade with about \$300-400/metric ton bulk price [152].

### 4.2.1 Screening Studies

Screening studies were conducted to elucidate the impact of glycerol: tert-butanol: methanol (G:T:M) ratios, catalyst type and concentration and conditions (temperature, pressure and time) on substrate (glycerol, tert-butanol and methanol) conversion, product (biodiesel-compatible top phase) yield and selectivity.

### 4.2.1.1 Variables and Experimental Design

For screening studies, the following variables were used:

| **Variable(s)** | **Levels** |
|---|---|
| Alcohols<br>Glycerol, Methanol, Tert-butanol | Glycerol: tert-butanol: methanol (G:T:M) of 1:2:1 and 1:1:2 |
| Catalysts<br>Sulfuric Acid, NaOH | 1% and 5% w/w |
| Temperature | 130-160 °C at 10 °C intervals |
| Pressure | (5-30) bar |
| Time | 4 hours |

The screening study was carried out as a $2^n$ design with 32 experimental units. JMP software was used to design and analyze data.

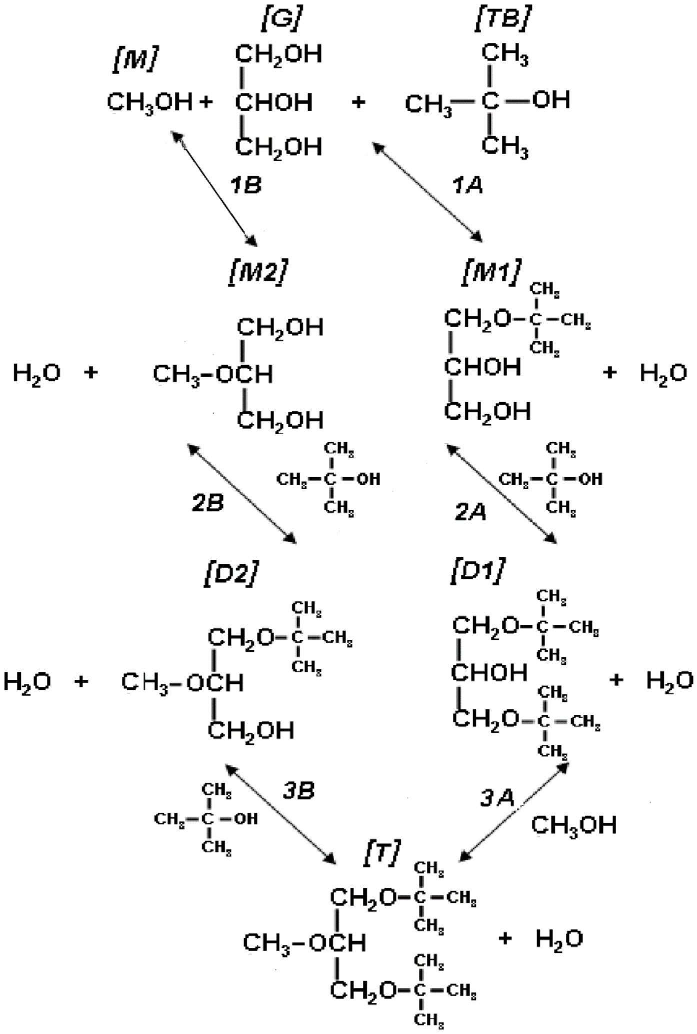
For calculating the response variables such as product yield and selectivity an idea of the chemical composition of the possible product is necessary. To help develop yield and selectivity relationships the following general equation for dehydration was used [4]:

ROH + R’OH + R’’OH ↔ ROR + ROR’ + R’OR + R’’OR’’ + ROR’’ + R’OR’’ $H_2O$ (Scheme 4.1)

Where R is methanol, R’ is tert-butanol and R’’ would be glycerol. More specifically, above reaction may proceed according to following elementary steps resulting in a mixture of ethers:

$$\left.\begin{aligned}
&ROH \leftrightarrow ROR + H_2O \\
&R'OH \leftrightarrow R'OR' + H_2O \\
&R''OH \leftrightarrow R''OR'' + H_2O \\
&ROH + R'OH \leftrightarrow ROR' + H_2O \\
&ROH + R''OH \leftrightarrow ROR'' + H_2O \\
&R'OH + R''OH \leftrightarrow R'OR'' + H_2O
\end{aligned}\right\} \quad \text{(Scheme 4.2)}$$

Using above schemes (4.1 & 4.2), based on previous work [151], and steric effects, a simplified product scheme, as depicted below was selected for reporting key responses, i.e., yield and selectivity:



**Scheme 4.3:** Etherification of glycerol, methanol, and tert-butanol

(developed from Pico, et.al, [153])

Where: $M_1$: 1-tert-butoxy propane-2,3-diol, $M_2$: 2-methoxy propane-1,3-diol.

$D_1$: 1,3-di-tert-butoxy propane-2-ol, $D_2$: 1-tert-butoxy-2-methoxy propane-3-ol

T: 1,3-di-tert-butoxy-2-methoxy propane

The stoichiometric equation given in Scheme 7 was used to represent a simplified system:

$$\underset{\text{Glycerol}}{C_3H_8O_3} + 2\ \underset{\text{tert-butanol}}{C_4H_{10}O} + \underset{\text{methanol}}{CH_3OH} \longleftrightarrow \underset{\text{diethylene glycol dibutyl ether}}{C_{12}H_{26}O_3} + 3\ H_2O \qquad \text{(Scheme 4.4)}$$

92g/mol 148g/mol 32g/mol 272g/mol 54g/mol

### 4.2.1.2 Theoretical Yield

Theoretical yield was calculated to discern the percentage of top phase obtained vs the top phase obtainable assuming that if the reaction went to completion as anticipated according to scheme 4.4. Theoretical yield was evaluated only during the screening studies (subsequent to screening studies, the nominal yield was used for reporting yields due to its increased relevance).

$$\text{Theoretical yield} = \frac{\text{Actual weight of top phase}}{\text{Theoritical amount of ether}} \qquad \text{Eq. 4.1}$$

### 4.2.1.3 Nominal Yield

Based on the results from the screening study, a new parameter, Nominal Yield was introduced that is more representative of the product system, and is calculated as follows:

$$\text{Nominal Yield} = \frac{\text{Actual weight of top phase}}{\text{Total weight of reactants}} \qquad \text{Eq. 4.2}$$

### 4.2.1.4 Selectivity Towards Ether

Due to the complexity of the top phase produced, the selectivity towards biodiesel-miscible (top) phase was defined as below:

Selectivity towards biodiesel-compatible (ether) phase

$$= \frac{(\text{weight of top phase})}{(\text{weight of top phase}) + (\text{weight of bottom phase})} \qquad \text{Eq. 4.3}$$

### 4.2.1.5 Conversion

The reactants' conversion was calculated as follows:

Glycerol Conversion:

$$\frac{n^0_{(\text{glycerol})} - n_{(\text{glycerol})}}{n^0_{(\text{glycerol})}} \qquad \text{Eq. 4.4}$$

Methanol Conversion:

$$\frac{n^0_{(\text{methanol})} - n_{(\text{methanol})}}{n^0_{(\text{methanol})}} \qquad \text{Eq. 4.5}$$

Tert-butanol Conversion:

$$\frac{n^0_{(\text{tert}-\text{butanol})} - n_{(\text{tert}-\text{butanol})}}{n^0_{(\text{Tert}-\text{butanol})}} \qquad \text{Eq.4.6}$$

### 4.2.1.6 Materials

Etherification experiments were carried out with glycerol, methanol, and tert-butanol using two types of catalysts, sulfuric acid, and sodium hydroxide. Sulfuric acid was obtained from J.T. Baker (95.9% assay) whereas sodium hydroxide was obtained from Avantor company as pellets (96-100% purity). The reactants, glycerol (purity >99%), methanol (purity 99.8%) and tert-butanol (99%), were obtained from Avantor, VWR, and Sigma Aldrich respectively.

### 4.2.1.7 Equipment

Etherification was conducted in a 25ml stainless steel Tiny Clave high-pressure reactor (Buchiglas USA) with a maximum rated pressure of 100 bar (@200-300 $^{o}$C). The vessel had ports to accommodate a PT-100 thermo-probe and a pressure gauge. Stirring and heating were accomplished using a magnetic stir-bar coupled with a stir hotplate. Weight measurements were obtained using high-sensitive microbalance (Cole-Parmer, PA 120 with 0.001g sensitivity). Quantitative analysis was carried out using a High-Performance Liquid Chromatography (HPLC) (Agilent Technologies, model 1120 compact LC). Ancillary studies via Gas Chromatography Mass Spectrometry (GC/MS) (Agilent Technologies 7890A/5975C) were conducted to verify the qualitative composition of the product spectrum.

#### 4.2.1.8 Procedure

Initially the tare weight of a 32-ml vial was recorded. Appropriate reactants, (i.e., alcohols) and catalysts were added sequentially while recording the weight/volume. Reaction mixture was then transferred to the pressure reactor along with a magnetic stir-bar. The vessel was securely tightened and heated while stirring in the stir-hotplate. Reaction timing, depending on the experiment, was initiated when the temperature reached the desired level.

Once the reaction time was complete, the products allowed to cool-down, depressurized, and were decanted to an extraneous container before final weight(s) were recorded. Product analyses were done instantly to minimize any losses due to volatility.

The bottom hydrophilic phase was analyzed using HPLC and top hydrophobic phase was analyzed using GC/MS. The bottom phase primarily consisted of unreacted glycerol, methanol, tert-butanol, catalyst, and resulting water from dehydration. The bottom phase was neutralized, centrifuged if needed and filtered to remove the catalyst before HPLC analysis. Neutralization was carried out using phosphoric acid for based catalyzed reactions, and NaOH for acid catalyzed reactions. After neutralization, the sample was filtered sequentially with three sizes of syringe filters, 0.8, 0.45, and 0.25 um respectively. Then, samples were diluted as appropriate to be compatible with HPLC column. The HPLC parameters are as follows:

- Column Information: Supelcogel 610H (30 cm X 7.8 mm).
- Flow rate: 0.5 ml/min.
- Mobile phase: 0.1% phosphoric acid.

Miscibility of the top phase of the product with biodiesel was evaluated by mixing with biodiesel at 1:1 ratio.

### 4.2.2 Optimization Studies

#### 4.2.2.1 Optimization Studies with NaOH

For optimization, the procedure was the same as screening studies except that NaOH was used as the catalyst while reaction times and other reaction conditions such as the molar ratios of reactants, temperature, and catalyst concentration were held constant based on the results from screening studies. These experiments were done as a full factorial design with three replicates. For optimization studies with NaOH, following variables were used:

| Variable(s) | Levels |
|---|---|
| Alcohols<br>Glycerol, Methanol, and Tert-butanol | Glycerol: Tert-butanol: Methanol (G:T:M) of 1:2:1 |
| Catalysts<br>NaOH | 5%, 7%, 9%, 10% |
| Temperature | 130 °C (held constant) |
| Pressure | <10 bar |
| Time | 1, 2, 3, 4 hours |

### 4.2.2.2 Optimization Studies with Sulfuric Acid and Amberlyst-36

For these studies, the procedure was the same as screening studies except that $H_2SO_4$ and Amberlyst-36 were used as a homogeneous and heterogeneous catalyst respectively. The reaction times and other reaction conditions such as the molar ratios of reactants, and temperature were held constant (unless stated otherwise) based on the results from screening studies and optimization studies on NaOH. The catalyst concentrations were 5% and 10%. These experiments were done as a full factorial design with three replicates. For optimization studies with $H_2SO_4$ and Ambyerlyst-36, following variables were used:

| Variable(s) | Levels |
|---|---|
| Alcohols<br>Glycerol, Methanol, Tert-butanol | Glycerol: Tert-butanol: Methanol (G:T:M) of 1:1:2 |
| Catalysts<br>$H_2SO_4$, Amberlyst-36 | 5%, 10% |
| Temperature | 130 $^oC$ (held constant) |
| Pressure | (5-30) bar |
| Time | 1, 2, 3, 4 hours |

#### 4.2.2.2.1 Fuel Quality Tests

Several fuel quality tests were conducted to assess its feasibility as a fuel additive. The purpose of these tests was to evaluate the compatibility of the additive with biodiesel and its fuel performance. The tests conducted are as follows:

##### 4.2.2.2.1.1 Cloud Point and Pour Point

Cloud Point is the temperature point at which the fuel starts to freeze whereas the Pour Point is the temperature at which the oil stops flowing. These are measured using the same apparatus (Figure 4.1).

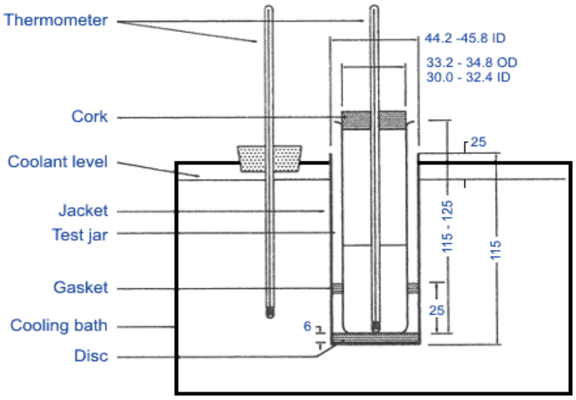


**Figure 4.1:** Fuel testing apparatus [3]

#### 4.2.2.2.1.1.1 Procedure

The procedure was conducted in compliance with ASTM D2500-05. The liquid sample was loaded into the test jar and the temperature was lowered (till the freezing point) while the sample was shaken mildly every 5 minutes. The point at which the bottom of the sample becomes cloudy was taken as the Cloud Point and that when the sample solidifies was taken as the pour point.

#### 4.2.2.2.1.2 Acid Number

This test is a measurement of acidity and is determined by the amount of KOH that is needed to neutralize the acids in one gram of sample.

### 4.2.2.2.1.2.1 Materials

- Isopropyl Alcohol, anhydrous (less than 0.9 % water)
- p-Naphtholbenzein Indicator Solution
- Potassium Hydroxide Solution, Standard Alcoholic
- Potassium acid phthalate solution (for standardization of alcoholic KOH)
- Phenolphthalein indicator solution (for standardization of alcoholic KOH)
- Toluene and Water
- Glasswares
- Burette, capacity 25 mL; Erlenmeyer flasks, 250 mL; Volumetric flasks, 1 L, 100 mL;

### 4.2.2.2.1.2.2 Procedure

The procedure was done according to ASTM D974-12 standard, which was as follows:

#### A. Preparation of Solutions

The Potassium hydroxide solution (standard alcoholic), 0.1 M and p-Naphtholbenzein Indicator solution will be prepared in titration solvent equal to 10 ± 0.01 g/L.  Titration solvent will also be prepared by mixing toluene, water, and anhydrous isopropyl alcohol in the ratio 100: 1: 99.

## B. Sample Titration

A weighed quantity of the Sample was introduced into an Erlenmeyer flask. Then, 100 mL of the titration solvent and 0.5 mL of the indicator solution were added and mixed until the sample is entirely dissolved. Then the sample was titrated with 0.1 M KOH (In the case of acidic samples, the orange color changes to a green or green-brown as the end point). The volume of KOH used was recorded (corresponds to A in the equation below). A blank titration was performed on 100 mL of the titration solvent and 0.5 mL of the indicator solution, adding 0.1-mL or less increments of the 0.1 M KOH solution until endpoint. The volume of KOH used is recorded (corresponds to B in the equation below).

## C. Calculations

The acid number will be as follows:

Eq. 16

$$\text{Acid number, mg of KOH/g} = [\,(A - B)\,M \times 56.1]/W$$

where:

A = KOH solution required for titration of the sample, mL,

B = KOH solution required for titration of the blank, mL,

M = molarity of the KOH solution, mole/L, and W = sample used, g.

#### 4.2.2.2.1.3 Viscosity

Viscosity measurements were done using ASTM D445-06 Standard. A Cannon (75-W613) viscometer was immersed in a water bath. The temperature of the bath was maintained at 40 $^oC$. The viscometer was inverted and immersed into the sample with vacuum applied to charge the sample into the meter. Then, the viscometer was up righted and placed in the water bath. A time lapse of 30 minutes was allowed until the viscosity measurement will be taken. Time of flow was recorded by letting the liquid flow through a bulb in the viscometer. This was done by applying the pressure on the liquid until it reached above the upper line of the bulb. The time counting started when the liquid passes the upper line and ends when the liquid passes through the lower line of the bulb. The viscosity will be simply the time of flow multiplied by the constant of the viscometer found in the standards of the equipment.

#### 4.2.2.2.1.4 Flash Point

To find Flash Point, the apparatus (Figure 4.2) was connected to a small propane tank, which is the source of the flame. The flame stays above the test cup in which the sample is placed. The flame is lit on and remains on till the end of the test. Underneath the test cup, there is a heater which heats up the sample to the desired temperature. Also, there is a temperature controller and a timer for intervals between each flash. Temperature is displayed and controlled accordingly.

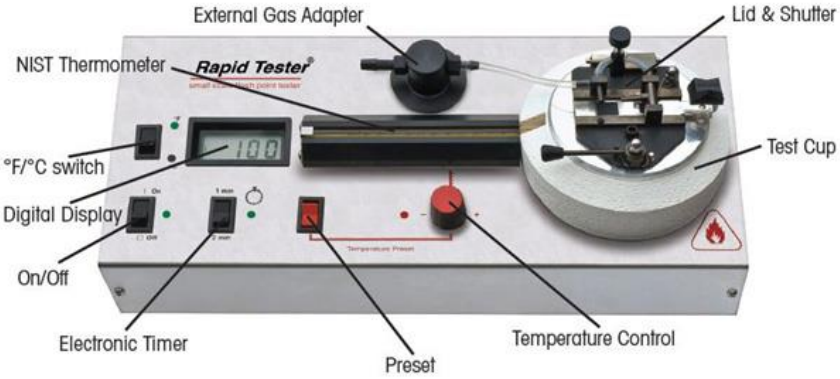


**Figure 4.2:** Flash point tester [1]

### 4.2.2.2.1.4.1 Procedure

The procedure was conducted according to ASTM D93 for flash point. The temperature was set close to the expected flash point of the product. The temperature set should be within the limits of ±5 $^{o}$C. Since the flash point of our sample was not known, an educated guess was made to set the initial setting. Once the desired temperature was reached, the sample was placed, the lid closed, and test flame was lighted. Moments later, the flame was inserted to check if there is a flash. The insertion of the flame was repeated until a flash occurs. Once a flash occurred, the temperature was reduced by 5 $^{o}$C until the flash point was determined.

### 4.2.2.2.1.5 Ash Test

Ash test was conducted using ASTM D482-07. This test consisted of a simple procedure where the sample is placed in an evaporating pre-weighed crucible, made of platinum; the crucible is capped and placed in a preheated oven up to 775 ±25 $^{o}$C for 10 minutes; the crucible cap is removed and the crucible is left for 4 hours; and the crucible is cooled to room temperature and weighed again. The mass of ash is calculated as follows:

$$\text{Mass } \% = (w/W) * 100 \qquad \text{Eq. 17}$$

Where:

w= mass of ash, g

W= mass of sample, g

### 4.2.2.2.1.6 Ultimate Analysis

This analysis is used to determine the elemental composition of the biofuel including C, H, N, S. The analyses were done adhering to ASTM D3176-15 [154]. Oxygen content was calculated by difference, i.e. (O%= 100 – the sum of all other elemental content). Also, the amount of the ash has been considered in the oxygen content calculations. The test was conducted using 1.688 mg of biodiesel and 1.9881 mg of glycerol ether.

###### 4.2.2.2.1.7 Energy Content / Heat of Combustion

Energy content (ASTM D240) of select samples (along with a biodiesel control) was determined externally at FOI Laboratories, Vancouver City, Washington State.

## 4.3 Results and Discussion

### 4.3.1 Screening Studies

Preliminary studies conducted with methanol and glycerol alone indicated that the products formed a single-phase hydrophilic phase which was immiscible with biodiesel under the catalyst types, concentrations and temperatures tested. These results indicated that any products resulting from methanol-methanol, methanol-glycerol, or glycerol-glycerol dehydration under the conditions tested do not produce products with any fuel-utility. These observations also helped simplify reactions (given in scheme 4.1) to develop equations for theoretical yield. Reacting glycerol with a mixture of methanol and tert-butanol (regardless of the glycerol: tert-butanol: methanol molar ratios) produced two phases of which the top phase being hydrophobic and compatible with biodiesel and bottom phase being hydrophilic and immiscible with biodiesel (Figure 4.3). Preliminary studies also confirmed that in the presence of glycerol, methanol or tert-butanol was immiscible with biodiesel and preferentially mixed with glycerol – indicating that the products formed were as a result of dehydration and not one of the unreacted substrates mixing with biodiesel. This study was conducted using $2^n$ design and one replicate.

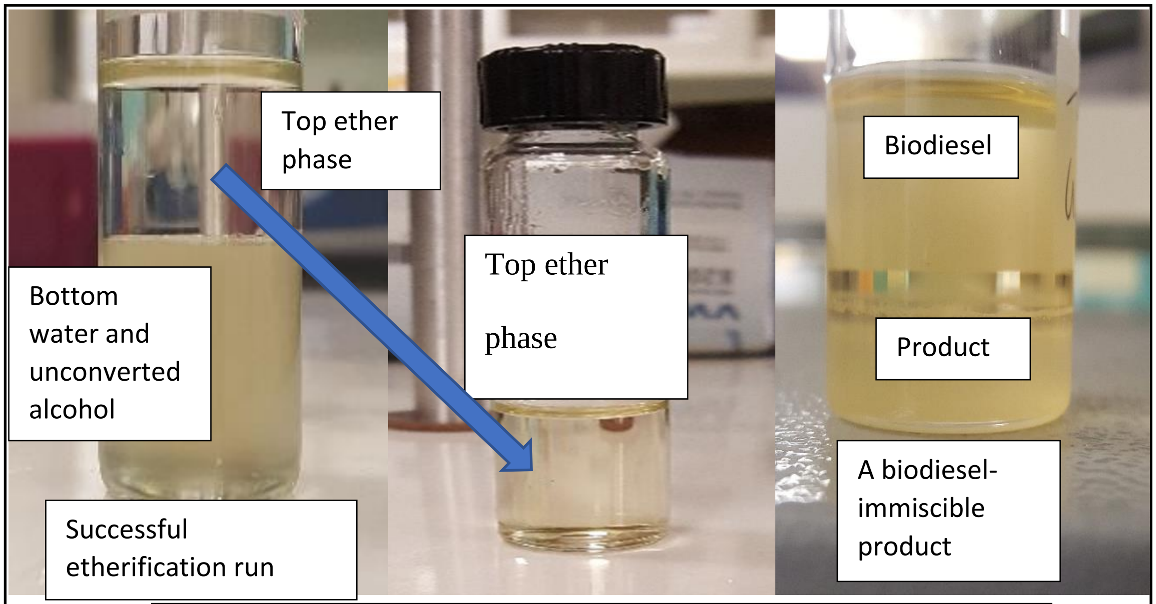


**Figure 4.3:** Biodiesel compatibility tests of top/bottom product phases

### 4.3.1.1 Spectroscopic Analysis to Confirm the Composition of Top Phase

In order to elucidate the composition, the top hydrophilic phase was analyzed with Fourier Transform Infrared spectroscopy (FTIR) (Thermo-Scientific Nicolet iS10). Then spectra from top phase were compared with control spectra of alcohols and ethers. To confirm the existence of ethers, the C-O peak shifts were analyzed. Figures 4.4 depicts C-O peaks of the top-phase with select alcohols (methanol, ethanol, and propanol) while Figure 4.5 depicts those of select ethers (methoxy propane, diethyl ether and di-propyl ether).

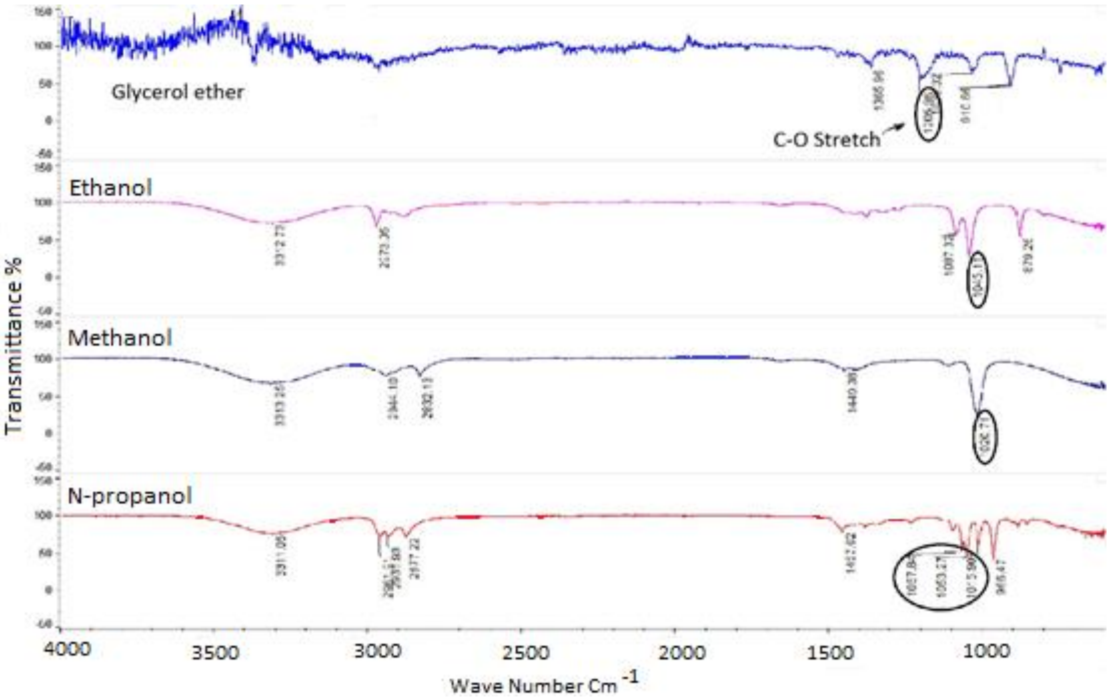


**Figure 4.4:** FTIR spectra of product and alcohol controls

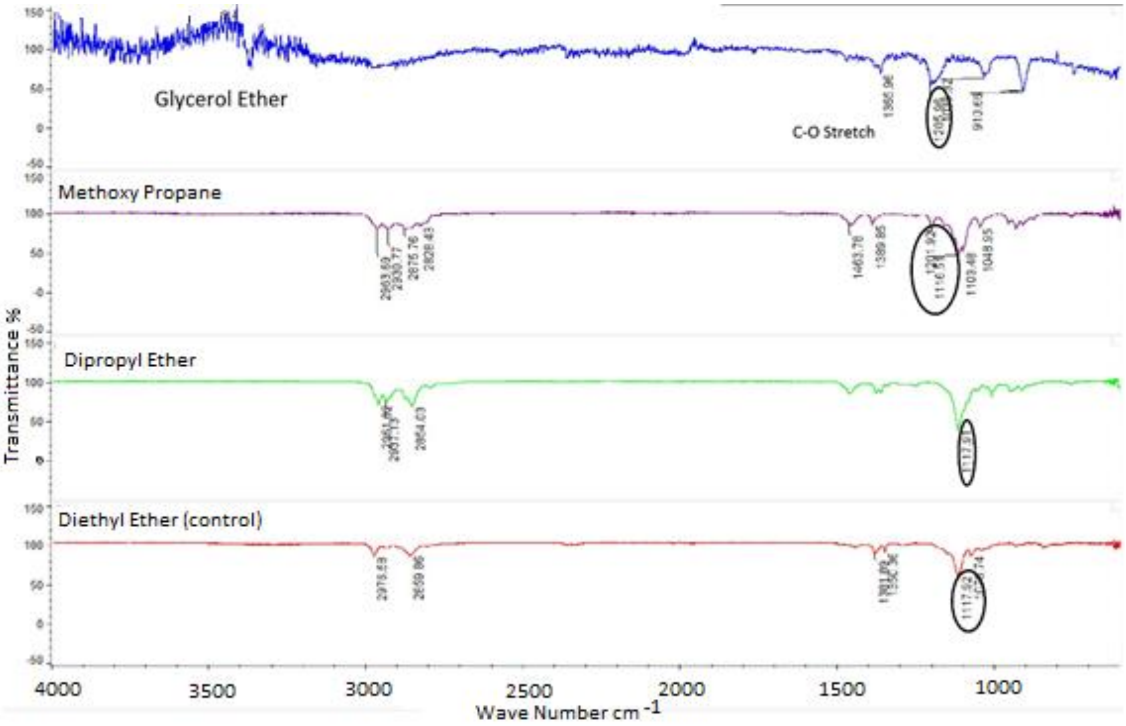


**Figure 4.5:** FTIR spectra of product and ether controls

It is noted that in general, C-O Stretch ranges between 1000-1300 cm$^{-1}$. The results show that the most prominent peak of the top phase is located within this range, specifically 1205.96 cm$^{-1}$. It is also noted that all ethers, the C-O stretch is tending > 1100 cm$^{-1}$ whereas alcohols tending < 1050 cm$^{-1}$ indicating a strong possibility of the top phase (1205.96 cm$^{-1}$) consisting of ether. Moreover, all alcohols have an O-H stretch at about 3300 cm$^{-1}$, whereas our product does not have that one giving us a firmer clue that what we have is more of an ether than an alcohol.

The impact of temperature, type of catalyst, catalyst concentration, substrate molar ratio and any interactions are depicted in Table 4.1. It is clear that, except for temperature, all the other factors significantly impacted the product conversion, ether yields and selectivity values. The type of catalyst had a significant impact on conversion of all the three substrates while was significant on theoretical yield or selectivity toward ethers. Catalyst concentration impacted conversion of methanol and glycerol (but not tert-butanol) and also theoretical yield and selectivity. Catalyst molar ratios impacted all responses except tert-butanol conversion. It was also noted that catalyst type and temperature had an interactive effect on glycerol conversion. Catalyst type and concentration had an interactive effect on all variables except methanol conversion. The molar ratios of the substrate alcohols and the catalyst type had an interactive effect on all the responses. The molar ratios of alcohols and catalyst concentrations had an interactive effect on all responses except for glycerol conversion.

**Table 4.1**: ANOVA of the effect of variables and their combinations on the responses conversion, yield and selectivity

| Responses | | | | | | |
|---|---|---|---|---|---|---|
| Factor | Conversion of Methanol | Conversion of Glycerol | Conversion of tert-butanol | Theoretical Yield | Nominal Yield | Selectivity towards ether |
| Temperature | P= 0.7096 | P= 0.1327 | P= 0.9395 | P= 0.9020 | P= 0.8809 | P= 0.9463 |
| Type of Catalyst | P= 0.0023 | P= 0.0212 | P= <0.0001 | P= 0.3213 | P= 0.1252 | P= 0.608 |
| Catalyst Concentration | P= 0.0005 | P= <0.0001 | P= 0.2891 | P= 0.0012 | P= <0.0001 | P= 0.0003 |
| Molar Ratio | P= 0.0018 | P= 0.1690 | P= 0.0015 | P= 0.0025 | P= <0.0001 | P= 0.0004 |
| Cat. type* Temp. | P= 0.7203 | P= 0.0379 | P= 0.4741 | P= 0.8579 | P= 0.8862 | P= 0.8989 |
| Cat. type* cat. Conc. | P= 0.5837 | P= 0.0385 | P= 0.0117 | P= 0.0038 | P= 0.0042 | P= 0.0222 |
| Molar ratio* Cat. Type | P= 0.0056 | P= 0.0007 | P= 0.0007 | P= 0.0013 | P= 0.0011 | P= 0.0137 |
| Molar ratio*Cat. Conc. | P= 0.0023 | P= 0.1943 | P= 0.0007 | P= 0.0003 | P= 0.0003 | P= 0.0010 |

*P: Probability value for significance. Green indicates significance (<0.05)

#### 4.3.1.2 Effects of Temperature on Responses

The impact of temperature, catalyst type and concentration and reactant molar-ratios on substrate conversion (Figure 4.6), theoretical yield and selectivity (Figure 4.7) are depicted below. Results indicate that of the four levels of temperature studied that ranged from 130-160 $^{o}$C at 10$^{o}$C intervals, the increase of temperature did not have any significant impact on any of the response variables indicating that the lowest temperature, i.e., 140 $^{o}$C could be utilized for etherification reactions. However, two clear exceptions were that in the case of $H_2SO_4$, glycerol conversion, theoretical yield and selectivity being highest at 160 $^{o}$C and the highest yields obtained with NaOH being also at 160 $^{o}$C.

#### 4.3.1.3 Effect of Catalyst Type and Concentration

The type of catalyst has a significant impact on substrate conversion; however, did not impact product yields and selectivity. Clearly, sulfuric acid was the preferred catalyst for tert-butanol conversion (~100%). For methanol conversion, the type of catalyst impact was more subtle - NaOH performed best at higher catalyst concentrations; however, overall regardless of catalyst concentration, $H_2SO_4$ performed more consistently resulting in >70% methanol conversion. Especially at higher methanol concentrations (i.e., glycerol: tert-butanol: methanol, i.e., G:T:M = 1:1:2) NaOH (~45%) performed much inferior to $H_2SO_4$ (~75%). Again, $H_2SO_4$ performed more consistently for glycerol conversion whereas, at higher glycerol concentrations, NaOH (~45%) performed much inferior to $H_2SO_4$ (>70%). Considering all three alcohols, the results indicate that $H_2SO_4$ to be the more consistent catalyst that contributes to higher conversions although NaOH was not that far off.

The amount of catalyst affected all responses other than tert-butanol conversion. In general, higher amounts of catalysts (regardless of type) favored alcohol conversion (regardless of type) and this observation was consistent at G:T:M of 1:2:1. However, at G:T:M of 1:1:2, higher amounts of $H_2SO_4$ tended to increase conversion, especially for glycerol and methanol and the impact of higher amounts of NaOH tended to be negative. Overall, usage of 4% (w/w) catalyst seemed to result in better conversions than 2% (w/w).

The impact of catalyst type on theoretical ether yield and selectivity were analogous. It was clear that the catalyst type did not have any impact on theoretical ether yield or selectivity; nevertheless, a clear pattern emerged with NaOH being superior at G:T:M of 1:2:1 whereas $H_2SO_4$ being superior when the alcohol ratios were 1:1:2. On the other hand, the amount of catalyst had a significant impact on both yield and selectivity. Clearly higher amounts of catalyst, regardless of type had a positive impact on both ester yields and selectivity. Overall higher concentrations of NaOH outperformed $H_2SO_4$ for G:T:M of 1:2:1 by producing >65% ether yields with >75% selectivity whereas $H_2SO_4$ was superior when the alcohol ratios were 1:1:2 with 10% ether yields and ~20% selectivity which were less attractive. This analysis overall suggests NaOH to be the better catalyst for etherification of the alcohol triad.

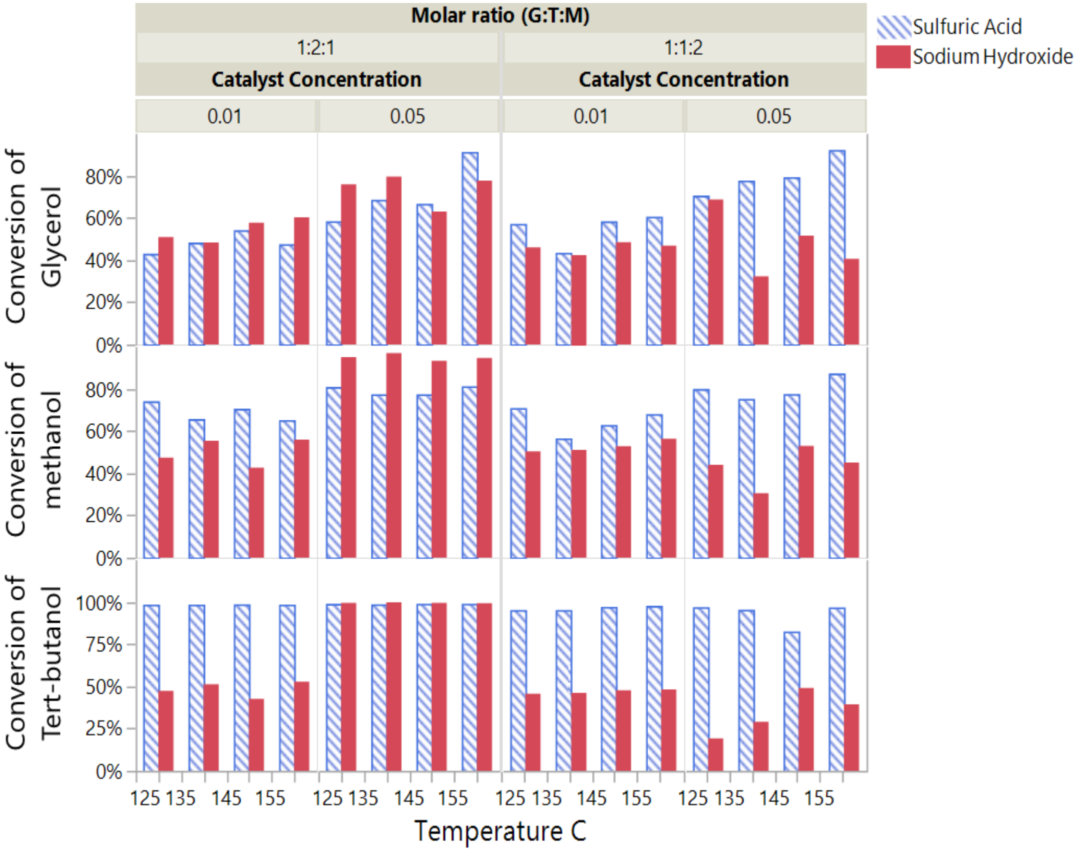


**Figure 4.6:** Effects of temperature, catalyst concentration and substrate molar ratios on substrate conversion

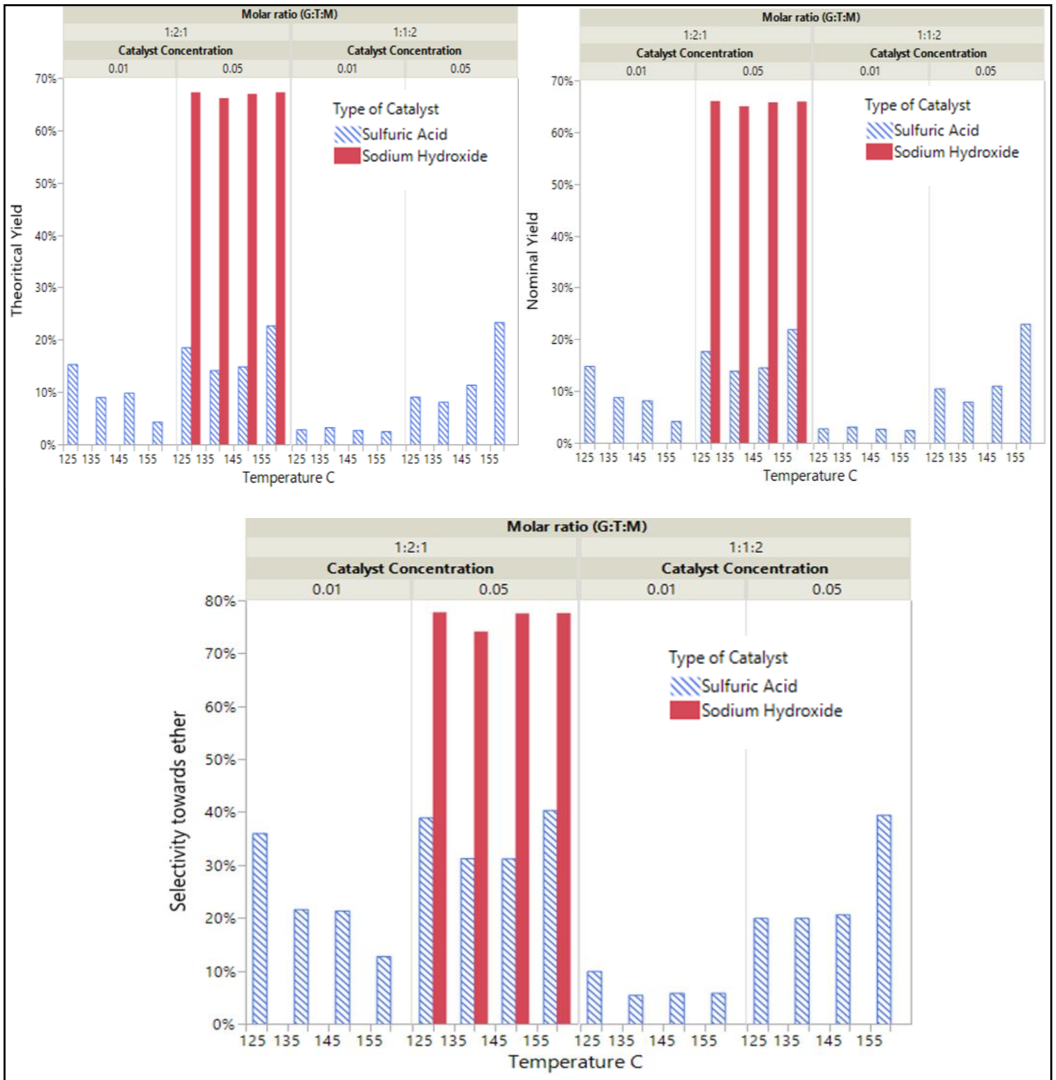


**Figure 4.7:** Effects of temperature, catalyst concentration and substrate molar ratios on product yield and selectivity

#### 4.3.1.4 Effects of The Reactant Molar Ratios

The G:T:M molar ratio had an impact on all variables with the exception of glycerol conversion. When catalyst type and amount is taken into account, the interactions: molar ratio vs catalyst type and molar ratio vs catalyst amount were all significant – stating that these combinations have a significant impact on substrate conversion and product yields and selectivity. It is clear that when $H_2SO_4$ is used, G:T:M 1:1:2 resulted in a better methanol conversion (72%) as opposed to 1:2:1 (61%). For NaOH it was the antithesis. Accordingly, NaOH would be the better catalyst when G:T:M is 1:2:1 is used for methanol conversion. For tert-butanol conversion, when $H_2SO_4$ was used, G:T:M 1:1:2 (84%) resulted in better conversion vs 1:2:1 (70%). For NaOH, it was the antithesis. For theoretical yield, when $H_2SO_4$ was used G:T:M of 1:1:2 (20%) resulted in better yields than 1:2:1 (7%). For NaOH again, the results were the antithesis giving better yields when G:T:M is 1:2:1. For selectivity, when $H_2SO_4$ was used G:T:M of 1:1:2 (27%) resulted in better yields than 1:2:1 (15%). For NaOH again, the results were the antithesis.

From this analysis it clear that when G:T:M is 1:2:1, NaOH is the better catalyst and when G:T:M is 1:1:2, $H_2SO_4$ is better. Here it should be noted that if the intention is usage of more methanol, $H_2SO4$ would be the better catalyst; however, the best yields are obtained when NaOH is used with 1:2:1 alcohol ratios (i.e., using more tert-butanol).

The ability of glycerol to react with tert-butanol has been confirmed by other studies where 1% sulfuric acid was used to produce mono-ethers from glycerol and tertbutyl alcohol [145]. It could be noticed that the highest yields obtained from sulfuric acid was ~25% at 160 $^oC$ and a catalyst concentration of 5%. The reason for this limited yield could be attributed to the water generated during the reaction hindering ether formation [150]. This has been proven in an earlier study with n-propanol/methanol etherification with $H_2SO_4$ as a catalyst. The water content of the bottom phase measured using Carl-Fischer titration was significant around 67%.

### 4.3.2 Optimization Studies with NaOH

Screening studies suggested the highest yield of top phase (that was miscible with biodiesel and likely consisted primarily with ethers) were highest when NaOH was used as the catalyst. Accordingly, it was decided to do an initial optimization study to find out best combination of process parameters favorable for the process.

The ANOVA for the impact of reaction time, catalyst concentration and any interactions are depicted in Table 4.2 It was revealed that reaction time had a significant impact on Nominal yield as well as selectivity toward ether; however, did not impact substrate conversion. It was interesting that catalyst concentration impacted all response variables while catalyst concentration and reaction time had an interactive effect on nominal yield and ether selectivity.

**Table 4.2:** ANOVA for the effects of variables on the responses, yield, conversion, and selectivity

| Factor | Conversion of Methanol | Conversion of Glycerol | Conversion of tert-butanol | Nominal Yield | Selectivity towards ether |
|---|---|---|---|---|---|
| Reaction Time (hr) | P= 0.0582 | P= 0.9415 | P= 0.0508 | P= 0.0045 | P= 0.0102 |
| Catalyst Concentration | P= 0.0035 | P= <0.0001 | P= <0.0001 | P= <0.0001 | P= <0.0001 |
| Cat. Conc. X React. time | P= 0.3626 | P= 0.290 | P= 0.0332 | P= 0.0034 | P= 0.5193 |

*P: Probability value for significance. Green indicates significance (P<0.05)

Generally, catalyst concentration has a diminishing impact for substrate conversion (Figure 4.8). In fact, in a number of instances, lowest or an intermediate concentration (5% or 7%) had the best positive impact on substrate conversion. Regardless of the substrate, high catalyst concentration (10%) did not bode well for substrate conversion.

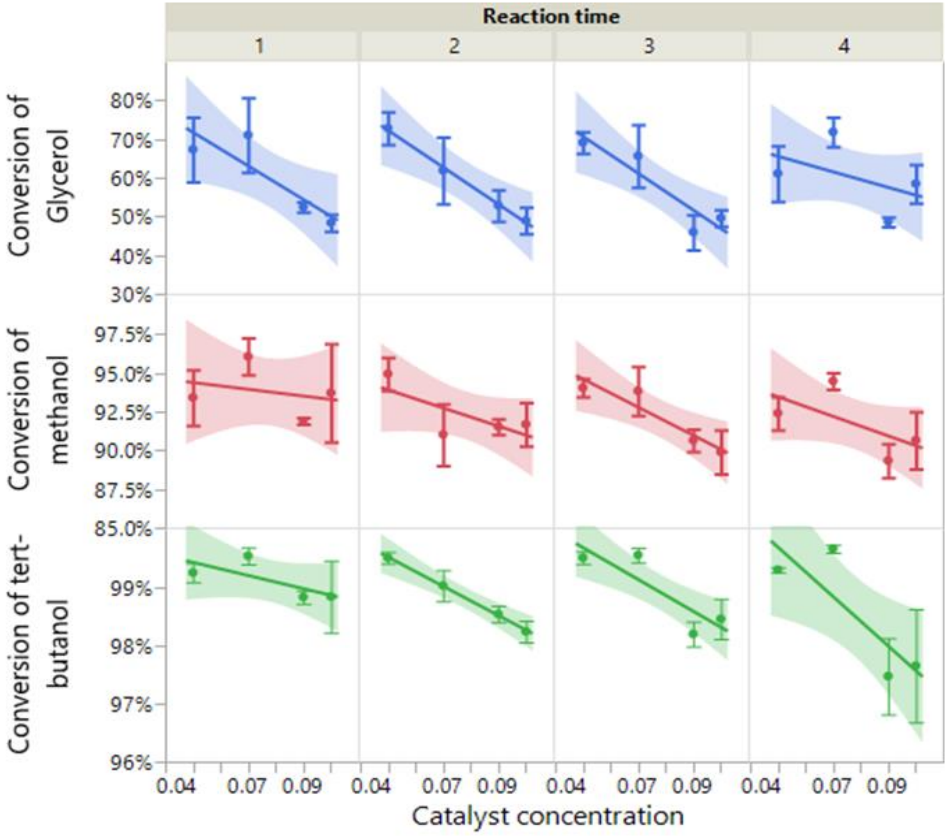


**Figure 4.8:** Impact of catalyst concentration over different reaction times on substrate conversion

The highest conversion for glycerol (87%) and methanol (95%) was achieved with 7% catalyst with a reaction time of 1 hour. For tert-butanol the highest conversion of 99.5% was achieved with the lowest amount of catalyst tested which was 5% and 1 hour reaction time. Results indicate that performing the reaction at 1 hour and lowest amount of catalyst is adequate to achieve maximum substrate conversion. The reduced substrate conversions at high catalyst concentrations and high reaction times allude to emergence of an unwanted and at this point an unknown reaction, possibly with NaOH as a substrate; higher NaOH resulting in saponification in biodiesel production is a well-known phenomenon [155].

The impact of catalyst concentration and reaction time on nominal yield as well as selectivity for the top biodiesel-miscible phase is given in Figure 4.9. It is clear that higher catalyst concentrations progressively reduced yield and selectivity of the top phase – which also implies increse of yield and selectivity toward the biodiesel immiscible bottom phase. The bottom-phase consisted of a gel-like substance which suggests an olygomerized/polymerized product. This observation is confirmed by other studies using glycerol alone [156]. It has been reported before that NaOH has a mild solubility in glycerol which decrease with concentration [156]. The lower activity of NaOH at higher concentrations may explain, at least partially the impact of low solubility on catalyzing the expected alcohol dehydration reactions.

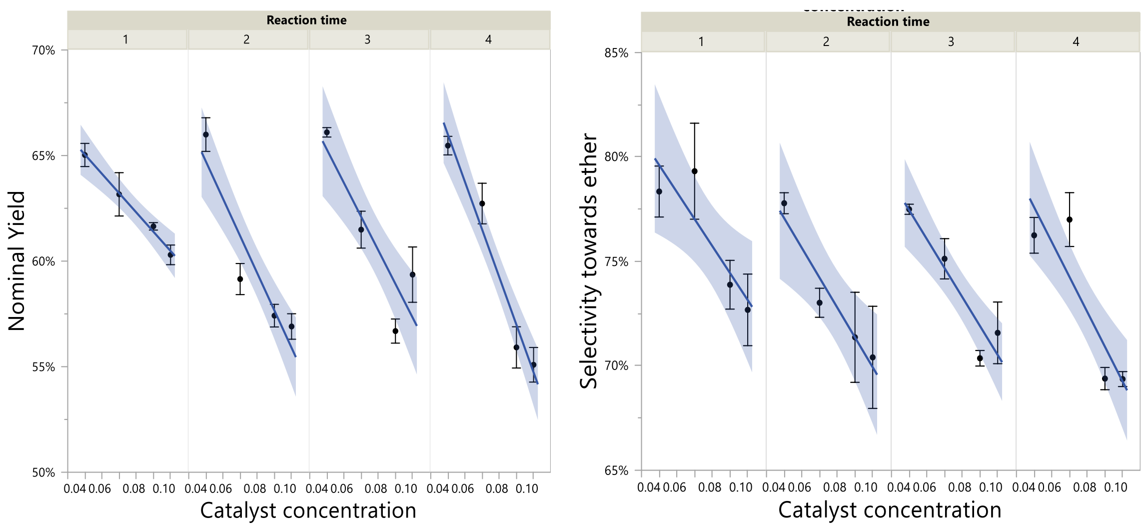


**Figure 4.9**: Effect of catalyst concentration and time on nominal yield and selectivity toward biodiesel-miscible top phase

#### 4.3.2.1 Fuel Quality Tests

Results from the fuel quality tests are depicted in Table 4.10. I could be noted that certain properties of the top phase were comparable or better than those of biodiesel, e.g., cloud-point, pour point, acid number, viscosity, sulfated ash, N%, C%, H%, S% and O%.

**Table 4.3:** Results of fuel properties test

|  | **Biodiesel (control)** | **Biodiesel miscible top phase via NaOH catalysis** | **ASTM Standard limitation for biodiesel [157]** |
|---|---|---|---|
| **Cloud point °C** | 1.5 - 5.5 | 0 – 15 | - |
| **Pour point °C** | - 2.5 | <-35 | - |
| **Flash point °C** | 175-180 | < 30 | 130 |
| **Acid number** | 0.21 | - | 0.8 max |
| **Viscosity CSt** | 3.96 | 2.94 | 1.9-6 |
| **Ash % wt** | 4.3 | 0.115 | 0.01 |
| **N%** | 1.317 | 0.945 | - |
| **C%** | 56.469 | 57.774 | - |
| **H%** | 8.376 | 12.478 | - |
| **S%** | 0.759 | 0.347 | - |
| **O%** | 28.779 | 28.341 | - |
| **Energy Content (BTU/gal)** | 128,642 | 86,166 | - |

As could be seen, the cloud point of the top phase varied widely as compared to biodiesel. However, the pour point was low compared with biodiesel which makes the additive effective for cold weather conditions. Acid number was unmeasurable with the top phase due to slight basicity of the product. The top phase was less viscous than biodiesel indicating that the product would improve fuel quality once blended. The increase of C and H and a reduction of O suggested better combustion properties. However, it was s less ash, nitrogen, and sulfur content. On the other hand, as it appears that it has a slightly higher, yet not significant, hydrogen and carbon content compared to biodiesel. Nevertheless, the oxygen content is less than of the biodiesel, which suggest that the reaction has moved further from etherification and dehydration to deoxygenation. The results in table 4.2 suggest that the glycerol ether is an efficient biodiesel additive in general.

The results for all studies conducted show that it is possible to have an ether produced and used as a biodiesel additive with different blending ratios. Type and concentration of catalyst were major variables affect the reaction significantly. Temperature and reaction time can also have significant effect on the process as well. However, the heat of combustion of the top phase (86,166 BTU/gal) was significantly low as compared to biodiesel (128,642 BTU/gal). The likely reason for this is the presence of water (that resulted from dehydration reaction as well as neutralization). Further miscibility studies confirmed the amphiphilic nature of the top phase - being miscible with water as well as biodiesel. This result presents advantages as well as challenges: the ability of the blend to abstract water may be beneficial in a high-humidity environment by keeping water as an emulsion in the fuel itself disallowing phase separation in a fuel tank. However, the presence of water dramatically reduces the blend's energy content while also requiring an additional dewatering step – which is energy intensive.

Due to above disadvantages, another optimization study was performed with $H_2SO_4$ and Amberlyst-36 as catalysts to ascertain the fuel quality of the product(s) formed using acidic catalysts.

### 4.3.3 Optimization Studies with Sulfuric Acid and Amberlyst-36

ANOVA results from optimization studies with $H_2SO_4$ and Amberlyst-36 are depicted in Table 6. As can be seen, the type of catalyst ($H_2SO_4$ vs Amberlyst-36) had a significant impact on glycerol conversion and product yields and selectivity. The catalyst concentration (5% vs 10%) had a significant impact on all of the response variables whereas reaction time (1, 2, 3 and 4h) influenced only yield and selectivity. Catalyst type and reaction time had an interactive effect on yields and selectivity while catalyst type and catalyst concentration had an interactive effect on almost all responses.

**Table 4.4**: Analysis of variance of catalyst type and concentration and reaction time

| **Factor** | **Conversion of Methanol** | **Conversion of Glycerol** | **Conversion of tert-butanol** | **Nominal Yield** | **Selectivity towards ether** |
|---|---|---|---|---|---|
| Type of Catalyst | P= 0.2158 | P= <0.0001 | P= 0.2859 | P= <0.0001 | P= <0.0001 |
| Catalyst Concentration | P= <0.0001 | P= <0.0001 | P= <0.0001 | P= <0.0001 | P= <0.0001 |
| Reaction time - hr | P= 0.9773 | P= 0.0685 | P= 0.2628 | P= 0.0173 | P= 0.0426 |
| Cat. type* reaction time | P= 0.0445 | P= 0.3127 | P= 0.2283 | P= 0.0048 | P= 0.0337 |
| Cat. type* cat. Conc. | P= 0.0212 | P= 0.3610 | P= 0.0088 | P= 0.0007 | P= 0.0047 |
| React. time*Cat. Conc. | P= 0.0023 | P= 0.7151 | P= 0.6838 | P= 0.8872 | P= 0.7014 |

* P: Probability values for significance. $P< 0.05$ is significant

### 4.3.3.1 The Effect of Catalyst Type

The effect of variables on substrate conversion is shown in Figure 4.11. As can be seen, $H_2SO_4$ was the more effective catalyst for glycerol conversion. Although not statistically significant, the dominancy of $H_2SO_4$ was evident for methanol and tert-butanol as well. When considering nominal yield and catalyst selectivity (Figure 4.12), clearly $H_2SO_4$ was far superior to Amberlyst-36. The superiority of $H_2SO_4$ may be two-fold: due to its homogeneity/miscibility with the reaction medium and having a higher number of protons per mass basis [137]. Sulfuric acid donates twice number of protons/mass to the reaction medium as compared to Amberlyst 36.

#### 4.3.3.2 The Effect of Catalyst Concentration

Catalyst concentration clearly had a positive impact on all responses, i.e., higher catalyst concentration (6%) resulted in improved substrate conversions, ether yield and selectivity.

#### 4.3.3.3 The Effect of Reaction Time

As mentioned earlier, the reaction time did not have an impact on substrate conversion. It was evident that all the reactants achieved almost full conversion during the initial hour. Tert-butanol by far was the most facile with ~100% conversion in the initial hour. The nominal yield increased with increased reaction time. The nominal yield that gives an indication of how much of the initial ingredients converted to the desired product was highest (~37%) after 4hrs with both $H_2SO_4$ and Amberlyst-36 (~13%). The highest yield that gives an indication of how effective the catalyst is in achieving the desired product against the potential maximum was highest after 4hrs for both $H_2SO_4$ (33%) and Amberlyst-36 (9%). The highest selectivity for both $H_2SO_4$ (~46%) and Amberlyst-36 (~20%) were also achieved after 4hrs of reaction time. Results from Figure 4.7 also alludes that there is no significant improvement to responses between 3h and 4h reaction time suggesting that 3h may be sufficient to achieve maximum yield and selectivity.

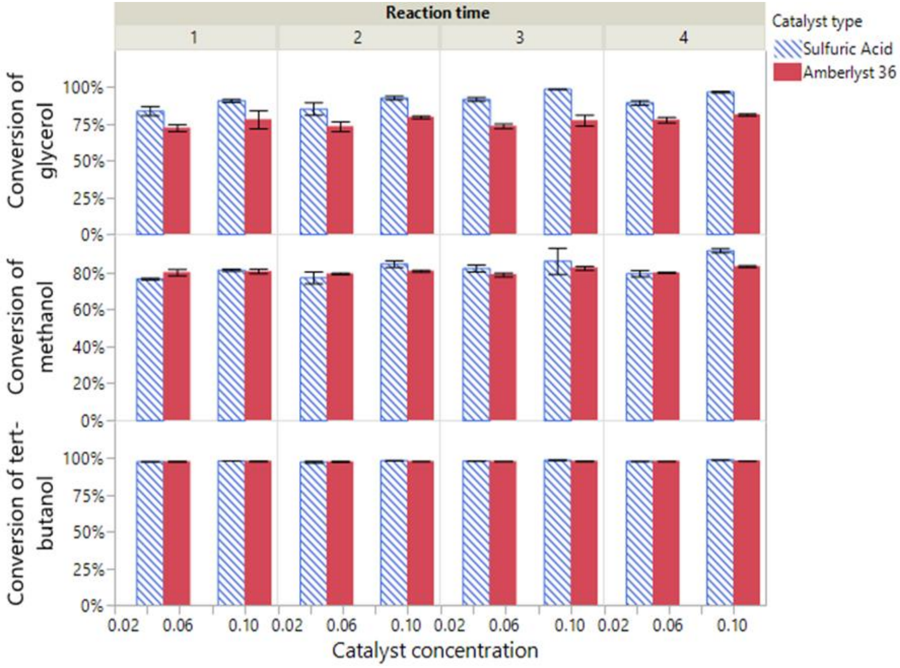


**Figure 4.10:** Effects of catalyst concentration and reaction time on substrate conversion

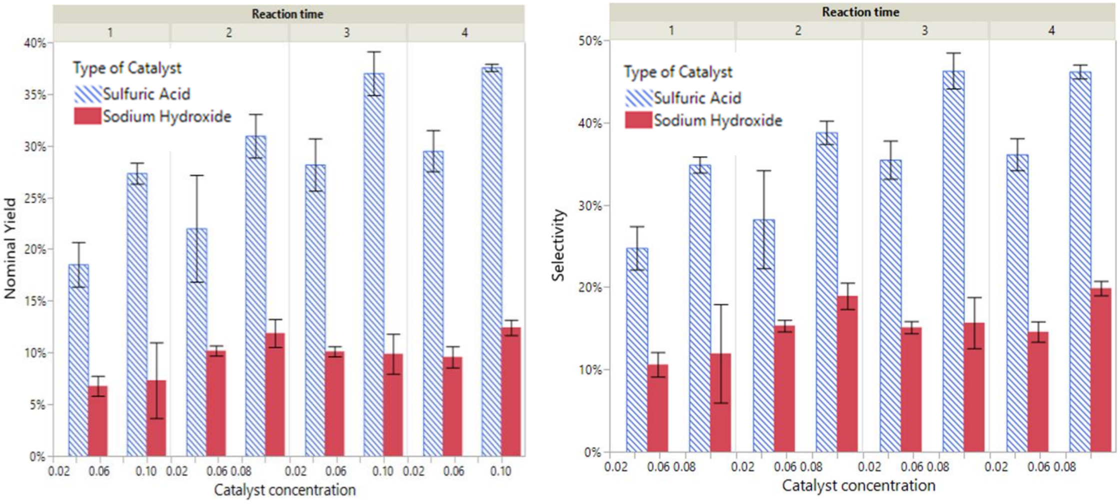


**Figure 4.11:** Impact of catalyst type and concentration on product yield and selectivity

### 4.3.3.4 Kinetic Studies

Figure (4.13) depicts the conversion trends of glycerol with 10% $H_2SO_4$ with data gathered from 0 to 4 h at 1 hour intervals. Each of the four charts refers to conversions transformed from zeroth order to the third order.

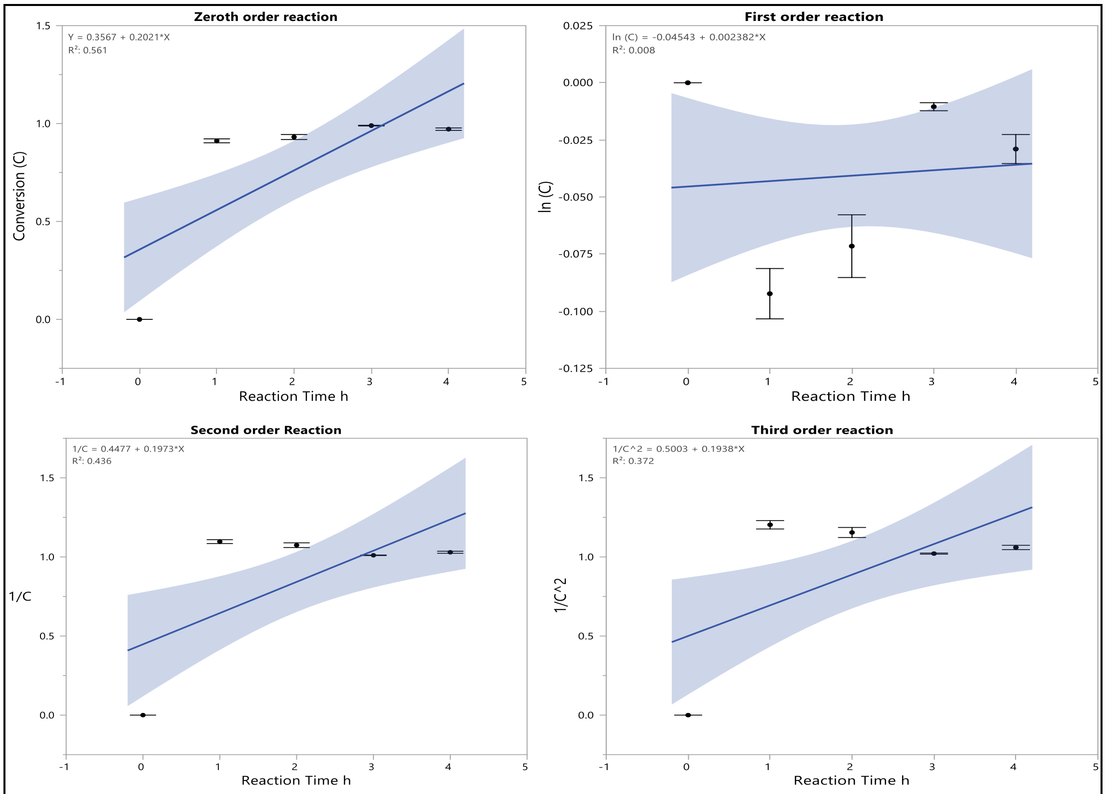


**Figure 4.12:** Kinetic parameters for glycerol conversion in the presence of $H_2SO_4$

The coefficient of determination ($R^2$) and goodness of fit statistics are given in Table 4.4. It should be noted that the correlation, though significant were not conclusive. The likely reason being most of the glycerol being converted within the first hour

**Table 4.5:** Statistical parameters pertinent to reaction kinetics

| Reaction order | R squared value | Goodness of fit | Probability value (Shapiro-Wilk) test |
|---|---|---|---|
| 0 | 0.561 | 0.5687 | <0.0001 |
| 1 | 0.008 | 0.8872 | 0.0610 |
| 2 | 0.436 | 0.5731 | <0.0001 |
| 3 | 0.372 | 0.6442 | <0.0001 |

Based on coefficient of determination ($R^2$) and goodness of fit statistics, the best-fit reaction order is assumed to be zero. The rate constant was obtained assuming that the reaction processes as follows:

$A \longrightarrow B$ Eq.18

$d[A] / dt = k * [A]^{\alpha}$ Where α is reaction order Eq.19

Since $\alpha$ = zero, then:

$d[A] / dt = k$ Eq.20

i.e: $[A] – [A]_o = kt$ Eq.21

then: $[A] = kt + [A]_o$ (Eq.13), which would be equivalent to the equation of the curve Y = mx + b; obtaining the equation from the graph A in figure 7:

$$Y = 0.3567 + 0.2021 * X \qquad \text{Eq.22}$$

Therefore, the rate constant $k = 0.2021$

### 4.3.3.5 Fuel Property Tests

Fuel property tests were conducted to a random sample that resulted in best yield/selectivity combination using $H_2SO_4$ (give reaction time and catalyst concentration). The cloud point and pour points were similar to that from NaOH results. However, the acid number was high as compared to that of biodiesel, likely due to residual acid. Viscosity of the ethers were lower than that of biodiesel indicating that the ethers were superior in this front. The ethers had 93% lower sulfated ash, 17% lower N, 16% lower S and an encouraging 72% reduction of O as compared to biodiesel. The Carbon and Hydrogen content of the ethers were increased by 41% and 14% respectively suggesting an increase of the energy content. Interestingly, supposition was confirmed by a 6% increase in energy content of ether as compared to biodiesel. The increase of energy also alludes to absence of water (as compared to the top phase that resulted via NaOH catalysis).

**Table 4.6:** Fuel property tests of analysis of variance of catalyst type and concentration and reaction time

| Property | Biodiesel (control) | Biodiesel miscible top phase via $H_2SO_4$ catalysis | ASTM Standards limitation for biodiesel [157] | Change +/(-) Remarks |
|---|---|---|---|---|
| **Cloud point °C** | 1.5 - 5.5 | - | - | - |
| **Pour point °C** | - 2.5 | <-35 | - | Vastly improved |
| **Flash point °C** | 175-180 | 80-100 | 130 | Highly volatile |
| **Acid number** | 0.21 | 5.78 | 0.8 max | High (could be reduced by neutralization) |
| **Viscosity (CSt)** | 3.96 | 6.96 | 1.9-6 | Increased |
| **Ash (%)** | 4.3 | 0.29 | 0.01 max | (93) - Significant improvement |
| **N%** | 1.317 | 1.088 | - | (17) - Significant improvement |
| **C%** | 56.469 | 79.652 | - | 41 - Significant improvement |
| **H%** | 8.376 | 9.558 | - | 14 – Significant improvement |
| **S%** | 0.759 | 0.636 | - | (16) – Significant improvement |
| **O%** | 28.779 | 8.776 | - | (72) – Significant improvement |
| **Energy Content (BTU/gal)** | 128,642 | 136,505 | - | 6 - Increased |

Based on the fuel property tests and being completely miscible with biodiesel, it could be surmised that the top phase resulting from reacting glycerol with methanol and tert-butanol in the presence of $H_2SO_4$ could be blended as an additive to biodiesel.

For optimization study 1 where the substrates (G:T:M = 1:2:1) were reacted in the presence of 5% NaOH catalyst at 130°C for 3h, about 69% ended up in the biodiesel-miscible and amphiphilic top phase whereas the remained ended up in a water/biodiesel immiscible gel-phase. In the optimization study 2 where the substrates (G:T:M = 1:1:2), were reacted under 10% $H_2SO_4$, at 130 °C for 3h about 44.3% ended up in biodiesel-miscible top phase.

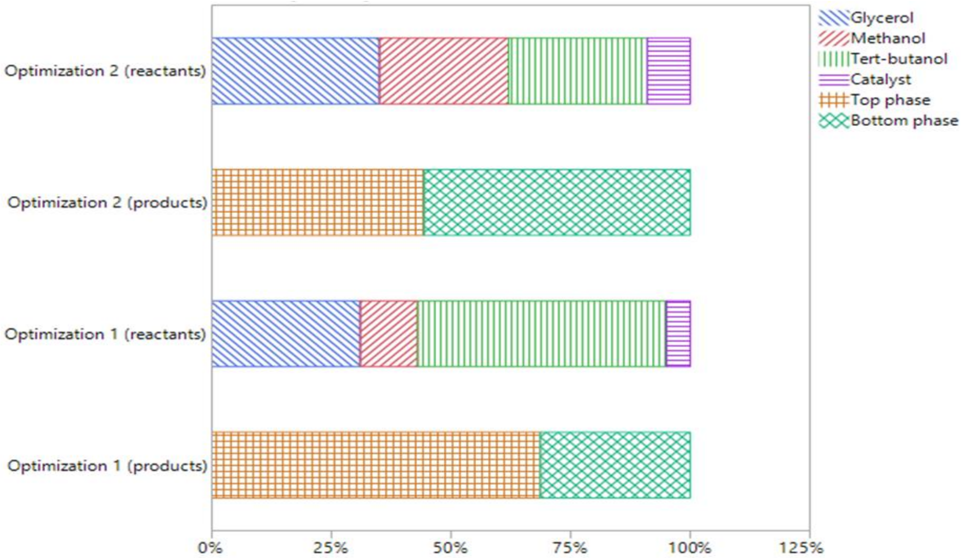


**Figure 4.13:** Amounts of initial reactants and products for the optimization studies

Although the yield of biodiesel-miscible top phase with NaOH was used was higher, the fuel quality of the top phase with $H_2SO_4$ was superior. Accordingly, it is surmised that the $H_2SO_4$-based process is better for producing biodiesel-compatible additive blends from glycerol-methanol-rich byproduct resulting from transesterification.

# CHAPTER V

# CONCLUSIONS

## 5.1 Conclusions from Studies Pertinent to Chapter III

Etherification experiments of propanol to di-propyl ether in the presence of sulfuric acid, Amberlyst 36 and titanium isopropoxide between temperatures 100–160 °C indicated that the type of catalyst had a significant impact on substrate conversion, product yield, and product selectivity. Of the three catalysts, sulfuric acid and Amberlyst 36 performed the best while titanium isopropoxide did not show any significant activity toward etherification. Propanol conversion, and ether yields & selectivity increased with increasing temperature but peaked around 140 °C. Further studies with sulfuric acid and Amberlyst-36 at 1 and 5% (w/w) concentrations with methanol and n-propanol substrates revealed that higher catalyst concentrations and higher temperatures favored substrate conversion. Of the two catalysts, sulfuric acid resulted in better substrate conversion, and ether yields. Regardless of the catalyst, higher temperatures favored ether yields. It was interesting to note that the selectivity of the two catalysts toward di-propyl ether under increasing temperatures was the antithesis to methoxy propane. A significant finding of this study is that when two different sized alcohols are present, preferential coupling, i.e., if the larger alcohols can couple together or larger ones with small ones, could be controlled by varying the type of catalyst (sulfuric acid or Amberlyst 36). These results pave the way to finding the correct catalyst type, concentration, and conditions for allowing coupling more complex alcohols such as glycerol and methanol which will allow use of byproducts from reactions such as transesterification to useful chemicals and fuels.

## 5.2 Conclusions from Studies Pertinent to Chapter IV

The ability of base (NaOH) and acid ($H_2SO_4$ and Amberlyst-36) catalyst dehydration of glycerol in the presence of methanol and tert-butanol was studied with the intention of utilizing the products as a fuel additive to biodiesel. Initial screening studies revealed that the resulting top phase after reacting glycerol with methanol alone was not miscible with biodiesel; however, that resulting with methanol and tert-butanol at glycerol: tert-butanol: methanol of 1:1:2 and 1:2:1 were miscible. All three catalysts were active for the process with NaOH performing best at glycerol: tert-butanol: methanol of 1:2:1 and $H_2SO_4$ performing better when glycerol: tert-butanol: methanol of 1:1:2.

An initial optimization study with NaOH revealed that from the catalyst concentrations tested (5%, 7%, 9% and 10%) low/intermediate (5% and 7%) concentrations being the most effective for maximum substrate conversion. Reaction time did not have an impact yield/selectivity of biodiesel-miscible top phase. The highest yield/selectivity was obtained at lowest NaOH concentration tested (5%). Fuel property tests indicated a top-phase which was miscible with and comparable to biodiesel; however, the presence of water (due to product being amphiphilic) and the need to dewater before being utilized as a biodiesel fuel additive reduced its utility.

Optimization studies with $H_2SO_4$ (homogeneous-acid) and Amberlyst-36 (heterogeneous acid) indicated that both catalysts performed well for substrate conversion with $H_2SO_4$ being the superior one. Overall, $H_2SO_4$ resulted in >99% tert-butanol, >80% methanol and >75% conversion under the conditions tested. $H_2SO_4$ also performed much superior to Amberlyst-36 on yield and selectivity toward ether. Increased catalyst concentration and reaction time had a positive impact on ether yields and selectivity. The highest ether yield of 37% and selectivity of 47% were obtained at 10% (w/w) $H_2SO_4$ catalyst concentration after 3-4hrs of reaction time. Fuel property and miscibility tests indicated that the ether-rich top phase resulting from reacting glycerol with tert-butanol and methanol (at 1:1:2 respectively) in the presence of $H_2SO_4$ was completely miscible with biodiesel and blended as an effective additive to biodiesel. The work paves groundwork for development of a fuel additive that can be blended on-site to biodiesel by for biodiesel manufacturers by utilizing the glycerol and methanol-rich byproduct stream from biodiesel production.

## 5.3 Recommendations

- Studies should be carried out with appropriate standards to specifically evaluate yields and selectivity of the complex array of products resulting from glycerol etherification.
- More extensive fuel property tests should be carried out to ascertain the fuel quality of the top ether-rich phase.

- The fuel property tests of various blends of ether-rich phase with biodiesel should be carried out.
- Economic study and evaluation for the process to see economic feasibility and the possibility to promote the reaction to commercial scale.
- It is also recommended to further work with actual transesterification byproducts (glycerol and excess alcohol with the catalyst) since our work was with model compounds.

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