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SYNTHESIS AND CHARACTERIZATION OF BIODIESEL FUELS FROM FURFURYL ALCOHOL AND SPENT COFFEE GROUNDS

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By

AMANDA LYNN RALEY, B.S.

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SYNTHESIS AND CHARACTERIZATION OF BIODIESEL FUELS FROM FURFURYL ALCOHOL AND SPENT COFFEE GROUNDS

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ABSTRACT

Biodiesel can be synthesized using several different triacylglycerides, alcohols, and catalysts. In this study, fatty acid methyl esters (FAMEs) and fatty acid ethyl esters (FAEEs) were produced from their respective alcohols and coffee oil, using either a basic (K_2CO_3) catalyst or an acidic catalyst (H_2SO_4). Fatty acid furfuryl esters (FAFurEs) were produced using commercially-purchased cooking oils (canola, olive, corn, sunflower, and peanut) with furfuryl alcohol, a basic (K_2CO_3) catalyst, a co-solvent (THF), and an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate). All samples were produced using either conventional heating methods (CH) or microwave-assisted heating methods (MW). All biodiesel samples were characterized using ^{1}H-NMR. FaFurE samples also underwent bomb calorimetry studies. Acid catalysis was unsuccessful at producing either FAMEs or FAEEs from coffee oil. Base catalysis, however, was successful. FAMEs were produced in 73% conversion and FAEEs were produced in 81% conversion under base-catalyzed conditions. FAFurEs were produced on varying amounts ranging from 19% for sunflower oil to 75.7% for olive oil. Microwave heating was unsuccessful at producing FAFurEs, whereas conventional heating did yield FAFurE products.

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I am also beyond thankful for anyone and everyone who spent any time around me during my graduate years at Stephen F. Austin State University, especially in the Spring of 2018. I was not the easiest person to be around. You all are the best.

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In Loving Memory of Dr. Sarah Christine Canterberry: Thank you for everything you've ever done for me. Rest easy sweet angel, and until we meet again.

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LIST OF ABBREVIATIONS

PD	Petrodiesel
BD	Biodiesel
CHT	Conventionally-Heated Transesterification
MAT	Microwave-Assisted Transesterification
TAG	Triacylglycerol
DAG	Diacylglycerol
MAG	Monoacylglycerol
FurOH	Furfuryl alcohol
SCG	Spent Coffee Grounds
FAAE	Fatty Acid Alkyl Ester
FAME	Fatty Acid Methyl Ester
FAEE	Fatty Acid Ethyl Ester
FAFurE	Fatty Acid Furfuryl Ester
FFAs	Free Fatty Acids
BMIM	1-butyl-3-methylimidazolium tetrafluoroborate
^{1}H-NMR	Proton Nuclear Magnetic Resonance Spectroscopy

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CHAPTER 1

Introduction and Literature Review

Countries worldwide rely on nonrenewable fossil fuels as their main source of energy for electricity, heating, and transportation. Due to the global demand for fossil fuels, and the political and economic instability of the world, the cost of a barrel of crude oil can vary drastically from year to year. A barrel of crude oil in the United States in 2005 cost, including inflation, only \$31.40, and today costs \$34.39, with a peak at \$102.00 per barrel in 2008 (1).

Biodiesel (BD) could be an attractive alternative to petrodiesel (PD), but is currently more expensive to produce.Biodiesel is a renewable energy source produced via transesterification reactions between triglycerides and short-chain alcohols. BD has very similar flow and combustion properties to petrodiesel, or diesel fuel derived from petroleum. Many properties are federally regulated closely for biodiesel and diesel usage in an average vehicle. One of these properties include viscosity. Viscosity of liquids is crucial for fuels because more viscous liquids atomize poorly. Bigger droplets within the fuel injector lead to incomplete combustion and the formation of soot. Two types of viscosity are studied: dynamic (or absolute) viscosity and kinetic viscosity. Dynamic viscosity is the ratio of shear stress of a fluid and the rate of which the fluid in sheared across a certain length

(49). Kinetic viscosity, however, is the measurement of resistance of a fluid to flow a specified length and can be found by dividing the dynamic viscosity by the fluid's density (49). Combustion properties include the heat of combustion (energy released when a compound is completely combusted), and energy content (energy stored within all bonds of a molecule). The flow and combustion properties of PD and BD are compared in Table 1 below.

Table 1: Flow and Combustion Properties of PD and BD.

Property	**Petrodiesel**	**Biodiesel**
Cetane Number[a]	40-55	50-65
Energy Density (MJ/kg)[b]	43	38
Dynamic/Absolute Viscosity(cSt)	2.98	4.31
Density (g/cm^3)	0.83-0.85	0.88
Kinematic Viscosity(cP)	3.50 – 3.59	4.90
Energy Content (BTU/gal)[c]	129K	118K
Cloud Point (^{o}C)	-5	20
Cold Flow	Baseline	Poor
Lubricity	Baseline	Excellent

[a] also seen as (CN), which is a measurement of how well the fuel ignites. [b] Energy within the biodiesel samples, also known as a biofuel's heat of combustion. [c] potential energy in a given fuel.

Because of these similar, albeit not identical, properties, in addition to BD's own advantages listed in a later section, BD has been considered as an attractive substitute for PD. BC can also be used in a blend with PD where the percentage of biodiesel is indicated as "Bx" where B20 consists of 20% biodiesel, B80 consisting of 80% biodiesel blend; B100 would indicate 100% biodiesel fuel (2, 3). Although there are several advantages and disadvantages to using biodiesel, the disadvantages are reduced when used in blends up to B20 (4).

Unlike PD, BD can be a part of a renewable closed carbon cycle. Extraction is used to separate vegetable or cooking oils from crops with high lipid content, and then this crude vegetable oil undergoes a refining process that includes water degumming, neutralization, bleaching, and deodorization (5). The refined oil product can then be treated with an excess of alcohol and a catalyst in a reaction known as transesterification to produce biodiesel and glycerol. The biodiesel can then be used as biofuel, while the glycerol has uses in other industries. A byproduct of the combustion of biodiesel is carbon dioxide, which, when consumed by plants along with water, can undergo photosynthesis, and the cycle can begin again. This cycle is known as a carbon-neutral cycle, since the carbon starts and ends in plant production. PD, however, releases excess carbon dioxide to the environment.

BD has been considered as an alternative to PD as a transportation fuel. In Europe, biodiesel production has increased from two million liters in 2009 to nearly four billion liters in 2012 (2). Other energy alternatives for electricity and heating include coal, nuclear, hydropower, and natural gas, but none of these alternatives are suited to be a biofuel (2, 3).

Biodiesel synthesis via transesterification can occur using either an acidic, a basic, or an enzymatic catalyst along with some heating source. Studies have been conducted in this laboratory in which biodiesel fuel mixtures were synthesized using multiple triglyceride sources and a variety of alcohols (7, 25, 26). The transesterification reaction has been performed using conventional heating as well as microwave heating. Analysis and characterization of biodiesel samples were done using ^{1}H-NMR Spectroscopy and GC-MS, which together, have yielded important structural information, conversion percentages, and the fatty acid composition profile of the biodiesel product mixtures.

One current source of controversy regarding biodiesel production is the usage of land and water to grow crops solely for biodiesel. Crops grown for biodiesel are also usually used for human consumption due to their high lipid content. In a world where nearly one million people are malnourished, many believe that arable land used to grow crops for biodiesel, rather than for food, could be considered inhumane (29). Solutions to this problem could be to use either crops that are not used for human consumption, or to use byproducts of other processes that are not useful in other industries. The objective of this research is to use two different byproducts from two different processes (furfuryl alcohol from lumber production and spent coffee grounds from brewed coffee) to produce biodiesel.

1.1 History of Biodiesel

Despite being a relatively new fuel alternative, triglycerides have actually been used in diesel engines for decades. Dr. Rudolf Diesel invented the diesel engine in 1892, which he presented at the Paris Exposition of 1900 (6, 7). Unbeknownst to those attending, the diesel engine presented ran exclusively on peanut oil. Dr. Diesel had been approached by the French government to explore the possibility of using vegetable oils as fuels. Although the diesel engine did run on peanut oil at the exposition, several problems were discovered after having used peanut oil to power the engine. These problems included the formation of deposits that increase friction and eventually lead to wear of the engine. In addition, the high viscosity of peanut oil led to ignition lag and reduced efficiency (less power per stroke), and a greater demand for fuel. Many suggestions were made in an effort to improve diesel engine performance when using vegetable oils as fuel. These suggestions included microdilutions, catalytic cracking, thermal decomposition, dilution, and transesterification. Microdilutions would be a “transparent, thermodynamically stable colloidal dispersion” made with vegetable oils, esters, and a co-solvent, or vegetable oils, an alcohol, a surfactant, and a cetane improver (50). Catalytic cracking or Fluid Catalytic Cracking (FCC) is a process in diesel processing in which heavy oils are pushed through a metal chamber under extreme pressure and heat conditions, along with a catalyst (alumina, silica, or zeolites). FCC breaks or “cracks” the larger, heavier oils into smaller, simpler units (51). Thermal decomposition, thermolysis or pyrolysis, is a process in which larger molecules are broken down by intense heat in the absence of oxygen or nitrogen (50). Dilution of vegetable oils is possible with diesel, ethanol, or other solvents, and can affect properties such as flash point and viscosity. Transesterification is a process in which biodiesel can be made from a triglyceride and alcohol source, usually with some sort of catalyst and heat source. Currently, transesterification is the primary reaction in producing biodiesel on a larger scale (40, 57). This reaction will explained in more detail in section 1.5.

The poor economy of the 1920s made PD a more attractive fuel for transportation due to its lower cost. Diesel engine systems were then modified in order to optimize performance using PD as the fuel. Ideas for using alternative fuel sources to power diesel engines were not seriously pursued until the energy crises of the 1970s (7).

1.2 Advantages and Disadvantages of Biodiesel

The use of BD by itself, or in a blend with PD has many advantages, which include: reduced emissions of sulfur oxides (SO_x), reduced CO_2 emissions, reduced soot and particulate emissions, lower reliance on foreign oil, better lubrication of the engine system, reduced toxicity (compared to PD), and increased flash point. In table 2 below, these variables are compared between biodiesel and petrodiesel.In addition, minimal changes are required to run biodiesel in current diesel engine systems.

Table 2: Property Comparison between Petrodiesel and Biodiesel (52)

Property	**Petrodiesel**	**Biodiesel (B100)**
Sulfur Content	< 10 ppm	< 5 ppm
NO_x emission (ppm)	237	248
Unburned hydrocarbon (ppm)	3	0
Particulate emission	2.9	1.1
Biodegradability	Readily	Poor
Toxicity	High	Low
Flash Point (^oC)	149 - 204	38-96
City mpg	20.1	22.3
Highway mpg	44.9	44.2

There has also been increased interest in lowering SO_x emissions after discovering that the combustion of fossil fuels is responsible for 73% of the sulfur dioxide (SO_2) in the lower atmosphere (2). SO_2 has been linked to several respiratory diseases such as asthma and bronchoconstriction (2). Due to these dangers to human health, the Environmental Protection Agency (EPA) of the United States lowered the 500 ppm standard for sulfur to 15 ppm in 2006 (8). However, the usage of biodiesel also has several disadvantages, which include: no reduction in nitrogen oxide emissions (NO_x), which can contribute to smog formation (53), the tendency to solidify in the fuel system at low temperatures (an average of approximately 1^oC), the possibility of saponification as a side reaction in production, competition with food crops for arable land, possible corrosion of the fuel systems and engines due to greater water solubility in BD, slightly higher fuel consumption due to the lower energy content, lower oxidative stability (so long-term storage should be avoided), and the fact that biodiesel fuel costs approximately 1.5 times as much as production for petrodiesel fuel. Nitrogen oxides, like sulfur oxides, are produced as a result of combustion, and can aggravate asthma-like symptoms. NO_x and SO_x alike can react with water and ozone in the atmosphere to produce acid rain (4, 9). It is worth mentioning, however, that a lot of these disadvantages are reduced significantly when PD and BD blends are used (4).

1.3 Triglyceride Sources

The triglyceride source used in industrial BD production usually depends on the geographical location of production. Rapeseed, in low fertility soils, usually gives moderate yields, typically within 40-50% in Europe. Rapeseed is also common in Central and South America, although it competes greatly with wheat for arable land. An acre used to grow crops for biodiesel is an acre not being used to grow food. This can prove to be problematic in certain areas of the world, where arable land is not in surplus. Canola, sometimes used synonymously for rapeseed, is a genetically modified version of rapeseed, originally developed in Canada. Rapeseed was modified to reduce erucic acid content (down to 2%) and decrease glucosinolate content. Erucic acid and glucosinolates both have been shown to be toxic in sufficient doses, and are known to cause heart disease in humans and other animals. The modified rapeseed was initially known as "double-zero" or "00 rapeseed" until the name "Canola" (for Canadian Oil Low Acid) was used more regularly. Canola oil, along with olive oil and sunflower oil, are commonly used for cooking as they are believed to reduce cholesterol levels in humans. Soybean oil is popular in the United States, Brazil, Argentina, China, and India with an oil content of around 18%. Oil Palm is also used due to the fact that it is possible to extract two different triglycerides from it: palm oil proper, from the pulp, and palm kernel oil, from the nut. Sunflower oil is another major oil used since it has a low content of linoleic acid and, therefore, can be stored for longer amounts of time (6). It also has an oil yield of 48-52%. Peanut oil is used often as well, but harvests between seasons can differ significantly due to the sensitivity of the peanut plant to weather conditions.

The type of vegetable oil used in biodiesel synthesis can affect the properties of the fuel itself. The carbon chain length of the starting molecule in the vegetable oil can affect the cetane number, the heat of combustion, viscosity, and NO_x exhaust emissions.

The amount of branching of these molecules can affect cetane number and pour point. The amount of unsaturation present in the molecule can affect NO_x exhaust emissions, oxidative stability, melting point, and lubricity. Table 3 compares various vegetable oils by their viscosities, densities, and percentage of saturated fatty acids.

Table 3 : Properties and Fatty Acid Composition of Various Vegetable Oils

Oil	Density (g/cm^3)	Absolute Viscosity	% saturated	% unsaturated	% monosaturated
Canola	0.918	0.0482	7.4	28.1	63.3
Soybean	0.920	0.0198	15.6	57.7	22.8
Peanut	0.930	0.0393	20.3	31.5	48.1
Olive	0.909	0.0272	13.8	10.5	73.0
Sunflower	0.918	0.0280	10.0	40.1	45.4
Corn	0.916	0.0185	12.9	54.7	27.6

Several studies have been reported in which biodiesel fuel mixtures were synthesized using waste cooking oil from restaurant fryers, but production yields were significantly lower than when virgin vegetable oils were used. It has been hypothesized that the free fatty acid (FFA) content of waste cooking oils is much higher than that of virgin oils. These FFAs can lead to catalyst degradation during the transesterification process (10).

However, the usage of these food vegetable oils has become increasingly controversial over time. With increasing global population causing increased demand for an energy source of electricity and transportation along with an increased demand for food crops, the use of land to grow crops for biodiesel has become a topic of debate. Food shortage aside, other arguments against the usage of edible vegetable oils include that it could cause significant sustainability issues, such as the division of arable land for that of food crops and biodiesel pre-reactants, deforestation to increase arable land, as well as possible food crop price increases (11). In order to reduce the demand on the use of arable land for fuel crop production, it has been suggested that other materials that have a high lipid content, but which are not used for human food, be used as alternative triglyceride sources. Examples of such materials include spent coffee grounds, acorns, and other non-edible nuts and seeds.

1.4 Spent Coffee Grounds (SCG) as a Triglyceride Source

Coffee is one of the most commonly consumed beverages in the world, behind water, tea, beer, and soda. Worldwide coffee consumption is estimated to be approximately 2.25 billion cups per day (5). When coffee is brewed, the spent coffee grounds (SCG) need to be disposed of appropriately. In countries where coffee is a major export, like Brazil, defective beans can decrease beverage quality and must be removed physically (32). Theseunsatisfactory beans occur naturally, are extremely common, and cannot be prevented entirely. They are not used commercially, but are reused to produce coffee grounds sold domestically. One side effect of this is that domestic coffee quality is decreased. SCG have many uses including animal feeds, organic fertilizer, anaerobic digestion, high-value compound removal, bioethanol production, and, bioethanol production, and, as work in this lab along with studies reported in the literature suggest, a triglyceride source for biodiesel production (11). It has been predicted that 1 billion liters of biodiesel could be produced per year based on how much SCG the world disposes of every year (11). Coffee beans have a high lipid content, some of which is partially lost during the brewing process. However, it is estimated that 11 – 20% of the remaining oil can be extracted from the SCG, depending on the source (33). SCGcontain an average of 15% usable lipid content that can be converted to a similar percentage of biodiesel successfully via transesterification (34, 35).

Coffea arabica, commonly known as Arabica, accounts for up to 75% of coffee production due to the fact that it is considered to be more flavorful and of higher quality (35). In comparison, *Coffeacanephoria*, commonly known as Robusta, contains twice as much caffeine, but is considered poorer quality and is used primarily for instant coffee. Due to their differences, Arabica and Robusta beans are commonly blended together (35). In research, 100% Arabica beans converted to biodiesel had conversions between 1.4% and 36.0% while 100% Robusta beans converted to biodiesel saw percentages between 1.2 and 44.0% (35). Biodiesel from coffee also contains high levels of antioxidants, which assist in oxidative stability and slow the rancidification process. In research, studies have used SCG with methanol and KOH conversion percentages of up to 100% (34). When an acid pretreatment is used before base-catalyzed transesterification, conversions of up to 96% can be obtained (36). Additionally, defective coffee beans from Brazil were used with methanol and ethanol with $NaOCH_3$ to reach percentage conversions of 70.1% and 64.2% respectively (32). A side product of the production of biodiesel is the remaining defatted coffee grounds, which can be used in soil as biochar

(36). Biochar can improve soil conditions by introducing more essential elements (carbon and nitrogen)into the soil,changing pH, increasing water retention, improving microbial populations, and enhancing efficiency of nutrient usage (36). Preliminary studies in this laboratory have been done in which BD mixtures have been synthesized from triglycerides extracted from SCG, albeit with low conversions. Plans for further work in this area will be discussed in further detail in section 2.4.2. Results from these preliminary studies can be found in Appendix A.

1.5 Transesterification

Transesterification is a reaction in which the alkoxy group from an ester is replaced by the alkoxy group of an alcohol. These reactions require some sort of catalyst (usually an acid or base) and a heat source to form a reasonable amount of product in a relatively short amount of time. Figure 1 shows the overall transesterification reaction, while Figure 2 depicts the stepwise process of forming three fatty acid alkyl ester (FAAE) molecules from a single triacylglycerol (TAG) molecule.

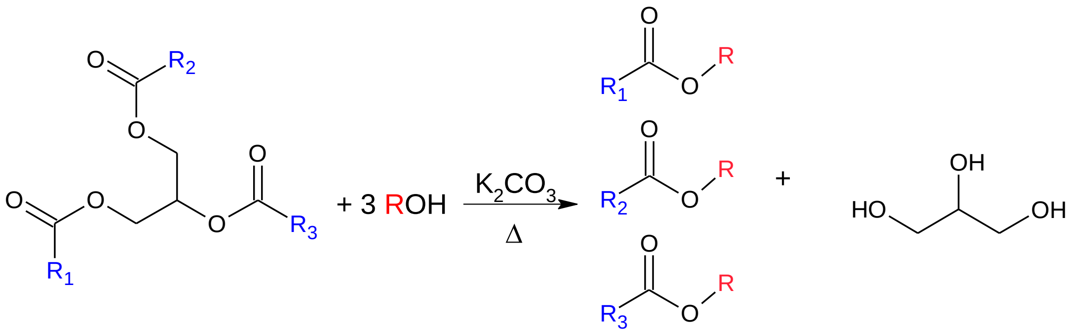

Figure 1: The transesterifcation process with a basic catalyst

Although a minimum 3:1 alcohol:triglyceride molar ratio is required stoichiometrically for the reaction, in practice alcohol:triglyceride molar ratios vary from 4:1 to 12:1 when the reaction is performed under base-catalyzed conditions. The alcohol:triglyceride ratio can be up to 20:1 when the reaction is performed under acid-catalyzed conditions (12). Typically, an alcohol:triglyceride ratio of 6:1 is used. Lower alcohol:triglyceride ratios can result in low conversion and higher alcohol:triglyceride ratios can increase the likelihood of undesirable side reactions, e.g. saponification (12, 13).

In transesterification, the excess alcohol also helps to drive a reversible reaction to favor the products. This is because there must be a conversion from triacylglycerol (TAG) to diacylglycerol (DAG) in reaction step I. This is followed by a conversion of the DAG to a monoacylglycerol (MAG) shown in step II, and finally the conversion of the MAG to glycerol. Each of these steps yields a fatty acid alkyl ester, (FAAE) (14). This entire process is shown in Figure 2.

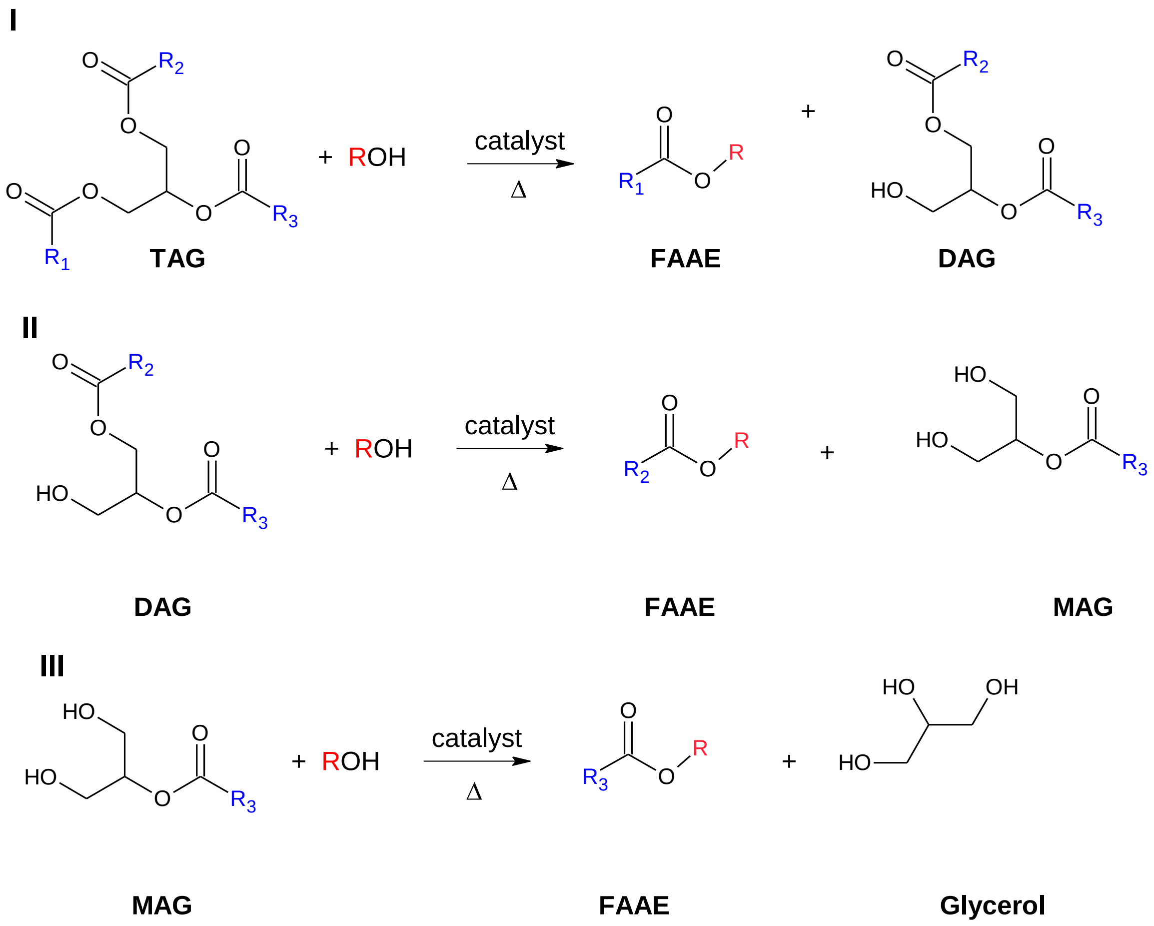

Figure 2: Sequential transesterification during biodiesel synthesis

Some literature reports have claimed that transesterification can occur without a catalyst (9). This could simplify the purification process, but such processes require much higher temperatures as well as larger excesses of alcohol (9). The current industrial production of biodiesel is performed using an acidic or basic catalyst. Acidic and basic transesterification occur via distinct addition-elimination mechanisms. The acid-catalyzed transesterification mechanism is shown in Figure 3; the base-catalyzed transesterification mechanism is shown in Figure 4.

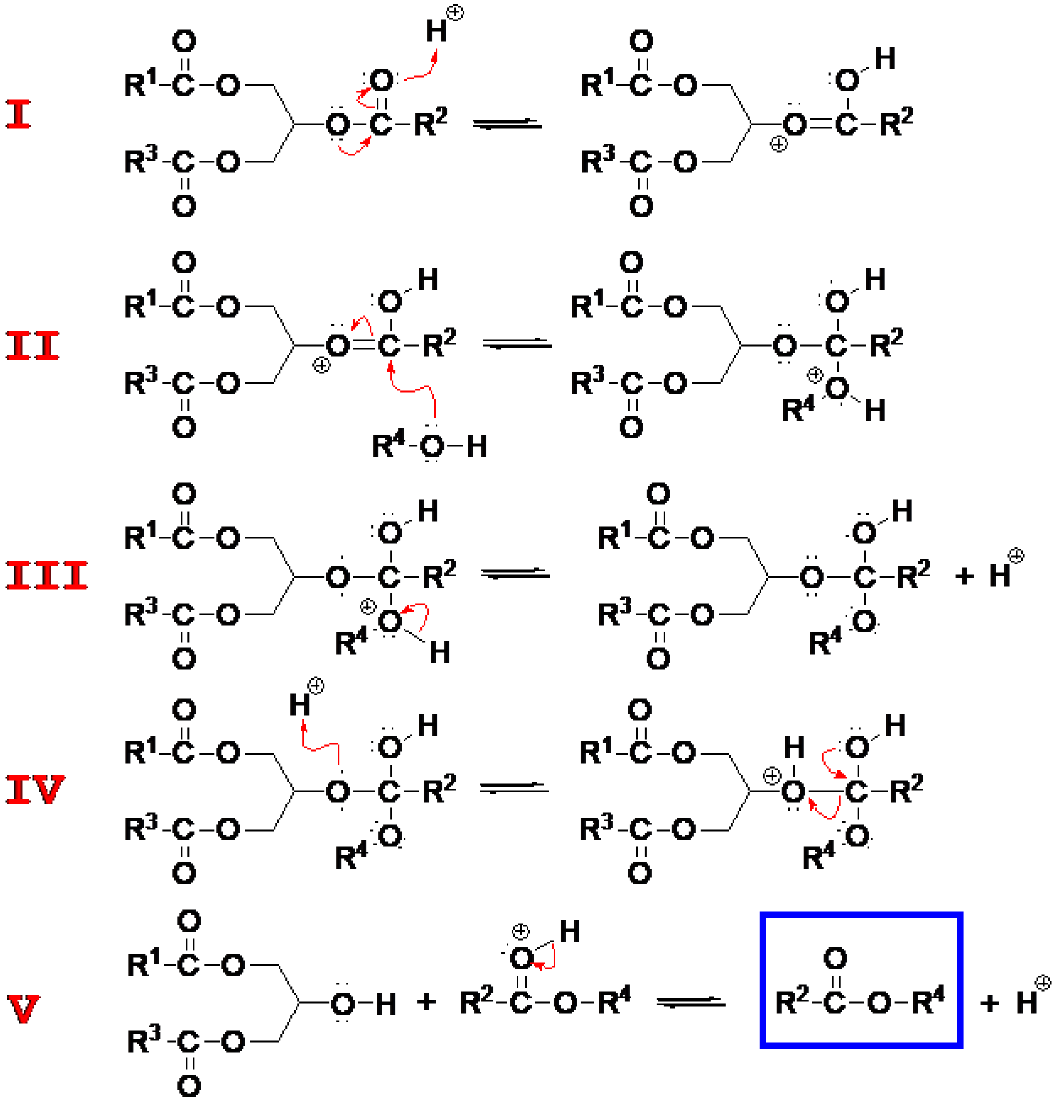

Figure 3: Mechanism for acid-catalyzed transesterification

The first step in acid catalysis is the protonation of the carbonyl oxygen of one of the carboxyl groups of the TAG. Then, nucleophilic addition occurs from the oxygen on the alcohol to the carbonyl carbon, producing a tetrahedral intermediate. This is followed by a series of proton-transfer steps: the first being loss of proton from species (B) and the second being protonation of the oxygen atom in species (C) to form intermediate (D). The conjugate acid of the FAAE product (E), along with the diacylglyceride (DAG) are formed via elimination from (D). The FAAE product is finally formed via deprotonation of (E).The base-catalyzed transesterification mechanism is similar to, but distinct from, the acid-catalyzed mechanism, as shown in Figure 4.

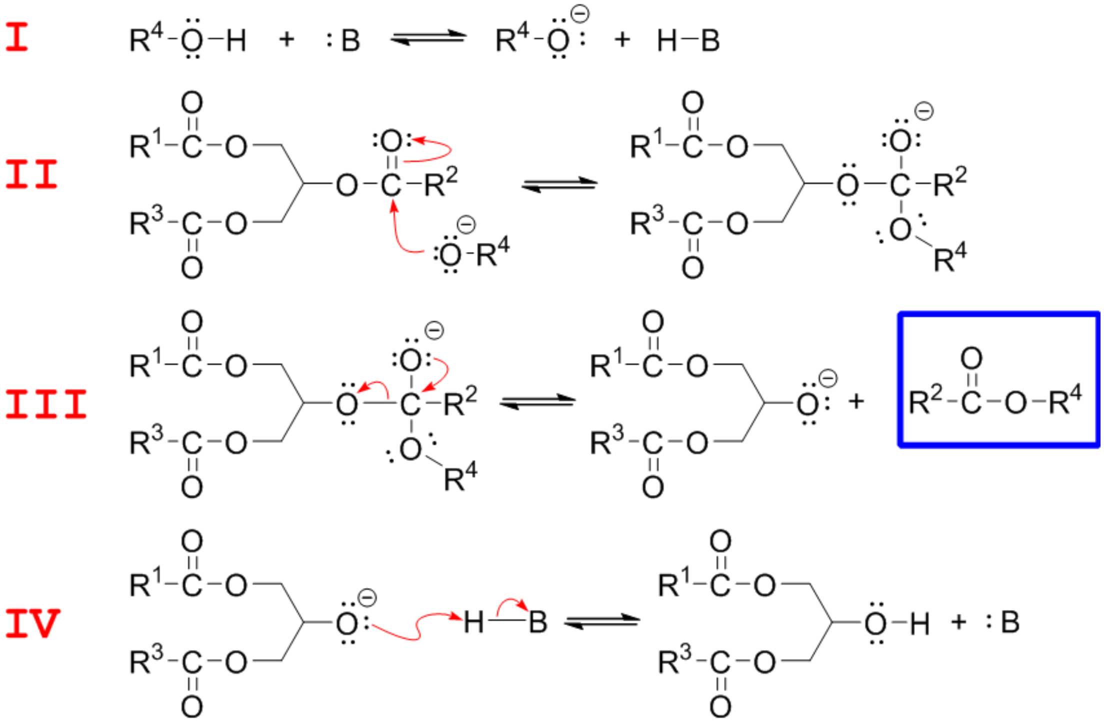

Figure 4: Mechanism for base-catalyzed transesterification

The first step in the base-catalyzed transesterification mechanism is the formation of the conjugate base of the alcohol (R^4-O^-) via deprotonation of the alcohol (Step I). The alkoxide anion then undergoes a direct nucleophilic addition to the acyl carbon of one of the carboxyl groups of the TAG. This forms the anionic tetrahedral intermediate species (F). The FAAE product, along with the DAG-conjugate base (G), is formed via elimination from intermediate (F). Protonation of (G) gives the neutral DAG.

As seen in the figures, the major differences between these two mechanisms is that protonation of the carboxyl group by the strong acid is necessary in order to allow the weakly-nucleophilic neutral alcohol to be able to do nucleophilic addition to the acyl carbon of the ester. In the base-catalyzed transesterification process, however, the alkoxide anion is sufficiently nucleophilic to be able to do nucleophilic addition to the acyl carbon of the ester without the need for prior activation (4, 15).

Although base-catalyzed transesterification does carry with it an increased possibility of saponification, it is much more commonly used for industrial-scale biodiesel production.This is due to the facts that acid-catalyzed transesterification requires more alcohol (30:1 mole ratio), higher reaction temperatures, and longer reaction times. In addition, acid catalysts are much more corrosive than basic catalysts (8).

Basic catalysts are used more often for large-scale BD production than acid catalysts. Solid bases are generally alkali metal oxides or alkaline-earth metal oxides mixed with zeolites. These solid bases typically offer higher conversions, but require much higher temperatures (at least $150^{o}C$) and higher pressures (20-40 bar) than metal hydroxides. Alkali metal hydroxides (e.g. NaOH, KOH) give lower percentage conversions, however, they are more cost efficient, and are used in industry much more commonly than solid basic catalysts (16).

Many base-catalyzed BD syntheses use strong bases, usually NaOH or KOH because the transesterification can occur with fairly low catalyst loading (0.5 mol %) and with high conversion (up to 98%) in a relatively short amount of time (30 min). Base-catalyzed transesterification requires anhydrous reaction conditions, and even in such conditions some water is still formed as a byproduct under the reaction conditions, as shown in Figure 5. This leads to the production of soaps, via saponification as the hydroxide ion from water reacts with triglycerides, which, as mentioned previously, makes the separation and purification of the product extremely difficult (10).

$$\mathrm{OH^- + CH_3OH \rightarrow H_2O + CH_3O^-}$$

Figure 5: Deprotonation of methanol by hydroxide ion

The saponification reaction is shown in Figure 6:

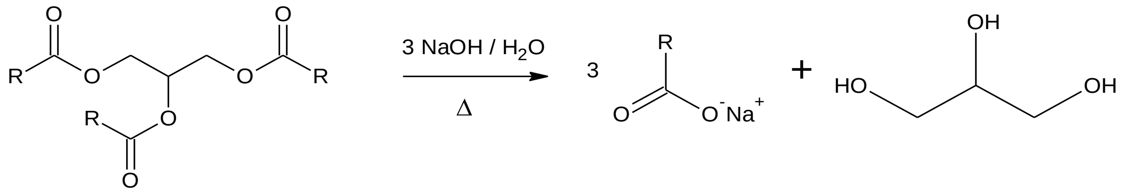

Figure 6: Saponification of a triaclyglycerol

In the saponification reaction, a fatty acid salt (soap) is produced instead of the desired FAAE product. The problem with soap formation is that the fatty acid salt has, by nature of its structure, considerable solubility in both phases: the low-polarity phase containing the TAG as well as the higher-polarity phase containing the alcohol, water, and some dissolved catalyst. This property is known as amphiphilicity, i.e. the fatty acid salt has a hydrophobic portion of its structure (the long fatty acid chain) and a hydrophilic portion of its structure (the carboxylate).

In order to avoid the formation of hydroxide ions, potassium carbonate was an attractive alternative catalyst in this experiment (27). The carbonate ion reacts with an alcohol to create the bicarbonate ion, which is less nucleophilic than the hydroxide ion. However, more carbonate catalyst is required (2-3%) compared to hydroxide catalyst (0.5%). This formation of the bicarbonate ion is shown in Figure 7.

$$\mathrm{CO_3}^{2-} + \mathrm{CH_3OH} \rightarrow \mathrm{HCO_3}^{-} + \mathrm{CH_3O}^{-}$$

Figure 7: Deprotonation of methanol by carbonate ion

Although there are many factors to consider when choosing a catalyst, one of the most important is the free fatty acid (FFA) content of the triglyceride source. If the FFA content is greater 1% (w/w), acid-catalyzed transesterification is preferable for BD synthesis. If the FFA content is below this threshold, then base-catalyzed transesterification is preferable. However, in either process, the biodiesel product must be purified by a slow and environmentally unfriendly washing stage with water (17). This is because upon production, there are still some contaminants in the product mixture. These contaminants can include unreacted alcohol, water, catalyst, glycerol, free fatty acids, soaps, monoglycerides, diglycerides, and some unreacted triglycerides (18).

In addition to acid and base catalysis,a third type of catalysis, enzymatic catalysis, has been studied for use in BD synthesis. Enzymatic catalysts, usually lipases, which do not require coenzymes, are reasonably stable and tolerate organic solvents. Another advantage is that enzyme catalysts are not as sensitive to the alcohol:triglyceride molar ratio as is the case for the acid- and base-catalyzed processes. They are, however, very sensitive to glycerol concentration. Glycerol can absorb to the surface of the enzyme, slowly negatively impacting the enzyme's activity and its capacity to be recycled (21). Despite their appealing properties, these enzymatic catalysts are still under development (8).

1.6 Furfuryl Alcohol as an Alcohol Source

The alcohols primarily used in biodiesel synthesis are short chained alcohols such as methanol and ethanol. They both have a low molecular weight, but methanol is cheaper. However, biodiesel made from methanol is not a true renewable resource since methanol is mainly produced from natural gas (38). In addition, methanol is toxic and hazardous and requires special precautions for industrial use (38). Bioethanol is more expensive but reaches higher percent conversions than methanol, and is a true renewable resource from corn and soybeans (38) However, this also plays a part in the usage of arable land controversy. A possible solution is the usage of furfurals (39).

In 1984, Le Bigot *et al*. filed a United States patent for the "Process For Preparing Esters of Furan By a Transesterification Reaction" (40). In their patent, they explained that a catalyst (aluminum butylate) was used with a polymerization inhibitor (40). The inhibitor is highly toxic and cannot be used in foodstuffs or pharmaceuticals, but in absence of the inhibitor, furfuryl alcohol will undergo spontaneous polymerization (40). It is now known that all resins made from furfuryl alcohol with an acidic catalyst can promote the polymerization reaction, but specific conditions can modify the kinetics of the reaction (41). These conditions include the strength of the acid, the amount of water in the reaction, and the temperature (41). Choura et al. discovered that this polymerization reaction occurred by the formation of polyconjugations through the terminal CH_2OH groups on furan rings with non-furanicunsaturations (41). Dunlop and Peters also discovered that, through dehydration (catalyzed by acids), a complete reaction removed nine grams of water per mole of furfuryl alcohol (42). Dunlop and Peters proposed the usage of *n*-butyl amine and piperidine to slow the reaction (42).

Furfuryl alcohol, unlike methanol or ethanol, is a heterocyclic alcohol that is a byproduct of sugar production, and can also be used to make polymers and resins in plywood and lumber production. Furfuryl alcohol also contains more oxygen than that of methanol or ethanol, which could lead to better combustion. Furfuryl alcohol is much heavier than the primary alcohols for biodiesel with a molecular weight of 98.10 g/mol, in comparison to methanol at 32.04 g/mol and ethanol at 46.07 g/mol (43). Furfuryl alcohol also has a much higher boiling point at $170^{o}C$ than that of methanol ($64.7^{o}C$) and ethanol (78.2^{o}C). Additionally, furfuryl alcohol is a much stronger acid with a pKa of 9.55 compared to methanol and ethanol with a pKa of 15.5 and 15.9 respectively (43, 44). Preliminary studies have been conducted with furfuryl alcohol in this laboratory and will stand as controls. Results from previous studies can be found in Appendix A and are explained in section 3.2.2.

1.7 Heating Methods

Microwave heating using a laboratory microwave oven will be the primary heating method in this research. It has been shown in the literature that microwave heating is more efficient than conventional heating methods (10, 19). There are two ways in which microwave radiation can interact with samples. The first way assumes that the sample molecule has a dipole moment. When the dipole moment of a molecule is exposed to the electrical field component of microwave radiation, the dipole tries to realign itself with this electric field, but the field is continuously oscillating, leading to motion of molecular bonds, resulting in friction which produces heat. The second way is if a molecule is charged, then the microwave radiation causes charge redistribution resulting from a distortion of the electron clouds. Because this heat is generated on a molecular level, and these molecules do not have a relaxation period, the heating is very efficient (10, 20). In a previous study in this laboratory, in which vegetable oils reacted with short straight-chained alcohols and a basic catalyst, it was seen that, compared to conventional heating, more effective over a shorter time period. Results of this study can be found in Appendix A.

1.8 Solubility

Preliminary studies in this laboratory using canola oil, furfuryl alcohol, and K_2CO_3 in the microwave, showed that the desired fatty acid furfuryl ester (FAFurE) products were formed, albeit with very low conversion. In the same study, another sample was produced using soybean oil instead of canola oil. Analysis of the product mixture using ^{1}H-NMR spectroscopy showed that the FAFurE product was formed with very low conversion. These preliminary results can be found in Appendix A. The much lower conversions might be due to the low solubility of the K_2CO_3 in the reaction mixture. In order to overcome this problem, the objective of this research is to investigate whether the addition of a co-solvent, e.g. THF, could improve the solubility of the catalyst in the reaction mixture and, thus, improve conversion.Another method by which the solubility of the catalyst in the reaction mixture might be improved is through the use of ionic liquids (21-23).

1.9 Ionic Liquids

Ionic liquids are salts that are in the liquid phase at room temperature (21). They differ from molten salts in that they are entirely ions in composition, are liquid below 100^{o}C, and are not relatively viscous (21). Initially, they were studied in the 1940s for aluminum electroplating, and in the 1970s, research of these liquids centered around their electrochemical applications. However, they were also studied as possible solvents for homogenous transition metal catalysts, and since the 1970s, have been studied in catalysis, synthesis, separations, and polymer electrochemistry (21, 22).

Their application as solvents or co-solvents was interesting due to their chemical properties, which differ greatly from organic solvents. These include very low vapor pressure, the ability to dissolve many compounds, the capacity to be used in two-phase systems, being nonflammable, having a wide liquid range, having high catalytic activity, potential recoverability, and having a high thermal stability (21, 23). In structural studies in the literature, it was discovered that dipolar solutes would interact with both the charged head groups and the nonpolar domains, making ionic liquids potentially excellent solvents for dipolar solutes (22).

In the literature, different ionic liquids have been synthesized and used for biodiesel synthesis either by taking place of a catalyst in methanol (24, 30) or ethanol (31), or in addition to an enzymatic catalyst (22) in methanol, all with percent conversions of at leat 87%. Ionic liquids can be recycled after the production of biodiesel. However, in the literature, two (tetraborates and hexafluorophorates) show higher decomposition rates in excess water (44). Additionally, 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([C_4C_1im][OTf]) had lower reactivities than other ionic liquids (45). It was proposed that the reactivity of [C_4C_1im][OTf] could be saved by using an acidic catalyst, but the reaction would require significantly more time (45).

CHAPTER 2

Methodology

2.1 Reagents

Commercially available canola, corn, peanut, sunflower, olive, and soybean oils were used in this study and were purchased from a local grocery store. Coffee grounds were saved from home-brewed coffee from both Folgers and Mountain Green K-Cups. Methanol (reagent grade Flinn Scientific), 95% ethanol, 100% ethanol (both reagent grade Flinn Scientific), and furfuryl alcohol (reagent grade Sigma-Aldrich) were used as alcohols. Potassium carbonate (K_2CO_3) (Fischer-Scientific) was used as the basic catalyst. Alumina gel (chromatography grade Flinn Scientific) was used to remove unreacted furfuryl acohol. Commercially-purchased vinegar was used in the washing stage.

2.2 Apparatus

All microwave-assisted transesterification reactions were performed using a Milestone START laboratory microwave oven with a color touch screen controller. The microwave oven kit includes a carousel that can heat up to 24 reactions at once. However, only a single holder was used as only one reaction was done at a time. A picture of the microwave apparatus can be seen in Figure 8.

Microwave-heated reactions were performed in 100-mL round bottom flasks (RBFs) with a magnetic stir-bar.The microwave oven parameter settings that were used for performing a particular reaction depended on the specific alcohol used.Table 4 lists the microwave oven parameters used for each alcohol.

Table 4: Parameters Used for Microwave Heating Experiments

Alcohol	**Microwave Procedure #**	**Temperature (°C)**	**Ramp time (min)**	**Hold time (min)**	**Cool down (min)**	**Total time (min)**
Methyl	1	55	2	9	10	21
Methyl	2	55	2	22	10	34
Ethyl	3	72	2	22	10	34
Furfuryl	4	88	2	13	19	34

Where “Microwave Procedure #” is the number programmed on the microwave for a specific set of parameters. “Ramp time” is the time, in minutes, at which the microwave increases the temperature in the vessel from room temperature tothe temperature at which the reaction is performed. “Hold time” is the time, in minutes, for which the vessel is held at the specified temperature. “Cool down” is the time, in minutes, at which the vessel is no longer heated and is allowed to cool. “Total” is the summation of ramp time, hold time, and cool down time.

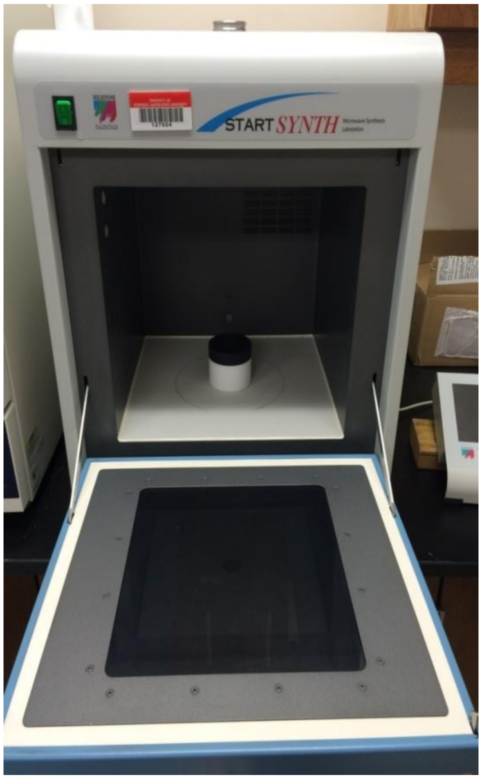

Figure 8: ***The Milestone START laboratory microwave***

Conventionally-heated reactions were performed in 100-mL RBFs using a thermowell heating mantle, a reflux condenser, and a magnetic stir bar. This apparatus can be seen in Figure 9.

Figure 9: Conventional-heated reaction apparatus

All products formed at the end of tranesterifcation were analyzed using ^{1}H-NMR Spectroscopy. The ^{1}H-NMR analyses were conducted using a JEOL ECS-400 spectrometer. All samples were dissolved in $CDCl_3$. The internal chemical shift reference used was tetramethylsilane (TMS).

2.3 Experimental Procedures

There were three major parts to this experimental design: synthesis, characterization, and bomb calorimetry. Synthesis was broken down further into two sections: with coffee oil as a triglyceride source or with FurOH as a alcohol source. Characterization was the same for all biodiesel samples produced. Bomb calorimetry was only used for FurOH biodiesels.

2.3.1 Commercially-purchased oils with FurOH:

It was crucial to fill the 100 mL RBF to a minimum of half of its total capacity in order for the IR sensor in the microwave to be able to monitor the temperature throughout the process.

According to literature and previous experiments from this lab, a 3:1 molar ratio was deemed the best for alcohol: oil ratios. Approximately 30 g of oil were used in each reaction (with the exception of reactions using coffee oil). This was the same for both microwave-heated reactions as well as for conventionally-heated reactions. The exact mass of oil was then used to calculate the amount of alcohol needed, based on a 3:1 molar ratio of alcohol to oil. The exact mass of oil was also used to determine the amount of K_2CO_3 that was needed for the reaction. In a similar manner, the exact amount of oil was also used to determine the mass of 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM) needed for the reaction, based on a 5 mol % ratio.

When coffee oil was used for a reaction, approximately 0.5-1.0 g of oil and 25 mL of alcohol were used. For acid-catalyzed reactions using coffee oil, 0.5 mL of concentrated (18 M) H_2SO_4 were used. For base-catalyzed reactions using coffee oil, a ratio of 5 mol % of K_2CO_3 was used to determine the amount of base needed.

2.3.2 CHT using commercially-purchased oils

All transesterification reactions using commercially-purchased oils were initially attempted using conventional heating methods. The reaction mixture was loaded into a 100-mL RBF. A stir bar was added, along with a reflux condenser. A simple reflux apparatus was constructed. The mixture was stirred at reflux for 3 h.

After the reflux period had ended, the apparatus was allowed to cool to room temperature. The stir-bar was removed, and THF was removed using rotary evaporation. Then, the remaining mixture was transferred into a separatory funnel. The reaction mixture was washed with vinegar (2 x 50 mL), followed by aqueous NaCl (2 x 50 mL), and finally DI water (2 x 50 mL). After each wash, the aqueous phase (the bottom layer) was removed. The organic phase was transferred into a 150-mL Erlenmyer flask and dried over anhydrous $MgSO_4$ for at least 2 h before being filtered through cotton into a new, dried 100-mL RBF.

Approximately 1 g of alumina gel was added to the RBF and the mixture was stirred vigorously and left to rest for 10 min. Then the mixture was filtered using a Buchner funnel into a tared vial and weighed. A small aliquot of the reaction mixture was then transferred to an NMR tube, $CDCl_3$ was added, and the sample was analyzed using NMR.

2.3.3 MAT using commercially-purchased oils

For all commercially-purchased oils, furfuryl alcohol was the only alcohol used. Therefore, only microwave procedure number 4 was used. The stir parameter was adjusted as needed in order to allow for rapid and thorough stirring of the reaction mixture. The other microwave parameters were set as specified in Table 4, Method number 4. After the sample was removed from the microwave oven, the sample was subjected to the purification/isolation protocol outlined in Section 2.3.2.

2.3.4 Drying protocol for SCG

Before transesterification, spent coffee grounds had to be first dried and then refluxed to extract the remaining lipids. Coffee grounds were initially dried by placing them in a thin layer on a paper plate and leaving them to dry overnight (approximately 18 h) in an oven set at 60 ^{o}C. Later, larger amounts of spent coffee grounds were placed in a disposable aluminum foil baking tray and left to dry in an oven set at 70 ^{o}C for 12 – 24 h.

2.3.5 Triglyceride extraction protocol for SCG

Approximately 100 g of dried coffee grounds were placed in a 500-mL RBF with about 250 mL heptane. The mixture was heated at reflux for 3 h. After 3 h, the mixture was filtered into a clean 500-mL RBF. A fresh portion of approximately 100 g of dried, spent coffee grounds were added to the RBF, along with additional heptane (as needed).The reflux-filtration process was repeated for a total of four times. After the fourth extraction, the coffee mixture was filtered into a clean 500-mL RBF. The heptane was removed using rotary evaporation. The coffee oil that remained in the RBF was transferred to a vial and sealed until needed.

2.3.6 CHT of coffee oil from SCG

Coffee transesterifications were attempted using acid catalysis as well as base catalysis. For acid-catalyzed transesterification, H_2SO_4 was used as the catalyst. For base-catalyzed transesterification, K_2CO_3 was used as the catalyst. Only methanol and ethanol were used for transesterification of coffee oil. No additional co-solvents or ionic liquids were used in transesterification reactions involving coffee oil.Base-catalyzed transesterification was carried out in a manner similar to that previously outlined in Section 2.3.2 for commercially-purchased oils.Acid-catalyzed transesterification reactions using coffee oil were heated overnight at reflux (typically 12-18 h).

The purification/isolation protocol used for coffee oil transesterification was similar to that outlined in Section 2.3.2, however, the alumina gel filtration step was omitted.

Acid-catalyzed reactions were washed first with aqueous $NaHCO_3$ (2 x 25 mL), then aqueous NaCl (2 x 25 mL), and finally DI water (2 x 25 mL). After every wash, the aqueous phase (the bottom layer) was removed. The organic layer was poured from the top into a 50-mL beaker and was dried over anhydrous $MgSO_4$ for at least 2 h. The dried product mixture was then filtered into a tared 100-mL RBF. Residual alcohol was removed using rotary evaporation. The product mixture was then transferred into a vial and stored until analyzed.

2.3.7 MAT of coffee oil from SCG

Microwave-heated transesterification of coffee oil was performed in 50-mL RBFs.The parameters for the microwave oven were set based on whether methanol or ethanol was used. Microwave procedure 2 was used for methanol; microwave procedure 3 was used for ethanol. The post-heating purification/isolation protocol outlined in Section 2.3.2 was used for these samples.

2.4 Analysis of Reaction Mixtures Using ^{1}H-NMR Spectroscopy

^{1}H-Nuclear magnetic resonance spectroscopy (NMR) was used to characterize product mixtures for all samples produced. A Jeol ECS-400 NMR spectrometer was used for all analyses. The raw NMR data were processed using the freeware SpinWorks 4.2.8 NMR processing software, which was designed by the Department of Chemistry of the University of Manitoba, Canada.

Specifically, integration data from the^{1}H-NMR spectrum of the product mixture can be used to determine percentage conversion using equations 1-3(24, 25, 45 - 48).

2.4.1 NMR analysis of FAME mixtures

Eq. 1 $$\%\mathrm{Conv} = \frac{(2\times \mathrm{I_{ester}})}{(3\times \mathrm{I_{\alpha CH_2}})} \times 100$$

In Eq. 1, "$\mathrm{I_{ester}}$" is the integration value of the methoxy protons of the methyl ester product (3.5-3.7 ppm). "$\mathrm{I_{\alpha CH_2}}$" is the integration value of the α protons of any unreacted TAG, DAG, or MAG that might be present in the product mixture as well as those from the FAME product. These protons are labeled in Figure 10 below.

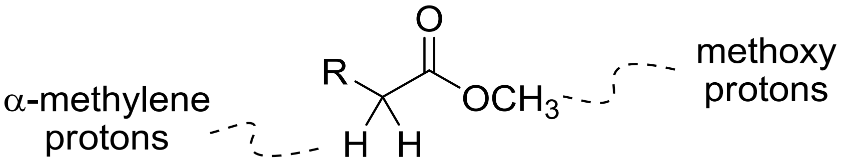

Figure 10: General FAME structure with key protons labeled

2.4.2 NMR analysis of FAEE mixtures

Eq. 2 $$\%\mathrm{Conv} = \frac{(8\times \mathrm{I_{C4}})}{(\mathrm{I_{DD}} + \mathrm{I_{EE}})} \times 100$$

In Eq. 2, "$\mathrm{I_{C4}}$" is the integration value of the specific ethyl ester peak at 4.08 - 4.09 ppm within the ethyl ester quartet and "$\mathrm{I_{DD}}+\mathrm{I_{EE}}$" is the integration value of the entire ethyl ester quartet that ranges 4.05 – 4.35 ppm (25). These protons are labeled in Figure 11.

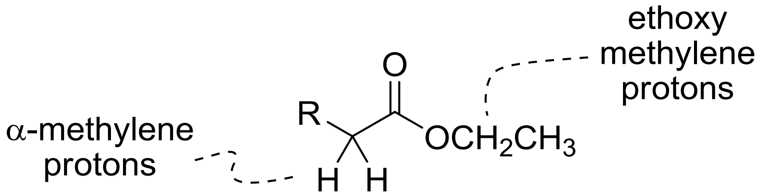

Figure 11: General FAEE structure with key protons labeled

2.4.3 NMR analysis of FAFurE mixtures

Eq. 3 $$\%\mathrm{Conv} = \frac{(\mathrm{I}_{\mathrm{FurEster}})}{(\mathrm{I}_{\alpha\mathrm{CH}_2})} \times 100$$

As was done for methyl ester percent conversion, $\mathrm{I}_{\mathrm{FurEster}}$is the integration value for the signal for the furfuroxy protons (5.05 ppm). Similarly, $\mathrm{I}_{\alpha\mathrm{CH}_2}$ is the integration value of the α methylene protons (2.30 ppm) from the fatty acid chain of any unreacted TAG, DAG, MAG, or FAFurE producct that might be present in the reaction mixture. These protons are labeled in Figure 12.

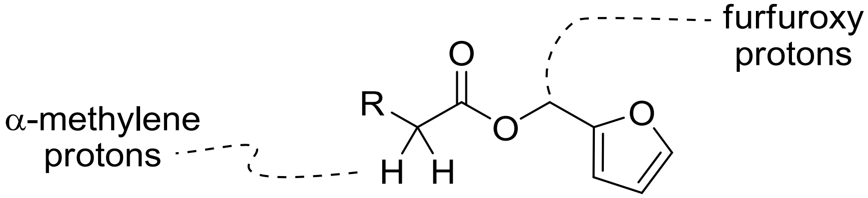

Figure 12: General FaFurE structure with key protons labeled

2.5 Combustion Analysis

Combustion analysis was conducted using a Parr Oxygen Bomb Calorimeter, Model 1331. In order to determine the heat of combustion of the biodiesel, it was necessary to standardize the bomb calorimeter unit itself. The settings of the bomb calorimeter are summarized in the following table.

Table 5: Data acquisition System Settings for Bomb Calorimetry Experiments (28)

Condition	**Value**
Preperiod Tolerance	0.002 ^oC
Mis-Fire Tolerance	0.05 ^oC
Preperiod Timeout	42 s
Postperiod Timeout	60 s

2.5.1 Standardization of bomb calorimeter

The standardization procedure was outlined in the Parr Manual(58). Benzoic acid (ΔE = -6318 cal/g) was used as a standard and is pressed into a pellet. Approximately 0.500 g of benzoic acid was pressed into a pellet. The exact weight of the pellet was recorded. A 10 cm sample, weighed exactly, of Parr Fuse Wire for Oxygen Bombs (ΔE = -1400 cal/g) was used to ignite the sample. The wire was wrapped around the pellet and then connected into the binding posts of the head of the calorimeter.

It is worth noting that the position of the wire is crucial. The wire must be touching the sample in order to get a proper combustion, but if the wire is touching the combustion pan, it will result in a misfire. When a misfire occurs, it is necessary to terminate the run and start over. The head of the bomb was attached to the bottom and screwed on tightly. The exhaust knob was twisted until resistance was felt. The bomb was filled with molecular oxygen, O_2, and purged three times before finally being filled to a pressure of 25-30 atm. This ensured a nearly pure oxygen atmosphere in the bomb and is essential for complete combustion of the sample. Next, the calorimeter was placed into the reaction chamber within a stainless steel bucket, and the fuse wires were attached to the calorimeter. The steel bucket was then filled with 2.0 L of DI H_2O. When the sample is combusted, the heat produced from the reaction causes the temperature of the water to increase. The temperature probe then feeds the temperature data to the Data Acquisition System (DAS) (#6772) which is a component of the calorimeter apparatus. The lid of the chamber was attached, and the stirring apparatus and the system was turned on. The experimental data was programmed into the DAS, and left to complete the trial. Once the trial was complete, the vessel was removed from the chamber, the exhaust knob was opened, the calorimeter was opened, and the remaining fuse wire was removed and weighed. The mass of the burned wire was entered into the DAS as the “fuse weight” and the final energy equivalent (EE value) of the system was calculated by the DAS.

After each run, the water in the steel bucket was changed out, and the inside of the calorimeter was dried throughout to keep moisture from accumulating on the walls. This process was repeated five times. The EE values were averaged and entered into the DAS as the Energy Equivalent of the reaction vessel in preparation for the combustion of the biodiesel.

2.5.2 Standardization of gelatin capsules

Biodiesel samples are liquid and must be contained within a gelatin capsule in order to be analyzed in the calorimeter.In order to determine the true energy of combustion of the biodiesel sample, the energy produced from combustion of the gelatin capsules used must also be accounted for. If this is not done, then the data will be inaccurate. The clear capsules used were purchased from a local pharmacy, and were stored in a dessicator until needed so the capsules would not disintegrate from the atmospheric humidity. Empty capsules were combusted using the same procedure outlined in section 2.6.1 for a total of five trials. The energy content was determined and entered into the DAS as the energy of the spiking material.

2.5.3 Determination of heat of combustion of biodiesel samples

A sample of 0.3000 – 0.3800 g of biodiesel was pipetted into a gelatin capsule that had already been weighed. It is important to note that biodiesel contains high energy bonds and produces a considerable amount of energy when combusted, so it was necessary to use a small sample. A sample too big could damage the calorimeter. The capsule was sealed by attaching both halves together. The entire assembled capsule unit was then weighed.

The difference between the final weight and the initial weight of the capsule by itself was also recorded, as this weight is the weight of biodiesel within the capsule itself. A tack was used to create holes in the capsule for two reasons: the first being to release pressure as combustion occurs, the second was to insert the fuse wire through the capsule and secure the capsule over the combustion pan. The sample was combusted using the method described in Section 2.6.1. A total of five replicate trials were performed. The average heats of combustion were recorded per biodiesel type.

CHAPTER 3

Results and Discussion

3.1 Introduction

Within this chapter will be the characterization results from biodiesel (FAMEs, FAEEs, and FAFurEs) via ^{1}H-NMR spectroscopy and the energy of combustion results via bomb calorimetry (only of FAFurEs) . However, coffee methyl and coffee ethyl ester production were both so low that only characterization could be done, so that only FAFurEs could be combusted.

3.2 Biodiesel Fuels from Furfuryl Alcohol

Furfuryl alcohol was used to convert five oils (canola, olive, peanut, corn, and sunflower) to biodiesel. Each oil underwent tranesterifcation using conventional heating in triplicate, and underwent microwave-assisted heating at least once.

3.2.1 NMR results for FAFurE synthesis

NMR analysis and percent conversions were calculated using the equation from section 2.5.3. Freeware SpinWorks 4 was used for integration. Table 6 contains the percent conversions of commercially-purchased oils with furfuryl alcohol, both conventionally and microwave heated.

Table 6: Percent Conversion Values for FAFurE Synthesis

	Conventional Heated (CH) (%)	**Microwave Heated (MW) (%)**
Canola	61.4 ± 17.1	40.1
Olive	75.7	0
Peanut	69.6	0
Corn	53.1 ± 13.0	0
Sunflower	19.3	3.9

3.2.2 Discussion of NMR results for FAFurE mixtures

Percent conversions for conventionally-heated FAFurE had a wide range. Sunflower oil had the lowest conversion at 9.7%. It is possible that this sunflower oil might have become rancid. Canola oil had the highest conversion at 61%. Again, standard deviations are very large here from non-consistent conversions. Microwave-assisted heating for FAFurE were very low, most oils having approximately 0% conversion. This might be because the final temperature for the microwave was set too low, or because the holding time was not long enough to let the reaction go to completion.

3.2.3 Calorimetry results for FAFurE mixtures

As previously noted, only fatty acid furfuryl esters (FAFurEs) were combusted due to higher production yields. It is worth mentioning, however, that some commercially-purchased methyl esters and ethyl esters were combusted for comparison. These prior results can be found in Appendix A, and will be referred to within this section. Another comparison will be made against the combustion energy of the canola furfuryl ester mixture made before the procedure improvements to include co-solvents and an ionic liquid.

All FaFurE samples were combusted within a calibrated Parr 1331 Oxygen Bomb Calorimeter as outlined in section 2.6.3 in the previous chapter.

The combustion of energy of petroleum diesel can range between 41.0 and 45.0 MJ/kg (55, 56). This will be the value used for comparison.

The results found for combustion energy are found in Table 7 below.

Table 7: Combustion Energies for FAFurEs

Energy of Combustion (MJ/kg)		
	Conventional Heated(CH)	**Microwave Heated (MW)**
Canola	36.5 ± 0.61	36.7 ± 2.46
Olive	37.8 ± 1.91	38.6 ± 0.21
Peanut	35.5 ± 0.11	34.2 ± 3.60
Corn	36.6 ± 0.12	36.9 ± 0.25
Sunflower	37.3 ± 0.55	36.8 ± 1.20

3.2.4 Discussion of calorimetry results for FAFurE mixtures

From these values, it safe to state that the combustion energy average for any and all of these biofuels is less than that of petroleum diesel. However it is worth noting that the different in the energy of combustion for either conventional heated or microwave heated biodiesel is relatively low (in MJ/kg).

In comparison with bomb calorimetry studies from biodiesel previously, found in Appendix A, the average of these biofuels energy of combustion is around 37 MJ/kg, whereas the other straight-chained alcohols have combustion energies ranging between

21-40 MJ/kg. It was assumed that the olive oil used in previous research might have gone bad between transesterifications, so the energy of combustion for the olive might be skewed.

The lower energy of combustion can be a result of many different factors. It is important to note that the composition of commercially purchased cooking oils, even if it is the same type of oil from different distributors, very drastically. Longer-tailed hydrophilic chains on a triglyceride can be more difficult to react due steric hindrance. Also, the deprotonated furfuryl alcohol molecule is much, much bigger than that of methanol and ethanol. Steric hindrance could make it difficult for the furfuroxide ion to attack the carbonyl carbon.

3.2.5 Conclusions on FAFurE work

Percent conversions were still relatively low. The first few reactions acting as controls had percent conversions around 20%. Those reactions were performed solely in the microwave. However, in this research, higher percent conversions occurred (other than for sunflower) for conventional heating. The microwave-assisted transesterification yielded approximately 0% for three of the five oils tested. It is possible that the parameters for microwave synthesis need to be changed. It is possible that the holding temperature was not high enough (not enough energy within the reaction), or that the running time was notlong enough (so the reaction could not go to completion). Calorimetry results show an average energy of combustion of 36.7 MJ/kg. This is similar to the values for biofuels already reported. Although lower than petrodiesel, these studies confirm that biofuels also have high energy content and could be used as a transportation fuel.

3.3 Biodiesel Fuels from SCG

Methanol and ethanol were used only in conversion of coffee triglycerides. Coffee oil was the limiting reagent in the production of both FAMEs and FAEEs. Microwave-assisted heating were only used for base-catalyzed reactions.

3.3.1 FAME synthesis from SCG

Fatty acid methyl ester (FAME) synthesis was attempted using both acid- and base-catalyzed transesterification. Conventional heating took precedent, but at least one reaction was done using microwave-assisted heating. Table 8 contains the calculated percent conversions from these reactions.

Table 8: Percent Conversion Values for FAMEs from Coffee Oil

	Catalyst	
	H_2SO_4	**K_2CO_3**
Trial 1	0	**51***
Trial 2	0	94
Trial 3	0	75
Average	0	73 ± 21.5

The reaction with an asterisk (*) was performed in the microwave.

3.3.2 FAEE synthesis from SCG

Fatty acid ethyl ester (FAEE) synthesis was attempted using both acid- and base-catalyzed transesterification. Conventional heating took precedent, but at least one reaction was done using microwave-assisted heating. Table 9 contains the calculated percent conversions from these reactions.

Table 9: Percent Conversion Values for FAEEs from Coffee Oil

	Catalyst	
	H_2SO_4	**K_2CO_3**
Trial 1	0	74.8
Trial 2	75.1	75.1
Trial 3	0	**92.1***
Average	25.0 ± 43.4	80.7± 9.90

The reaction with an asterisk (*) was performed in the microwave.

3.3.3 Discussion of results from FAME and FAEE synthesis from SGCs

Acid catalysis for FAME production showed no conversion and relatively low conversions for FAEE production. FAEE production had a large standard deviation, giving the impression that conversions were not consistent. Base catalysis for FAME production showed moderate conversion with an average of 73%. Standard deviations for base catalysis are still relatively high at 21%, still proving that the conversions are not going to completion. Results from base-catalyzed FAEE production from coffee oil were higher, with an average percent conversion of 81% and a smaller standardization of

9.90%. Results from that previous study can be found in the Appendix A.

Low conversions for acid catalysis could be accounted for in many ways. Firstly, coffee reactions were very small and it is possible that there just was not enough catalyst used within the reaction as only a few drops were used. Also, acid catalyzed transesterifications do typically take a significantly longer amount of time to reach completion, and it is possible that the reaction was stopped before it could go to completion.

3.3.4 Conclusions from SGC work

Acid-catalyzed reactions resulted in very low percent conversions. All but one reaction was found to have 0% conversion from the ^{1}H-NMR spectra. Acid-catalyzed reactions cannot be performed in the microwave and must be given efficient time to complete the reaction. Reaction times for acid-catalyzed tranesterification are long, usually overnight (between 18 – 24 h). It is possible that acid reactions were not given enough time to run. Another interesting find is that ethyl esters (81%) showed higher conversions than that of methyl esters (73%). Although neither is ideal, ideally conversions would be 95-99%, ethyl esters are much closer to full conversion. This has also been seen in the preliminary studies. Results for that study can be found in Appendix A.

3.4 Overall Project Summary and Conclusions

Although conversions are low, these are mostly (again, with the exception of sunflower oil) higher than what was seen previously. Microwave parameters could be changed to have a higher final temperature, a longer running time, or both. It is also crucial to be positive that the stir-bar is aggressively agitating the reaction mixture. If the reaction mixture does not mix properly, the reaction will not go to completion, if at all.

Ethanol was found to be a better solvent between it and methanol. Ethyl ester conversion topples methyl ester conversion by almost 10%. This could be because ethanol is a short enough alcohol (like methanol) to dissolve in the aqueous phase, but also long enough (like propanol or higher) to also dissolve in the organic phase as well. This can quicken the reaction and help the reaction go to completion.

Future studies for FaFurE and coffee methyl and coffee ethyl esters will have to be conducted.

CHAPTER 4

Conclusions and Future Work

4.1 Conclusions

Biodiesel is an attractive alternative fuel source due to its renewability, non-toxicity, and biodegradability. The most common procedure used commercially for biodiesel production is transesterification. Commercially produced biodiesel is made with shorter chained alcohols (methanol and ethanol) due to their prices, availabilities, and eco-friendly natures.

However, with green chemistry on the rise with the fear of depleting of the world wide fossil fuels, furfuryl alcohol could be used for transesterification in the future. Furfuryl alcohol, like ethanol, has an eco-friendly background. It is a byproduct of sugar production and can be recycled into biodiesel production. Likewise, spent coffee grounds, which would either be thrown away or used in compost, can be used as an eco-friendly triglyceride source.

Catalysts used in biodiesel production can be acidic, basic, or enzymatic. Base catalysts are used more commonly due to their fast reaction times and higher yields, but they cannot be used with fatty acids with high FFA content. However, insolubility of the basic catalyst can cause low percent conversions. In order to overcome this problem, this study suggested using co-solvents (such as THF) and ionic liquids (1-butyl-3-methylimidazolium tetrafluoroborate). Conventional heating and microwave-assisted heating were both used to perform transesterification. Multiple cooking oils were used (canola, corn, olive, peanut, and sunflower) with furfuryl alcohol, THF, 1-butyl-3-methylimidazolium tetrafluorobortae, and K_2CO_3 to make fatty acid furfuryl esters (FAFurE). Another extracted triglyercide source was from spent coffee grounds. Coffee oil underwent transesterification with methanol or ethanol and K_2CO_3 to create fatty acid methyl esters (FAMEs) and fatty acid ethyl esters (FAEEs).

All fatty acid esters were analyzed by ^{1}H-NMR to determine percent conversions using equations 1, 2, and 3 in section 2.5 depending on the alcohol used in production. However, due to low percent yields, coffee FAMEs and FAEEs were not available for bomb calorimetry, and only FAFurE were analyzed by bomb calorimetry.

Percent conversions for FAFurE synthesis ranged for conventional heated transesterification ranged from 9.7% for sunflower oil up to 75.7% for olive oil. Percent conversions for FAFurE in microwave-assisted transesterification ranged from 0% for corn, peanut, and olive oil and 40.1% for canola oil. Percent conversions for FAMEs from coffee oil ranged from 0% for acid catalysis to 94% for base catalysis, and percent conversions for FAEEs from coffee oil ranged from 75.1% for acid catalysis to 92% for base catalysis. Most percent conversions had large standard deviations, giving the impression that conversion was not consistent.

Bomb calorimetry was used to measure the heat of combustion for FAFurE of commercially-purchased oils with furfuryl alcohol for both conventional-heated and microwave-assisted transesterification. The energy of combustion for conventional-heated transesterifications ranged from 35.5 MJ/kg to 37.8 MJ/kg while energy of combustion for microwave-assisted transesterifications ranged from 34.2 MJ/kg to 38.6 MJ/kg. The average of all biofuels, both microwave-assisted and conventionally-heated, was found to be 36.7 MJ/kg, significantly lower than the 45 MJ/kg average for petroleum diesel. The differences between conventional-heated and microwave-assisted energies of combustion were not significant.

4.2 Future Work

Furfuryl alcohol as well as spent coffee grounds can still be a crucial players in biodiesel production. Their environmentally friendly uses are attractive for greener chemistry in the lab as well as renewable energy sources. Biodiesel can be synthesized using the following methods in the future.

- GC-MS can be used to identify fatty acids within neat coffee oil
- Low solubility of the basic catalyst caused low conversions. Therefore, trying different basic catalysts may improve conversions.
- In order for biofuels to be used commercially, they must first follow all the specifications outlined in ASTM D6751. Some regulations include viscosity, ester content, and acid number. These properties can be studied.

- Conventionally-heated reactions last at least 3 h up to 10 h. The microwave is set for 30 min reaction times. It may be useful to have microwave reactions last up to 1 or 2 h, and still be faster than conventionally-heated.
- In literature, 1-butyl-3-methylimidiazolium was mentioned as a possible player in biodiesel production, but other ionic liquids may be used. For example, methyltrioctylammonium chloride can also be helpful.
- Coffee oil underwent transesterification with methanol and ethanol. The goal is to make the most eco-friendly biodiesel while still maintaining the regulations in ASTM D6751 and having relatively similar energy of combustion as that of petroleum diesel. It is possible to have coffee oil and furfuryl alcohol together for transesterification.

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APPENDIX A

Table 10: Combustion Energies for FAMEs and FAEEs from Microwave Heating

	FAME	**FAEE**
Canola	37.3 ± 2.95 MJ/kg	38.7 ± 0.08 MJ/kg
Olive	38.8 ± 0.70 MJ/kg	20.9 ± 0.67 MJ/kg

Table 11: Literature Values for Combustion Energies of FAMEs and FAEEs

	FAME	**FAEE**
Canola	39.4 MJ/kg	39.5 MJ/kg
Olive	39.2 MJ/kg	39.9 MJ/kg

Table 12: Preliminary Conversion Values for FAMEs from Coffee Oil

Conditions	**Method**	**% Conv.**
Coffee oil, acid, MeOH	Heating mantle	42.35
Coffee oil, base, MeOH	Microwave	2.21
Coffee oil, base, MeOH	Heating mantle	4.05

Table 13: Preliminary Percent Conversion Values for FAME and FAEE Synthesis

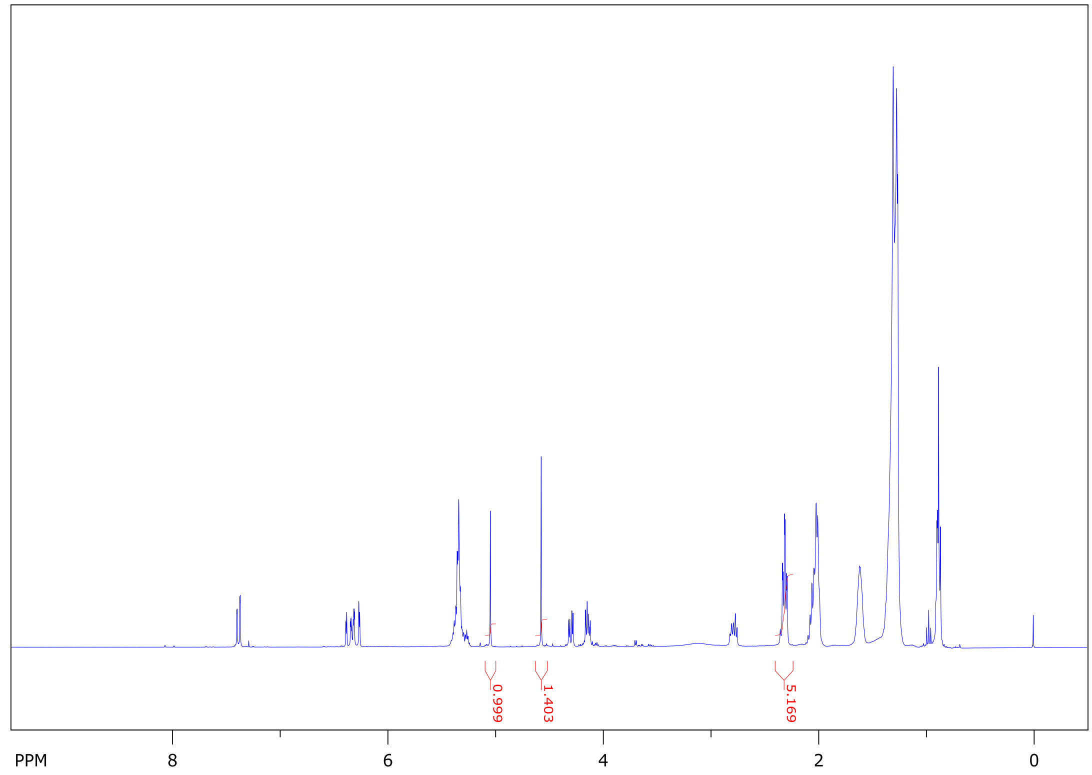
Oil	**MeOH (% conv)**		**EtOH (% conv)**	
	Heating mantle	**Microwave**	**Heating mantle**	**Microwave**
Canola	51.71	58.28	61.17	28.60
Olive	36.99	63.84	77.44	62.16
Soybean	56.34	78.48	35.68	74.03
Sunflower	23.32	69.33	53.67	79.44

APPENDIX B: NMR SPECTRA

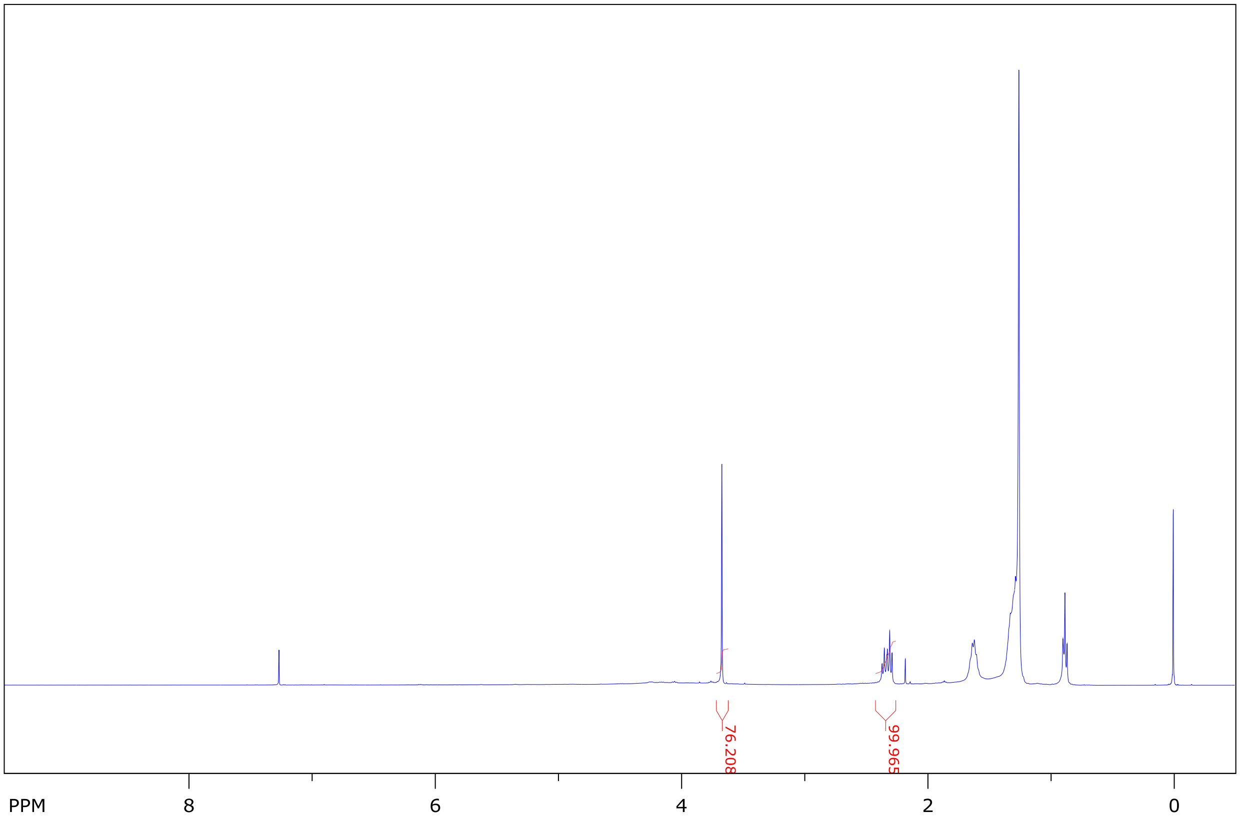
Table 14: List of ^{1}H-NMR Spectra

NMR#	Oil	Alcohol	Catalyst	Heat	THF	BMIM
1	Canola	FurOH	Base	MW (#4)	no	no
2	Coffee	MeOH	Base	CH	no	no
3	Soybean	FurOH	Base	MW (#4)	no	no
4	Coffee	MeOH	Base	MW (#2)	no	no
5	Canola	FurOH	Base	CH	yes	yes
6	Canola	FurOH	Base	CH	yes	yes
7	Coffee	EtOH	Base	MW (#3)	no	no
8	Canola	FurOH	Base	MW (#2)	yes	yes
9	Canola	FurOH	Base	MW (#1)	yes	yes
10	Olive	FurOH	Base	CH	yes	yes
11	Coffee	EtOH	Acid	CH	no	no
12	Olive	FurOH	Base	CH	yes	yes
13	Olive	FurOH	Base	CH	yes	yes
14	Corn	FurOH	Base	CH	yes	yes
15	Canola	FurOH	Base	CH	yes	yes
16	Corn	FurOH	Base	CH	yes	yes
17	Canola	FurOH	Base	CH	yes	yes
18	Sunflower	FurOH	Base	CH	yes	yes
19	Olive	FurOH	Base	MW (#4)	yes	yes
20	Coffee	MeOH	Base	MW (#2)	no	no
21	Coffee	EtOH	Base	(MW#3)	no	no
22	Canola	FurOH	Base	MW (#4)	yes	yes
23	Sunflower	FurOH	Base	MW (#4)	yes	yes
24	Peanut	FurOH	Base	MW (#4)	yes	yes
25	Corn	FurOH	Base	MW (#4)	yes	yes
26	Canola	FurOH	Base	CH	yes	yes
27	Peanut	FurOH	Base	CH	yes	yes
28	Coffee	EtOH	Base	CH	no	no
29	Peanut	FurOH	Base	CH	yes	yes
30	Peanut	FurOH	Base	MW (#4)	yes	yes

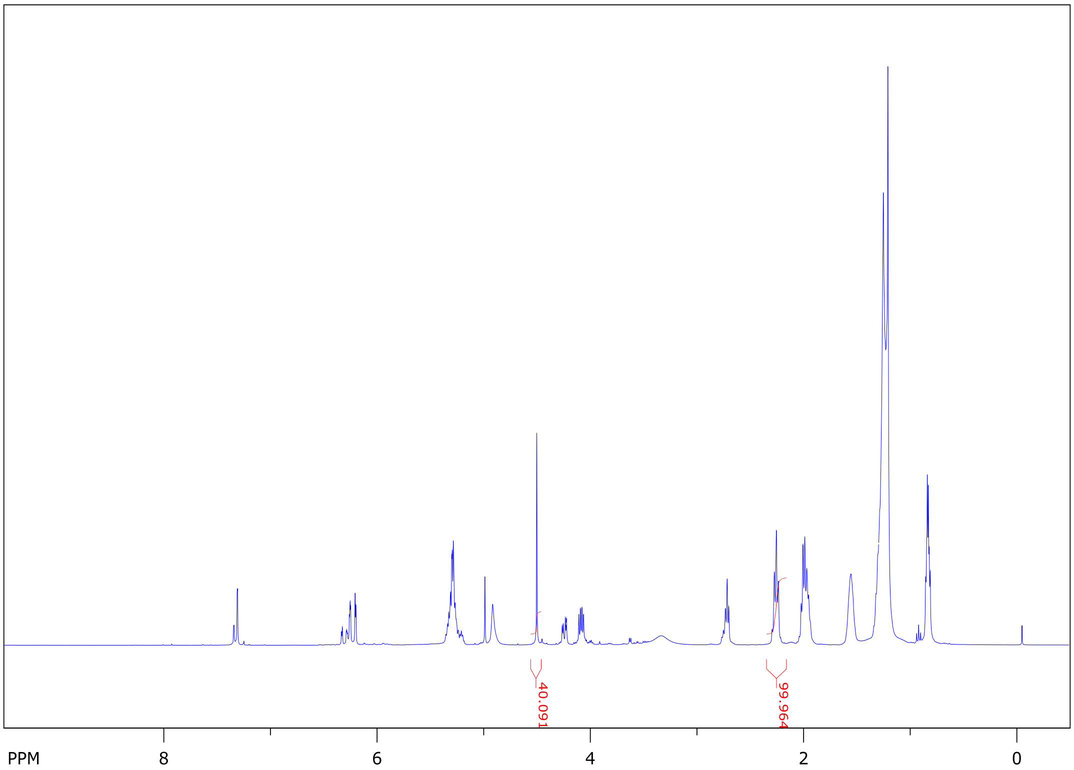
1.) ^{1}H-NMR Spectrum of Canola, FurOH, K_2CO_3, MW. (Control)



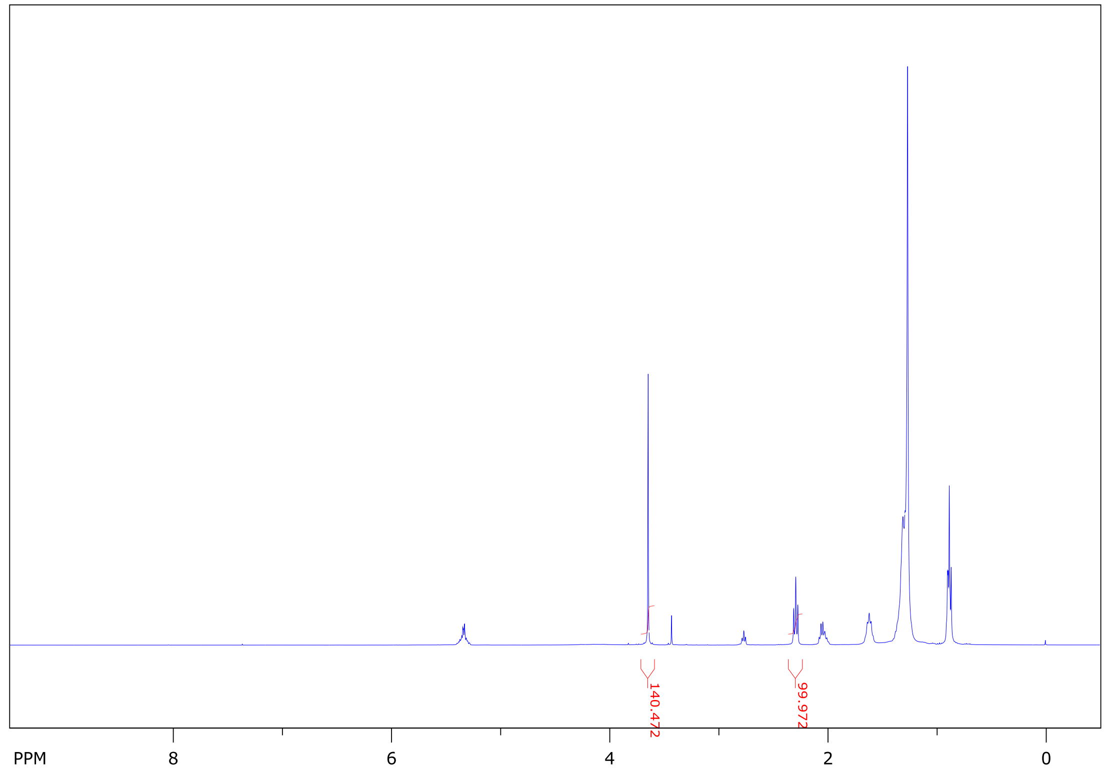
2.) ^{1}H-NMR Spectrum of Coffee, MeOH, K_2CO_3, CH.



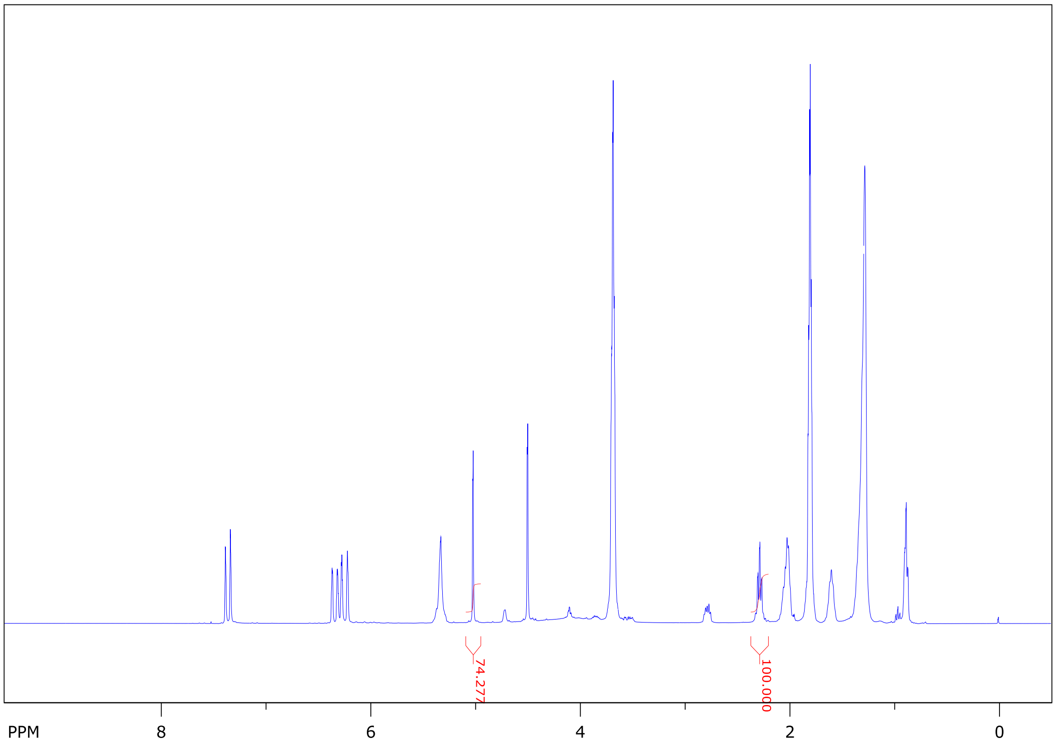
3.) ^{1}H-NMR Spectrum of Soybean, FurOH, K_2CO_3, MW



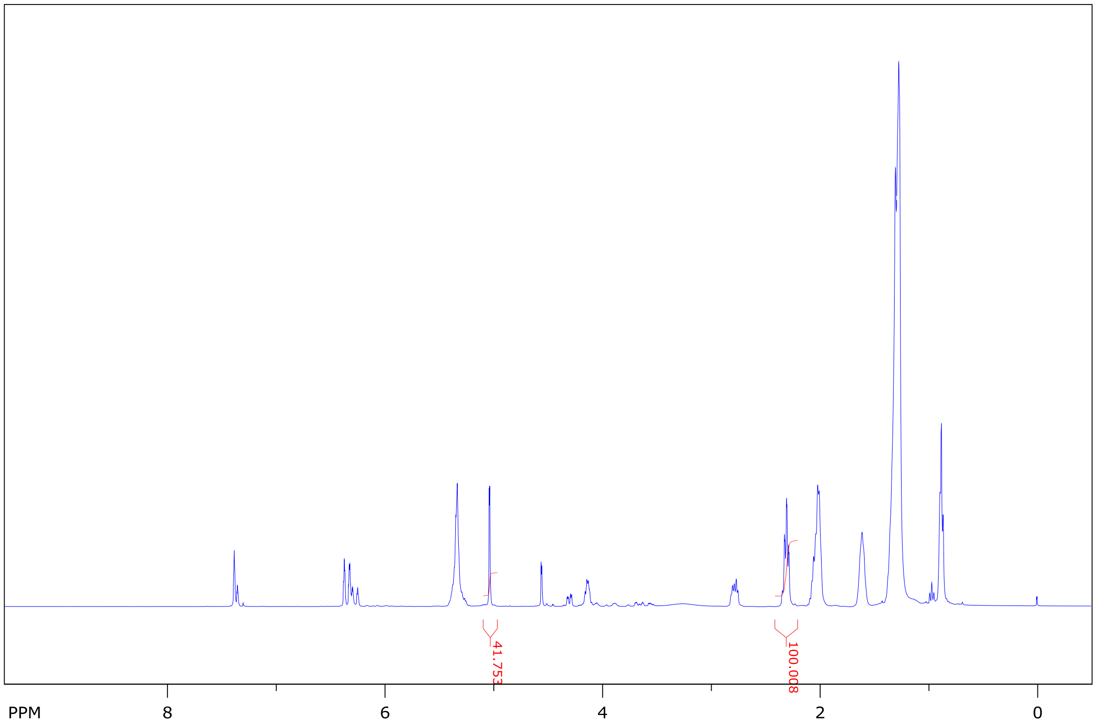
4.) ^{1}H-NMR Spectrum of Coffee, MeOH, K_2CO_3, MW



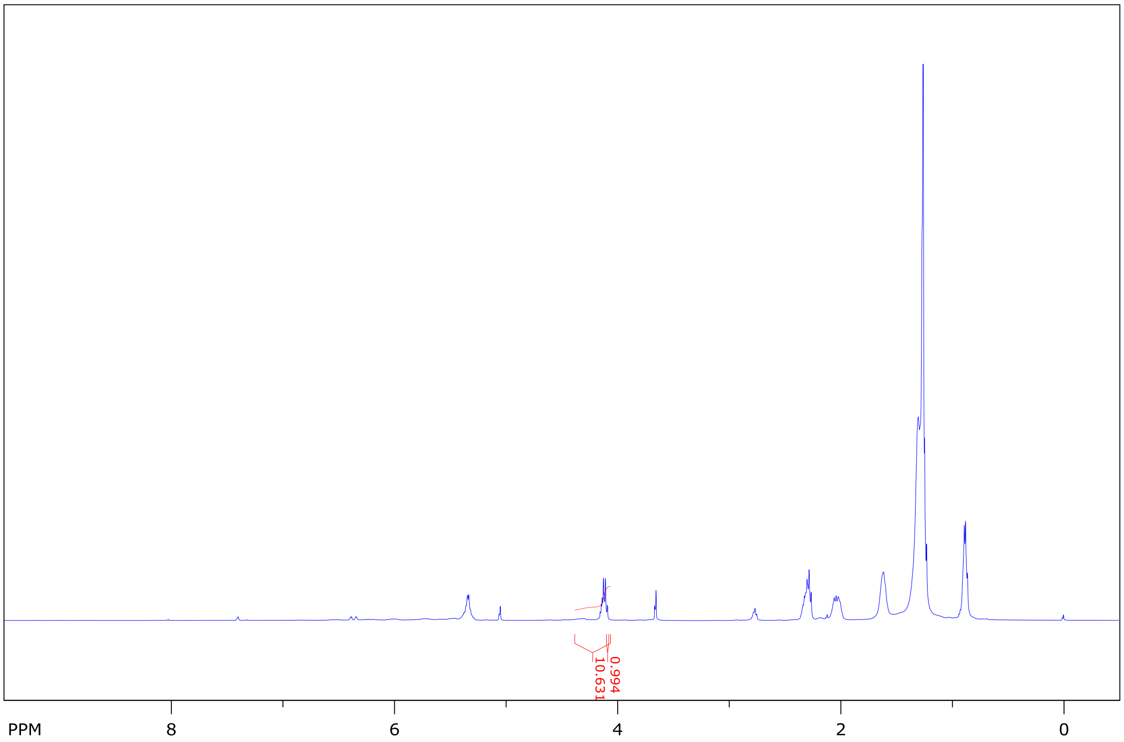
5.) ^{1}H-NMR Spectrum of Canola, FurOH, THF, BMIM, and K_2CO_3. CH



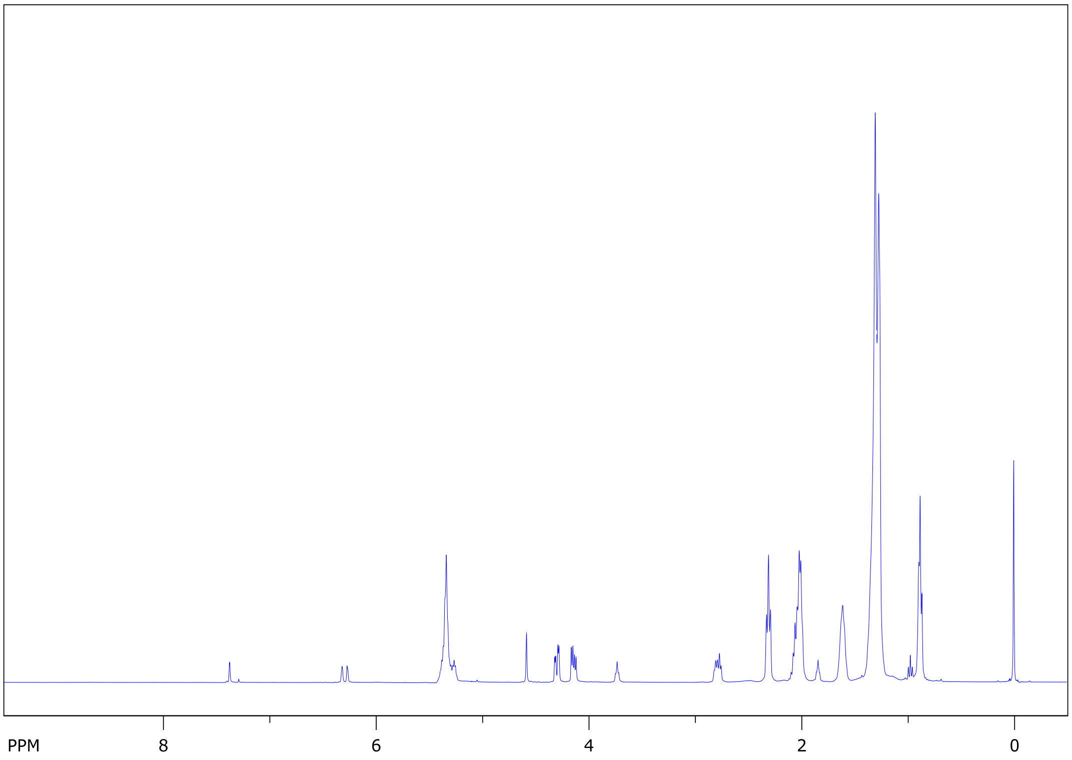
6.) ^{1}H-NMR Spectrum of Canola, FurOH, K_2CO_3, BMIM, and THF. CH.



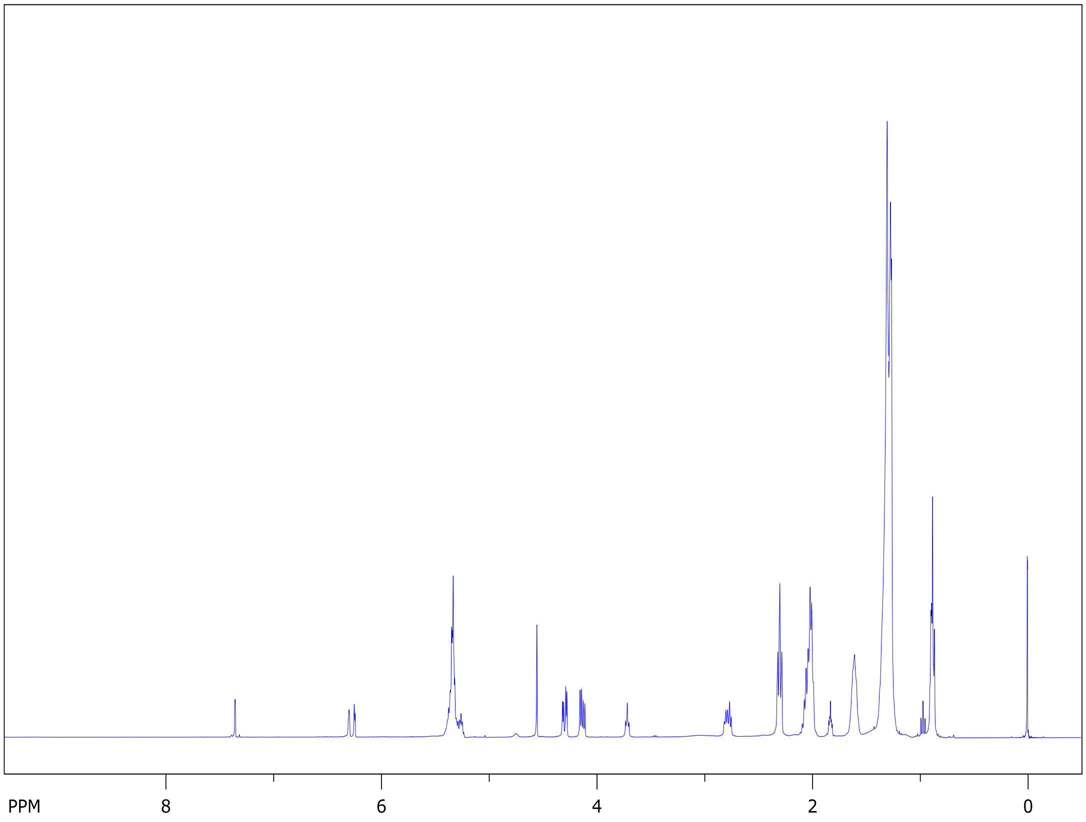
7.) ^{1}H-NMR Spectrum of Coffee, EtOH, K_2CO_3, MW.



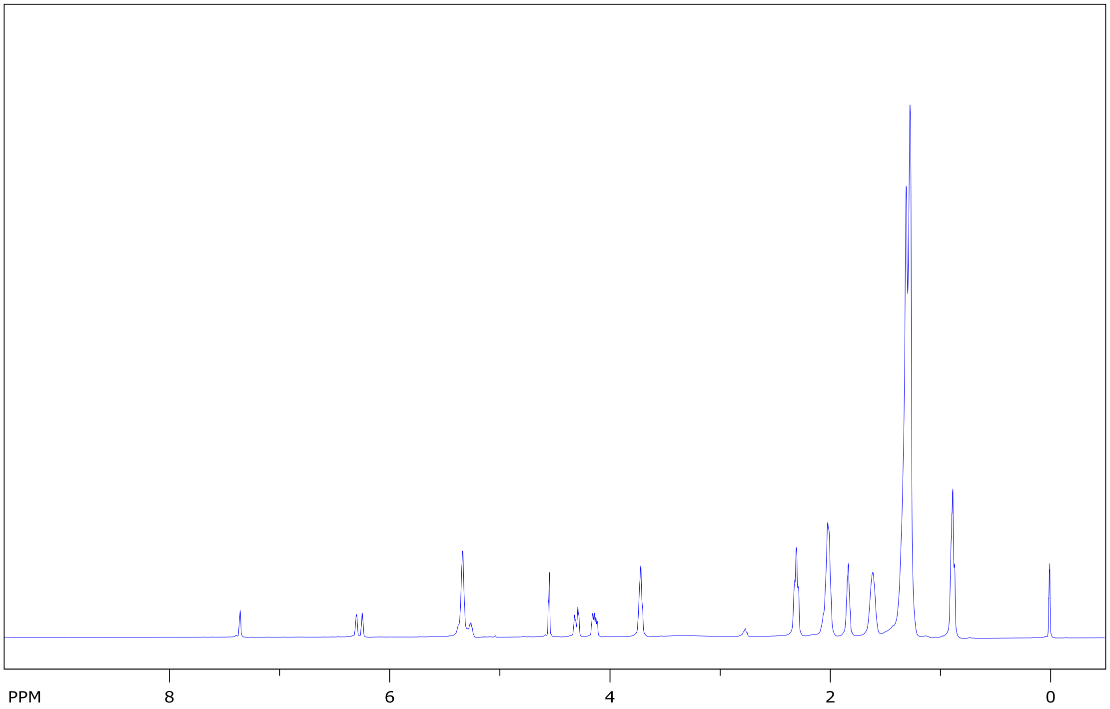
8.) ^{1}H-NMRSpectrum of Canola, FurOH, K_2CO_3, BMIM, and THF. MW(#2)



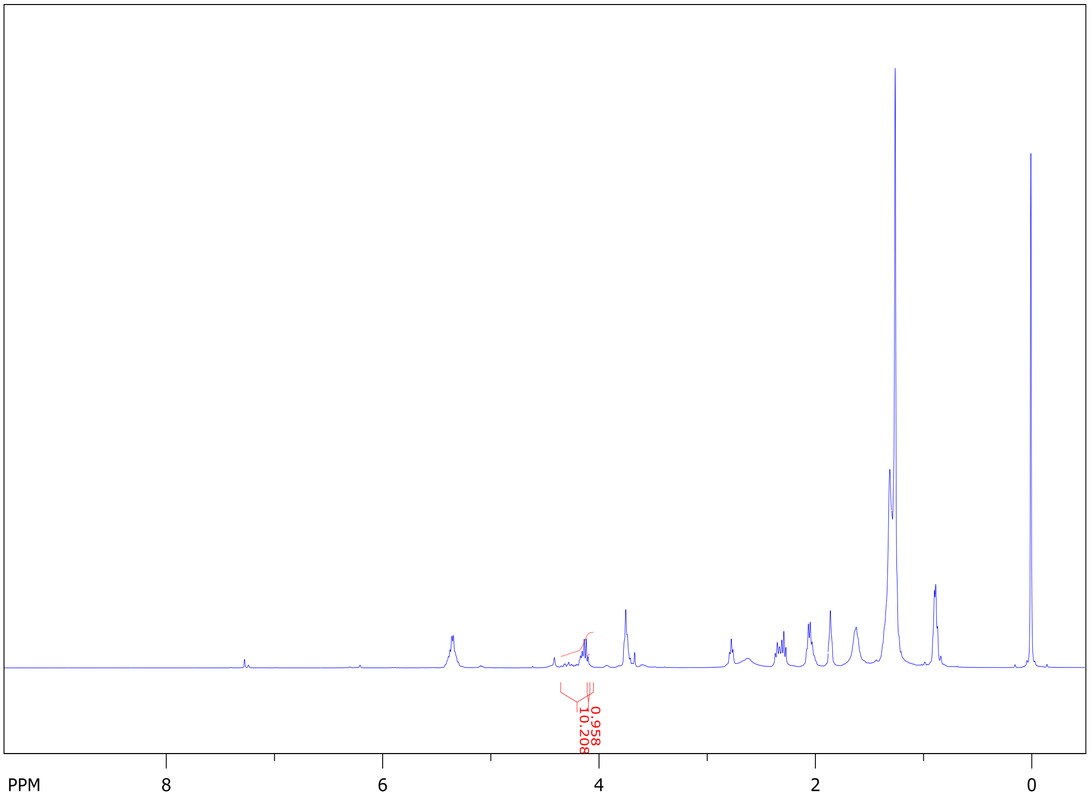
9.) ^{1}H-NMR Spectrum of Canola, FurOH, K_2CO_3, THF, and BMIM. MW(#1)



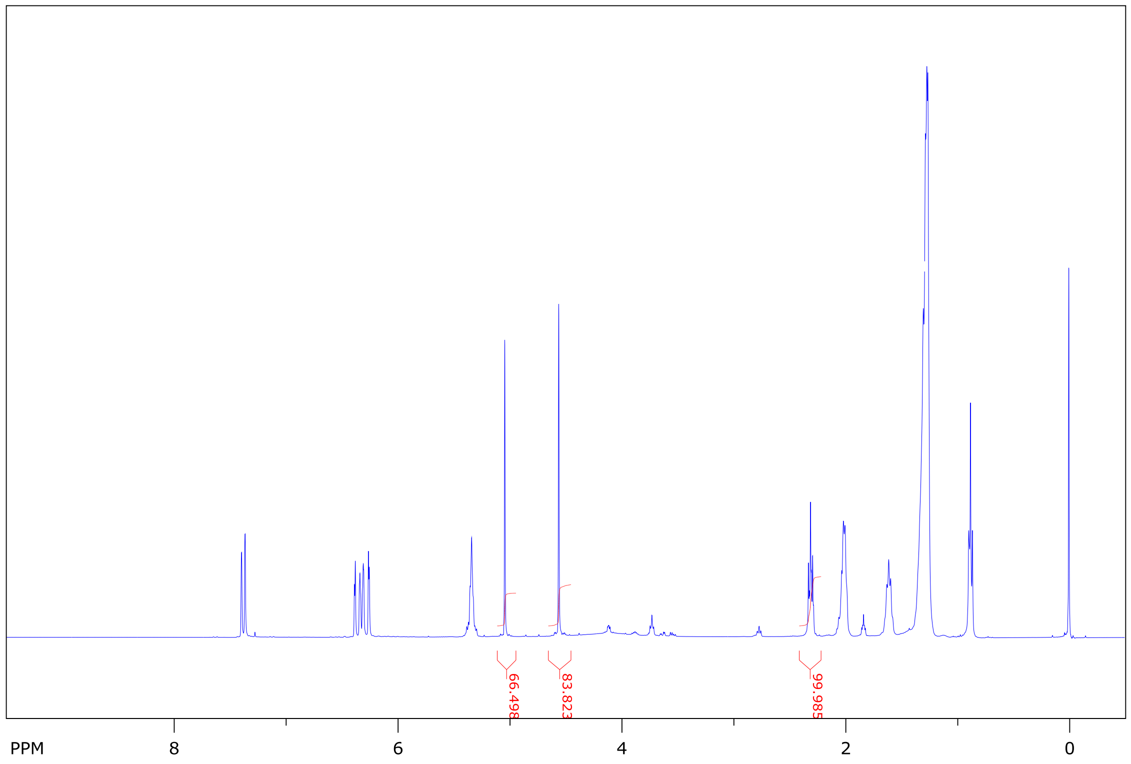
10.) ^{1}H-NMR Spectrum of Olive, FurOH, K_2CO_3, BMIM, and THF. CH.



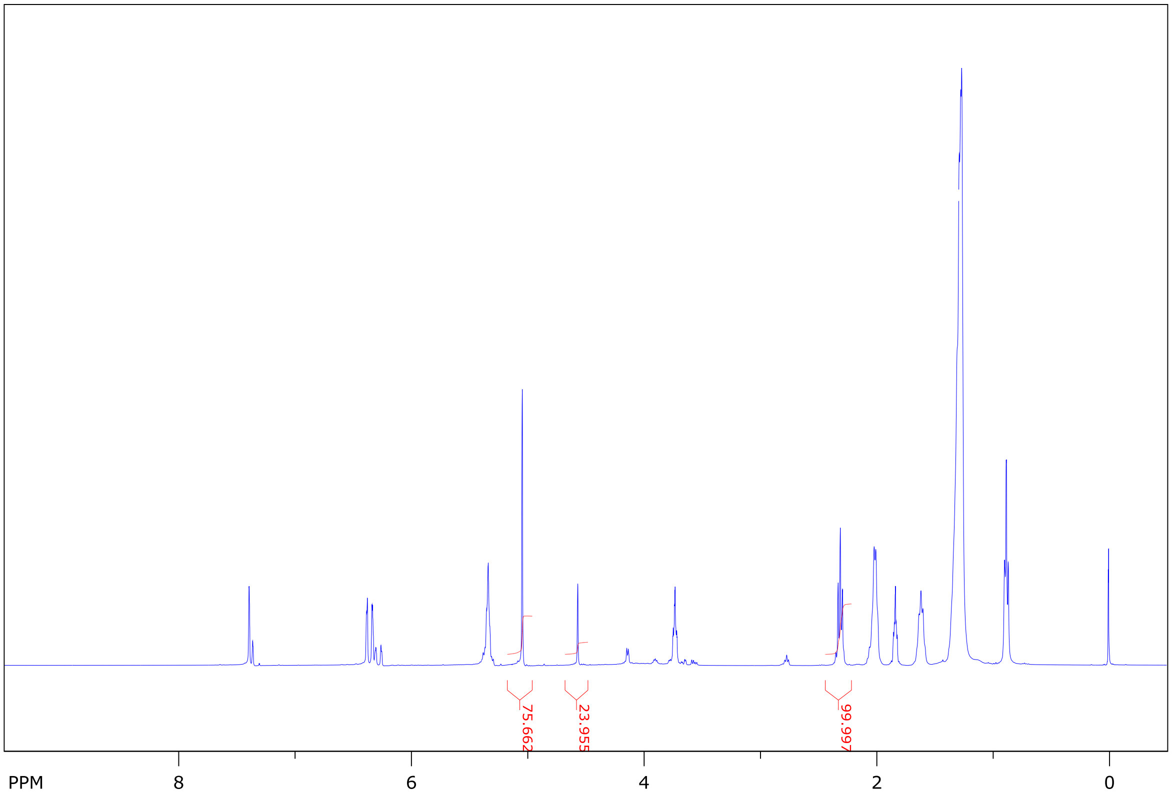
11.) ^{1}H-NMR Spectrum of Coffee, EtOH, H_2SO_4 CH.



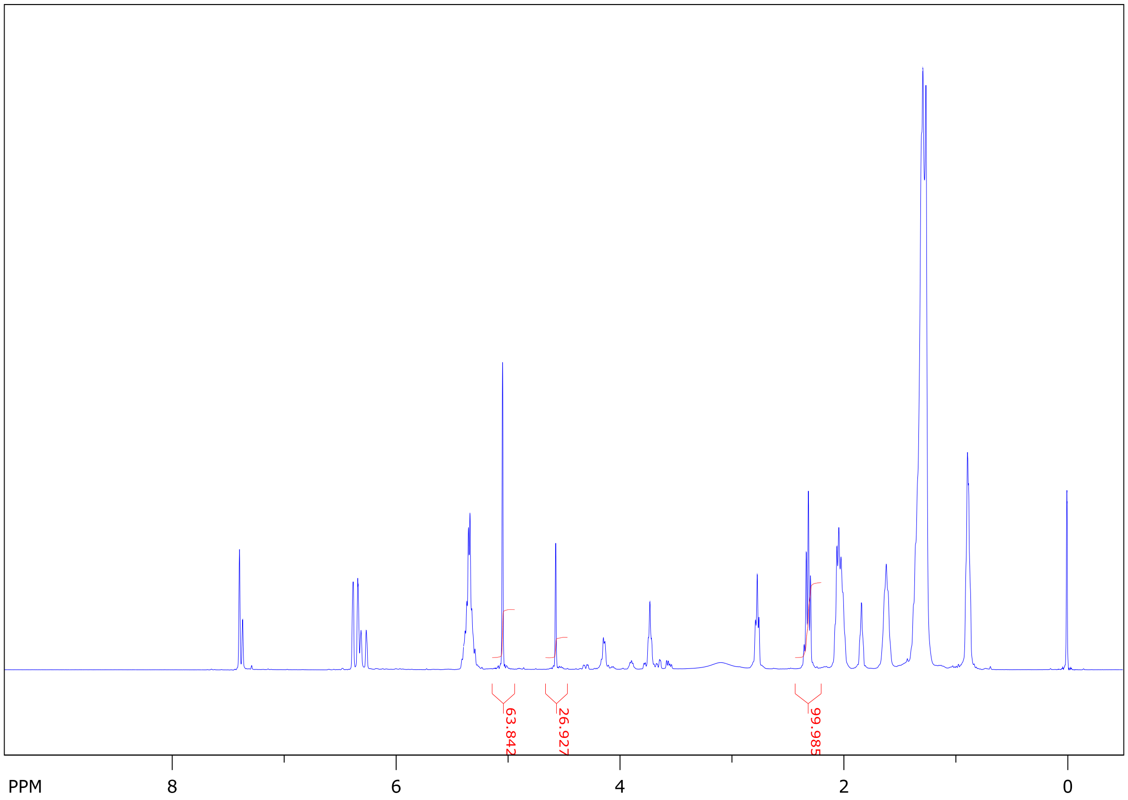
12.) ^{1}H-NMR Spectrum of Olive, FurOH, K_2CO_3, THF, BMIM. CH.



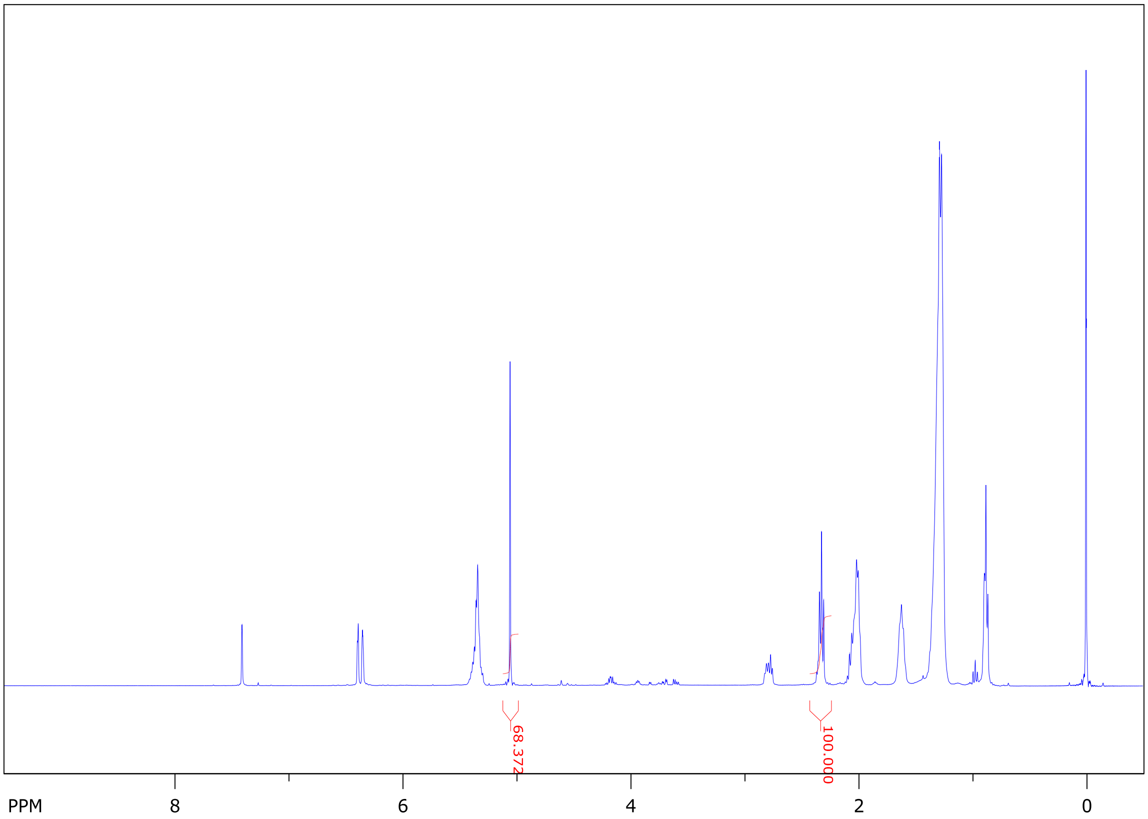
13.) ^{1}H-NMR Spectrum of Olive oil, FurOH, K_2CO_3, THF, BMIM. CH



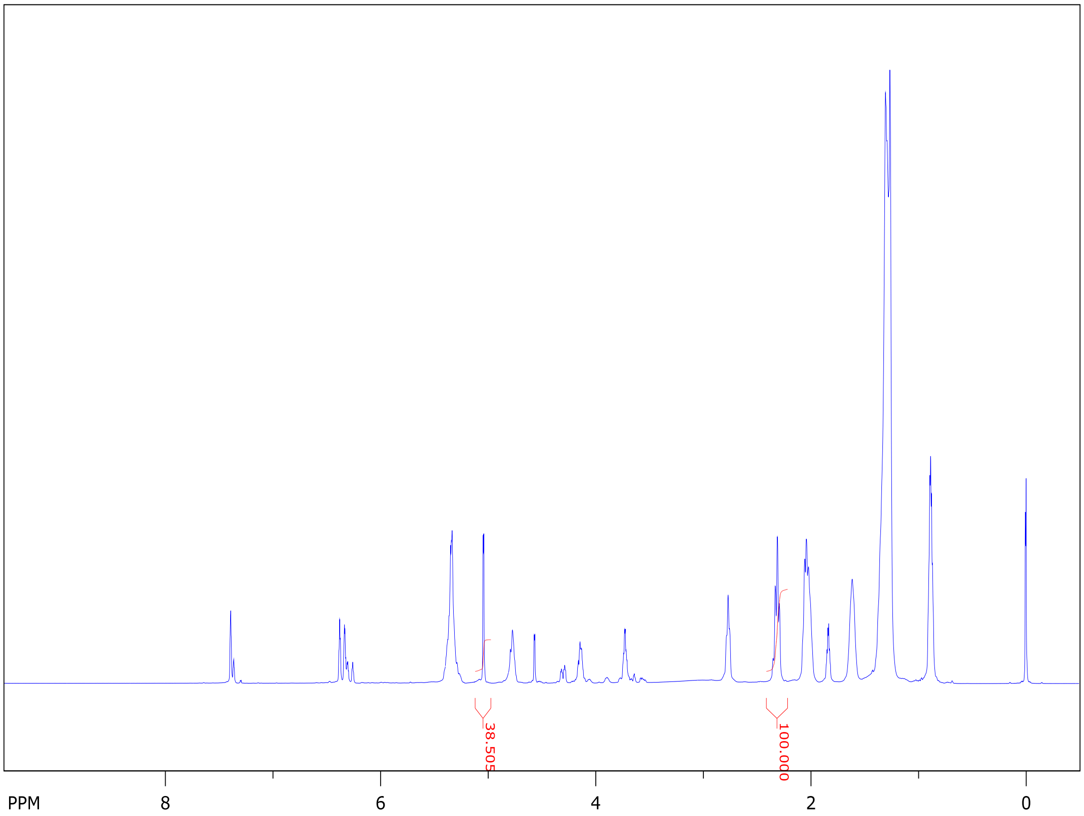
14.) ^{1}H-NMR Spectrum of Corn, FurOH, K_2CO_3, THF, and BMIM. CH.



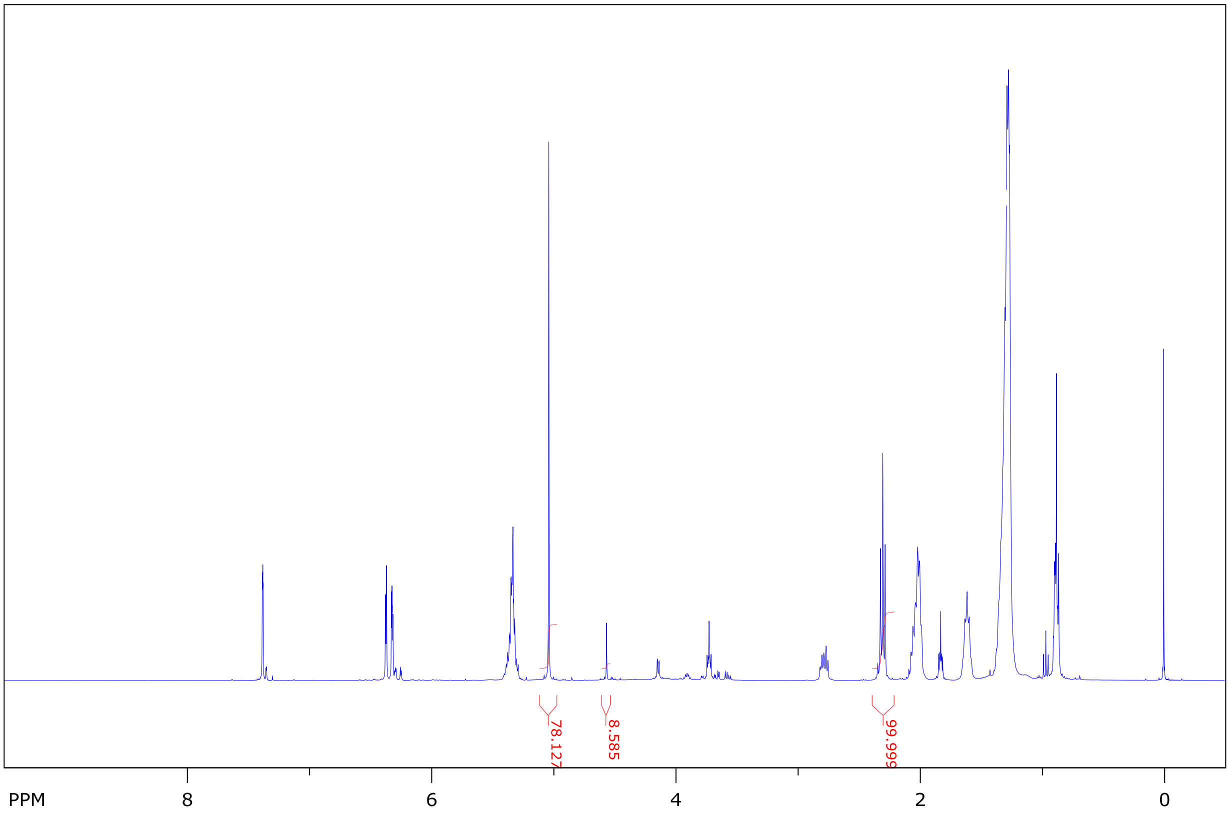
15.) ^{1}H-NMR Spectrum of Canola, FurOH, K_2CO_3, THF, and BMIM. CH.



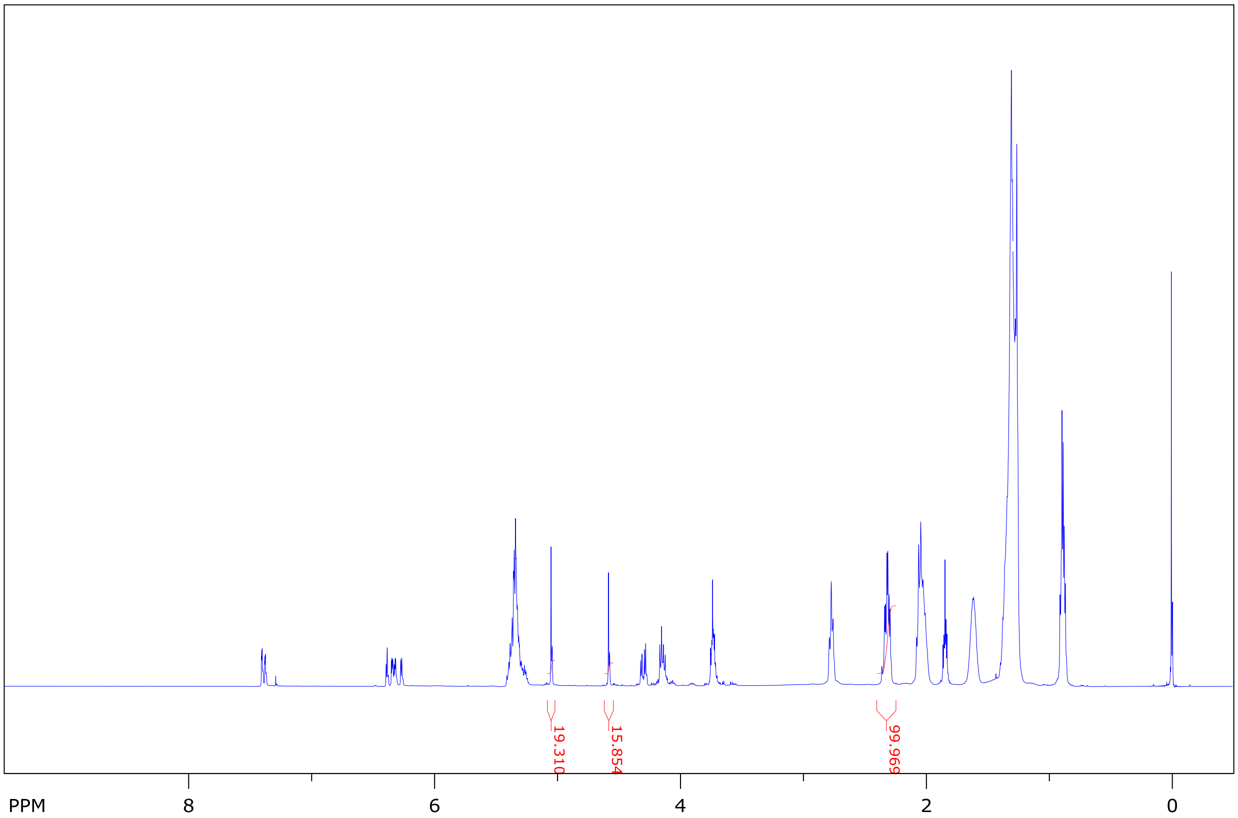
16.) ^{1}H-NMR Spectrum of Corn, FurOH, K_2CO_3, BMIM, and THF. CH



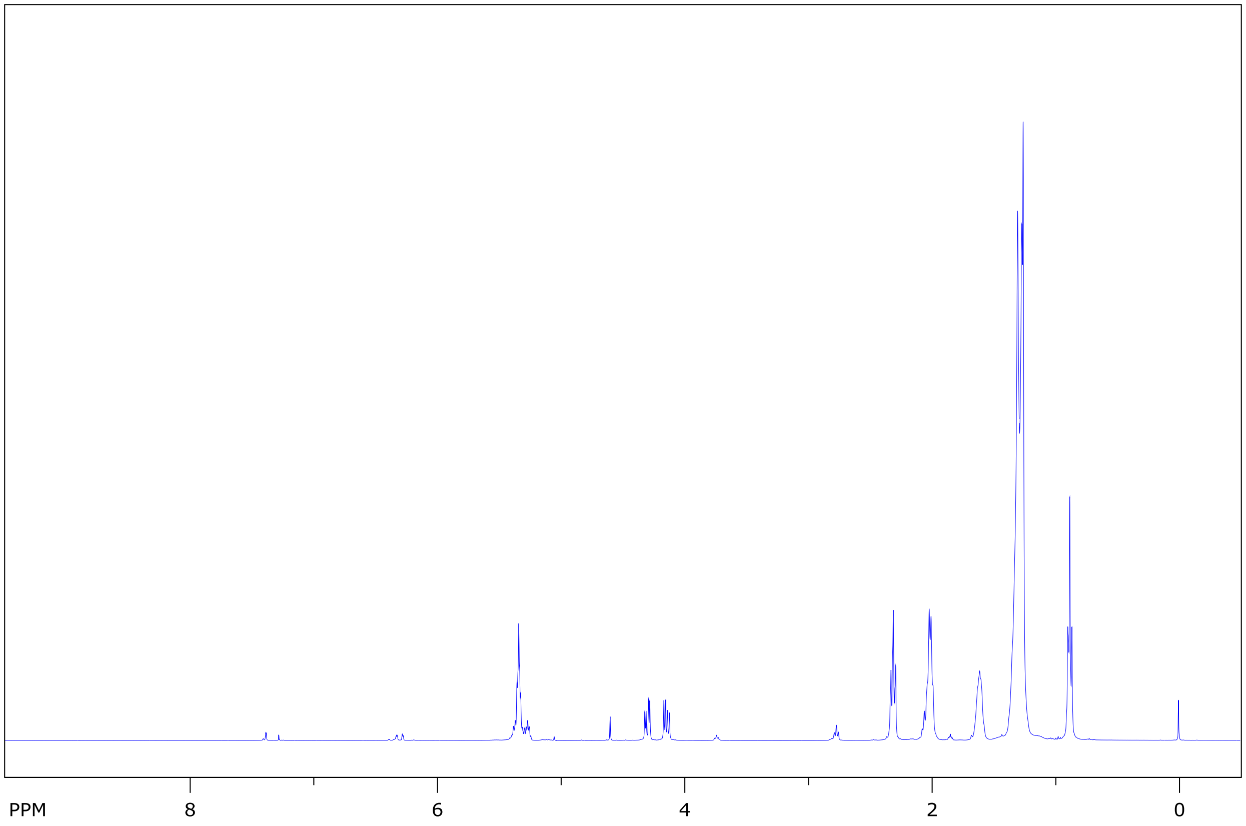
17.) ^{1}H-NMR Spectrum of Canola, FurOH, BMIM, THF, and K_2CO_3. CH.



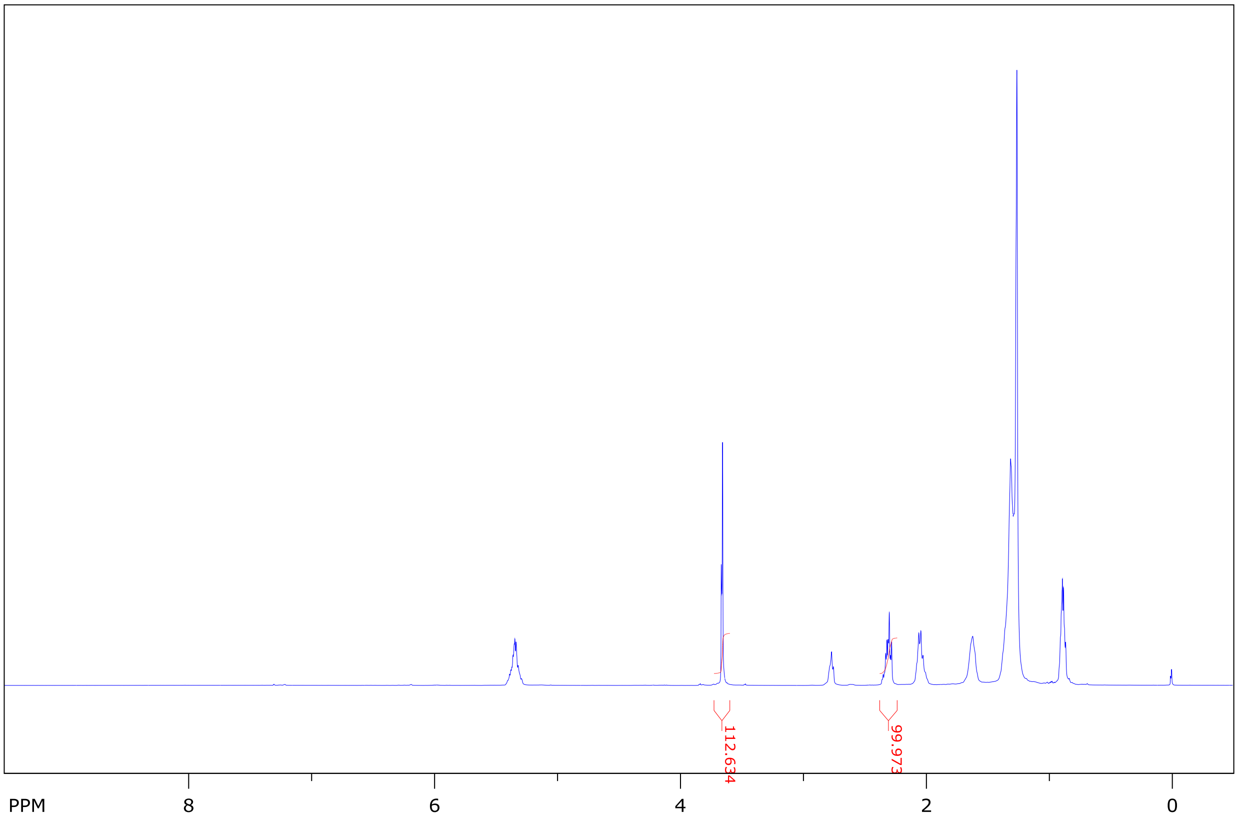
18.) ^{1}H-NMR Spectrum of Sunflower, FurOH, K_2CO_3, THF, BMIM. CH



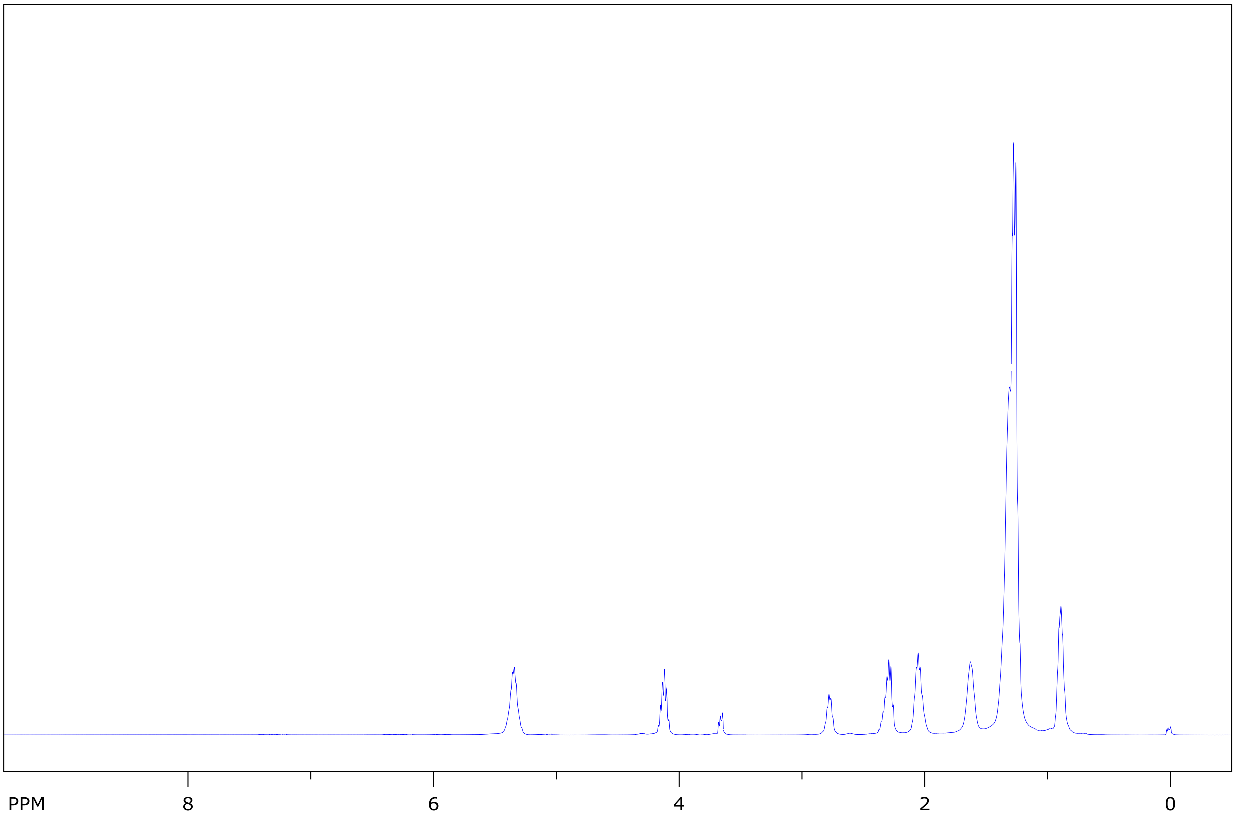
19.) ^{1}H-NMR Spectrum of Olive oil, FurOH, K_2CO_3, THF, and BMIM. MW.



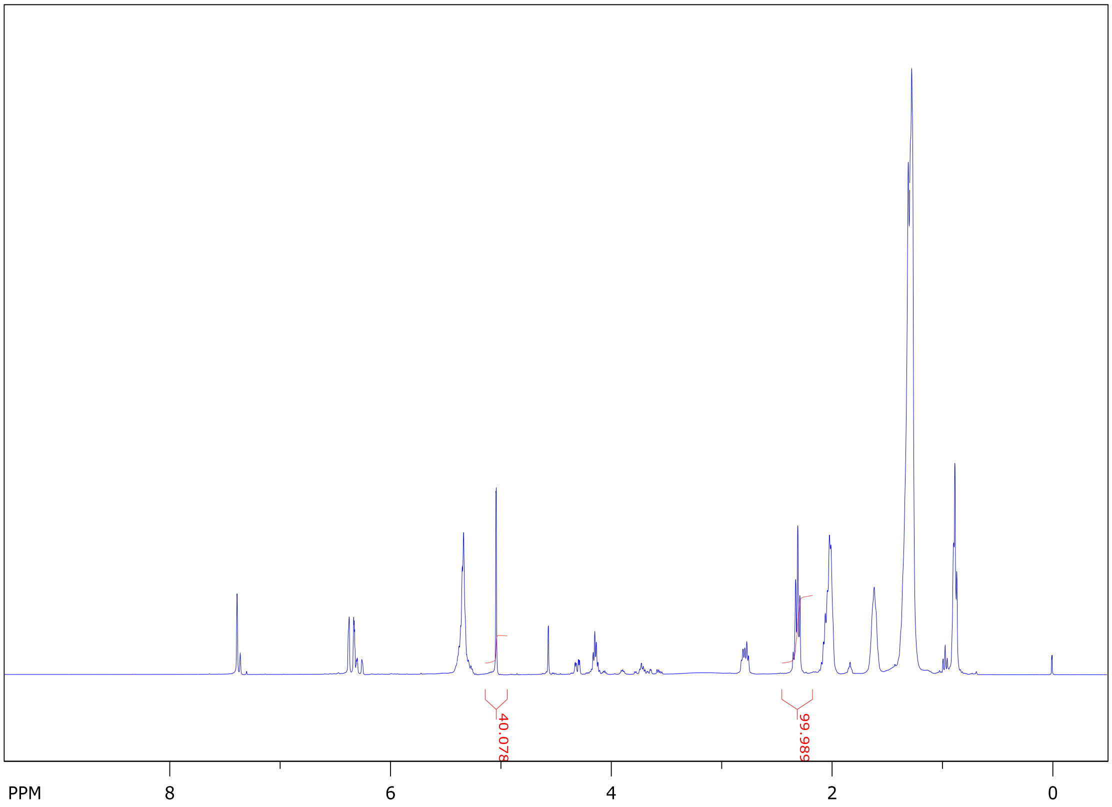
20.) ^{1}H-NMR Spectrum of Coffee, K_2CO_3, MEOH. MW.



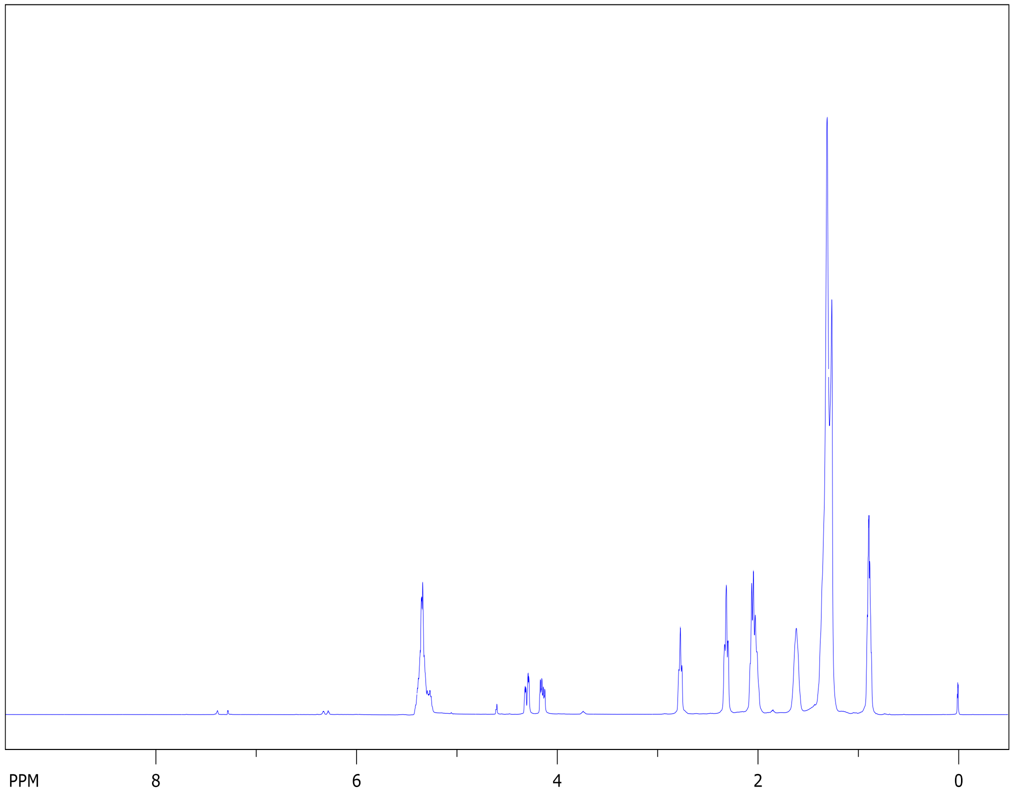
21.) ^{1}H-NMRSpectrum of Coffee, K_2CO_3, EtOH. MW



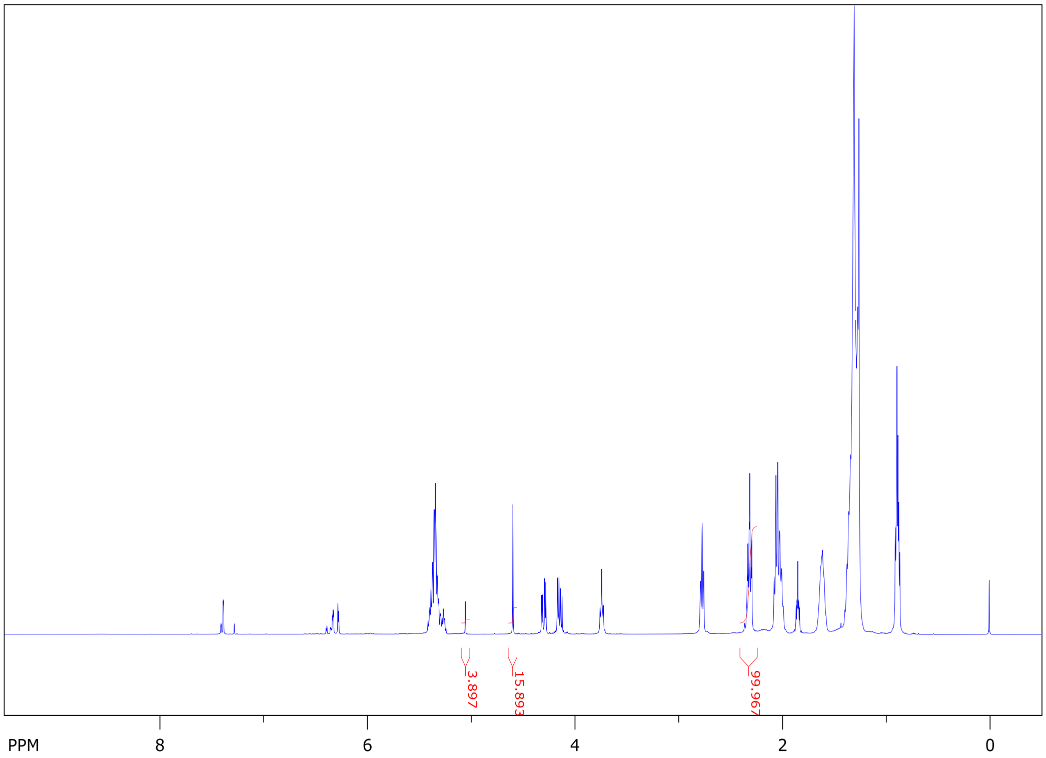
22.) ^{1}H-NMR Spectrum of Canola, FurOH, K_2CO_3, MeOH, and BMIM. MW



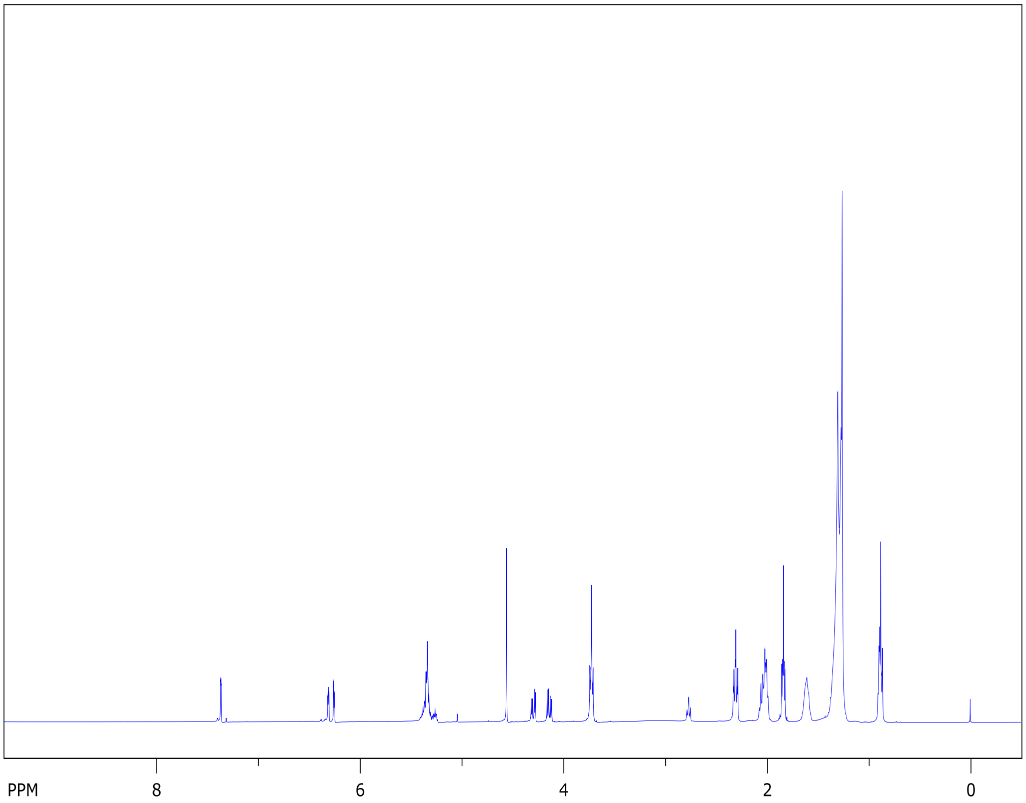
23.) ^{1}H-NMR Spectrum of Sunflower, K_2CO_3, MeOH, BMIM, and THF. MW.



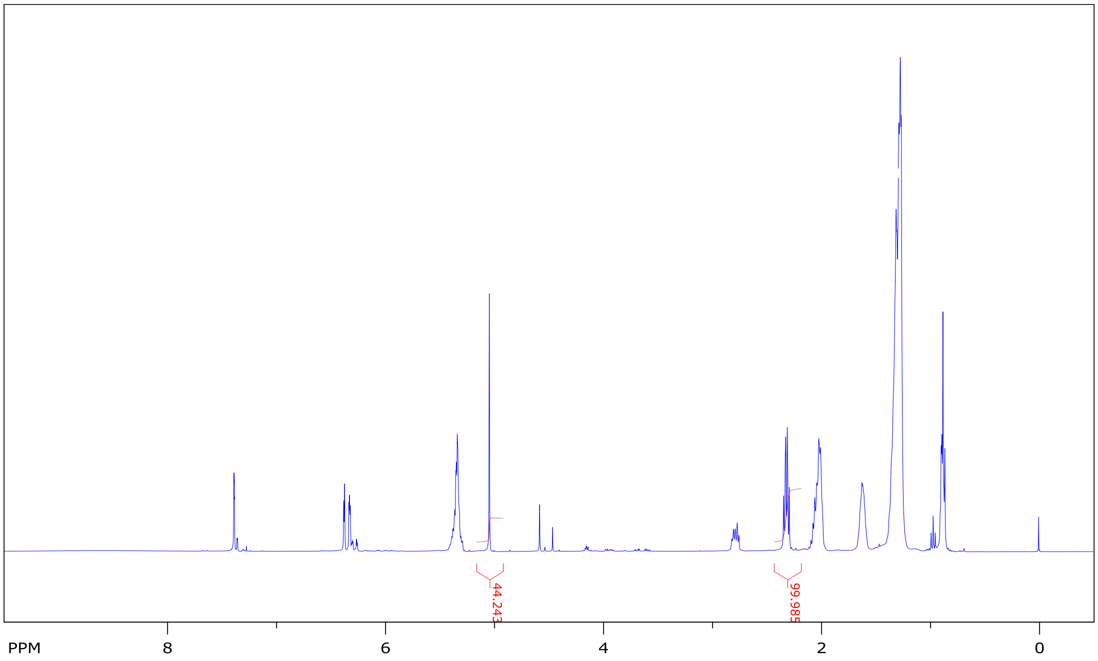
24.) ^{1}H-NMR Spectrum of Peanut, K_2CO_3, MeOH, BMIM, and THF. Mw.



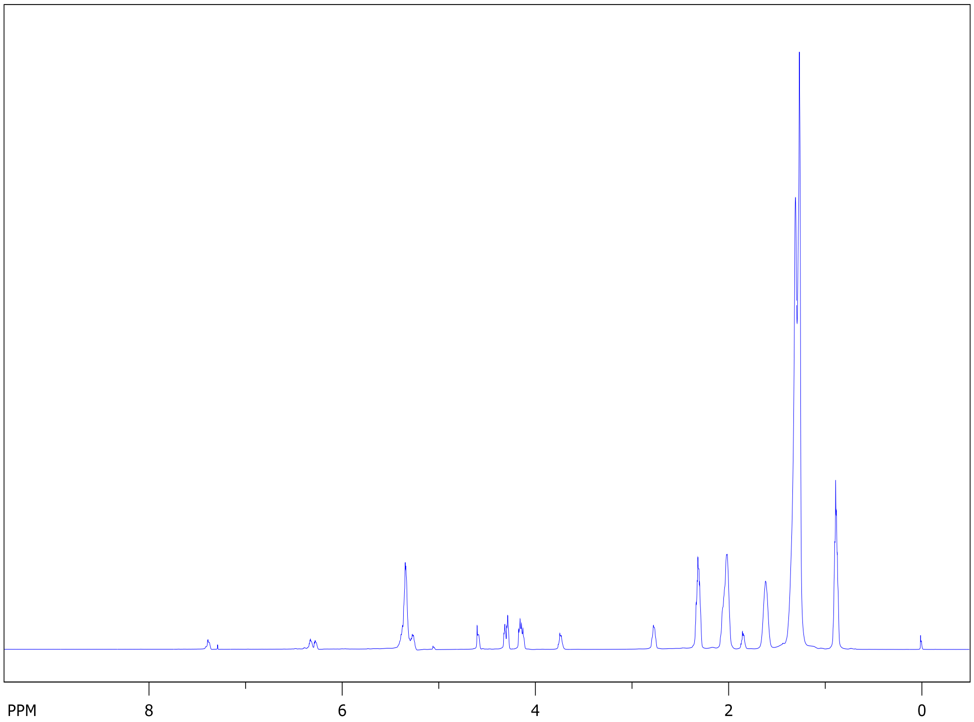
25.) ^{1}H-NMR Spectrum of Corn, K_2CO_3, MeOH, BMIM, and THF. MW



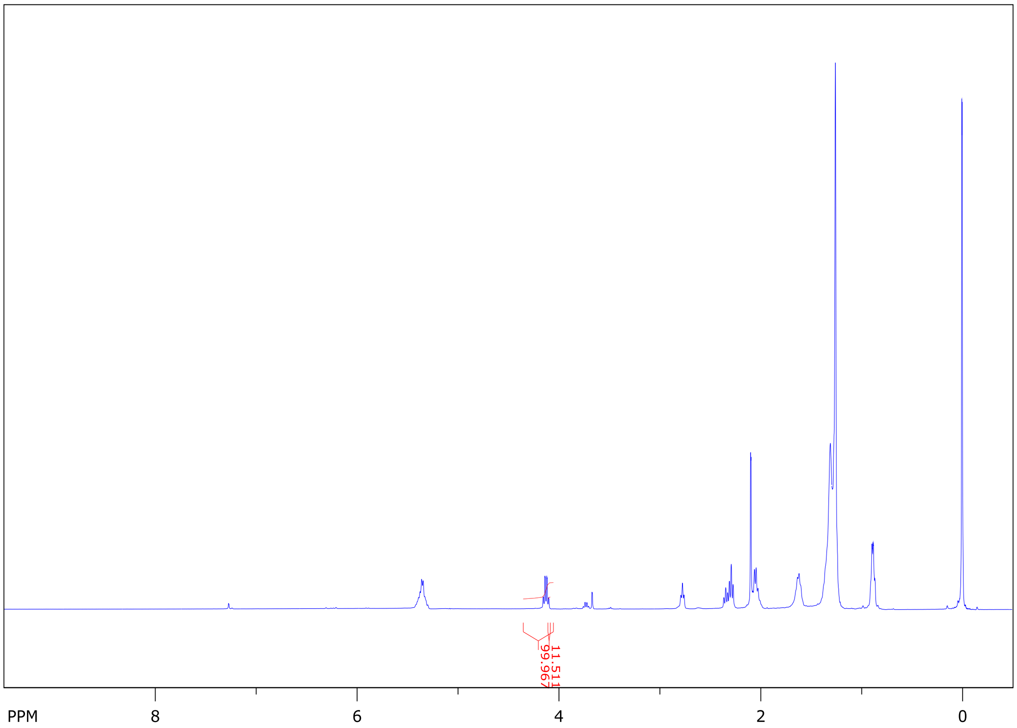
26.) ^{1}H-NMR Spectrum of Canola, FurOH, K_2CO_3, THF, and BMIM. CH.



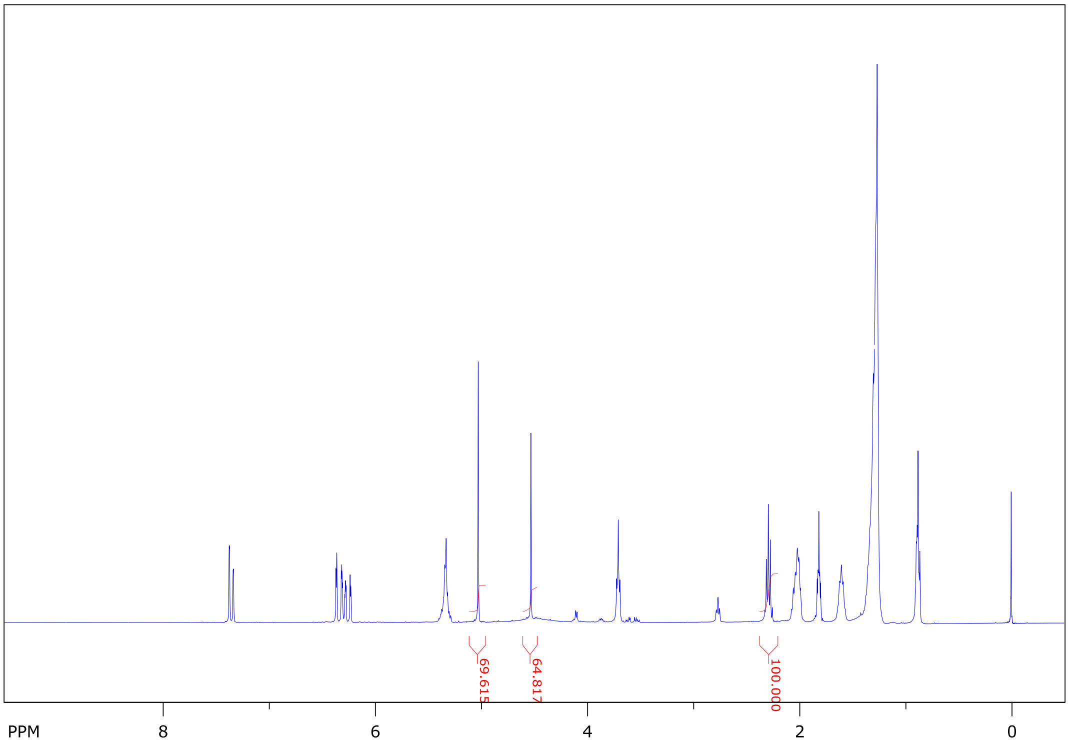
27.) ^{1}H-NMR Spectrum of Peanut, FurOH, K_2CO_3, THF, and BMIM. CH.



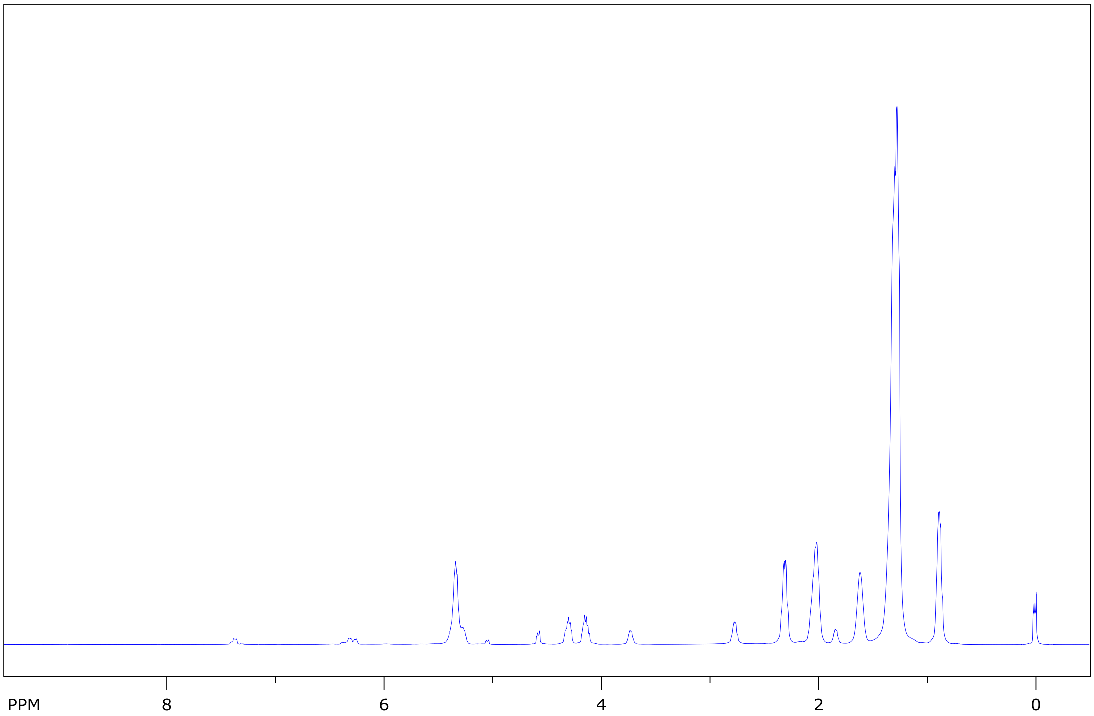
28.) ^{1}H-NMR Spectrum of Coffee, EtOH, K_2CO_3, MW.



29.) ^{1}H-NMR Spectrum of Peanut, FurOH, K_2CO_3, THF, and BMIM. CH.



30.) ^{1}H-NMR Spectrum of Peanut, FurOH, K_2CO_3, THF, and BMIM. Mw.



VITA

After receiving her diploma from Plano Senior High School in 2012, Amanda Lynn Raley began pursuing a degree at Stephen F. Austin State University in Nacogdoches, Texas. She received the degree of Bachelor of Science in chemistry from Stephen F. Austin State University in May 2016. Immediately after graduation, Amanda began to pursue a Master of Natural Science degree—emphasis in chemistry, at Stephen F. Austin State University. Amanda is expected to graduate May 2018 and begin her pursuit for a Ph.D. in biochemistry at the University of Arkansas in Fayetteville, Arkansas.

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This thesis was typed by Amanda Lynn Raley.