

Senior Project Coversheet

Title

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**Synthesis of Biodiesel Using Liquid Morpholine as a Homogeneous
Basic Catalyst**

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List of Symbols

GC-MS – Gas Chromatography with Mass Spectroscopy, an analytical instrument used to identify substances based on retention time and ion mass.

^1H NMR – Proton NMR, an analytical instrument used to identify the location of hydrogens in a substance using a magnetic field.

^{13}C NMR – Carbon 13 NMR, similar to Proton NMR but, instead of locating hydrogen with this setting the magnetic field is used to locate Carbon isotopes.

SO_x – Sulfur Oxides.

CO₂ – Carbon Dioxide.

FFA – Free Fatty Acids.

Biodiesel – Methyl Esters produced from a transesterification reaction of Fatty acid and methanol.

Glycerides – commonly known as fat or oil. Commonly 3 fatty acids attached to a glycerol molecule.

Morpholine – a stable heterocyclic basic molecule used in the project to catalyze the biodiesel reaction.

KOH – potassium hydroxide, a strong inorganic base.

CH_x (CH₂, CH₃, CH=) – alkanes, carbon bonded to multiple hydrogens.

CH_x-O (CH-O, CH₂-O, CH₃-O) – alkoxy groups, alkanes with oxygens bonded to the carbon in the place of a hydrogen.

ABSTRACT

Synthesis of Biodiesel Using Liquid Morpholine as a Homogeneous Basic Catalyst

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The described technique can be used to produce biodiesel from pure canola oil, waste vegetable oil, or animal fat. The method described in the project uses excess of methanol and liquid morpholine as a catalyst. With this method the biodiesel is produced without soapy water and in less corrosive reaction conditions. The excess methanol can be recovered by distillation and the recovery of morpholine while not currently very successful (52%) can be improved with a more powerful vacuum in a vacuum distillation. This method uses a new catalyst that reduces the problems in the purification of biodiesel and glycerol. The described method uses simple liquid liquid extraction to separate the biodiesel produced from the glycerol. Once extracted purification involves filtration and evaporation. The final part of the method is testing using GC-MS, ^1H NMR, and ^{13}C NMR for the presence of biodiesel.

Introduction

Biodiesel is an alternative to petroleum diesel for reducing emissions of gaseous pollutants such as CO₂, SO_x, organic compounds, and particulate matter. Considering that it is made from renewable sources, its production provides a method of recycling CO₂ (1). It is a fuel comprised of alkyl esters of long chain fatty acids.

Currently, alkaline bases are used as a catalyst for the reaction. The reaction is shown in figure 1. Commonly, biodiesel is prepared from triglyceride sources such as virgin, used oils, and animal fat.

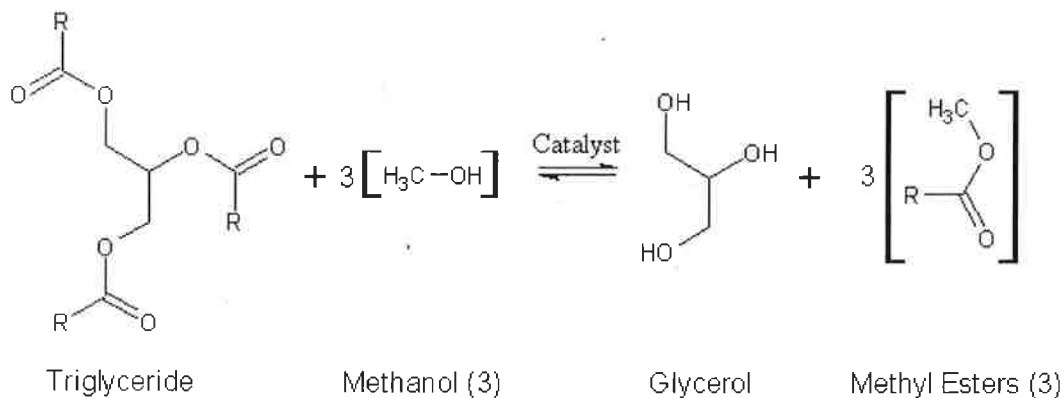


figure 1. Biodiesel Reaction

Inexpensive feedstock, such as waste oil, contains high levels of free fatty acids (FFAs) can be used only after neutralization, which increases the amount of catalyst required for the reaction and increases the time required. This is because catalysts require anhydrous conditions and low levels of FFAs in the fats and oils used.

Organic liquid amines are not as corrosive as the commonly used hydroxide bases and allow for the synthesis of biodiesel without the production of soapy water during purification, an additional byproduct which must be disposed of. Although the literature

describes methods for biodiesel production using low boiling amines (2-5), these examples are rare, the catalyst necessary for the reaction is not recovered due to its high volatility, and take place at sub-critical methanol temperature

The present work studied biodiesel production using morpholine, a liquid amine with a relatively high boiling point (129 °C) which makes it easier to recover. In addition, a series of commercially available resins containing morpholine were examined as potential heterogeneous catalysts.

Experimental

Reagents

Methanol and Morpholine were purchased from Fisher Scientific (Atlanta, Ga). Methanol was dried over molecular sieves prior to use.

Pure canola oil was purchased from Wal-Mart, local restaurants donated animal fat and used vegetable oil.

Raw materials characterization

Prior to the reaction, a titration of the vegetable oil or animal fat was performed with an aqueous solution of KOH (1g/L) to determine the concentration of the FFA. The fuel stock solution used in the titration was prepared by dissolving 1g of used vegetable oil or animal fat in 10mL of 2-propanol. The acid value for used vegetable oil was 2.5 mg of KOH/g of oil, and for animal fat was 1.93 mg of KOH/g of fat.

Pretreatment

The only pretreatment of the fuel stock necessary was filtration of the used vegetable oil and animal fat to remove any solid residue.

Synthesis of biodiesel

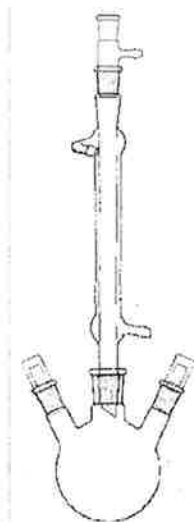


Figure 2. Aparatus

A round bottom flask (250 mL) (figure 2.), containing 30 g of oil or animal fat, methanol and morpholine was used as a reactor. In all reactions, a mass ratio of 10:3 methanol/triglyceride was used. The mass % of morpholine used was 9.1% for pure canola oil, 10.3% for used vegetable oil and 14% for animal fat. The additional quantity of morpholine necessary for the reaction of used vegetable oil is 0.027 g of morpholine per gram of oil and per mL of KOH solution (1g/L) required in the titration of waste oil. An additional 0.14 g of morpholine were added per gram of fat per mL of KOH needed when titrating the fat. The reaction mixture was heated at reflux (65 °C).

NMR was used to follow the progress of the reaction. Each hour, a 1 mL aliquot was collected from the reaction mixture and analyzed using ^1H NMR (Anasazi 90 MHz FT NMR). The reaction times required for complete conversion were: 33h for pure vegetable oil, 36h for used vegetable oil, and 41h for animal fat.

When the reaction was complete, excess methanol was recovered using distillation. A portion of the morpholine was also recovered by vacuum distillation. Then the reaction mixture was extracted with ethyl acetate, and the solvent was evaporated under vacuum. The organic layer was then purified by filtration through silica gel using hexane as the eluent. In the case of animal fat, the solid residue was isolated after this filtration and then filtered using ethyl acetate as the eluent. The solid residue was a mixture of methyl esters, free fatty acids, and glycerides. The yield for the reactions was

calculated using the formula: $\text{weight}\% = (\text{mass of biodiesel} / \text{mass of triglyceride}) \times 100$.

Analysis

Analyses of the products of the reactions were done using ^1H NMR and ^{13}C NMR (Anasazi 90 MHz FT NMR).

Pure canola oil:

^1H NMR (90 MHz CDCl_3) δ : 0.63-0.88 (m, CH_3); 0.10-1.60 (m, CH; CH_2); 1.99-2.03 (m, CH_2); 2.21 (t, CH_2CO); 2.29-2.37 (m, CH_2); 4.13-4.28 (m, CH-O; CH_2 -O); 5.32 (t, CH=).

^{13}C NMR (90 MHz CDCl_3) δ : 14.59 (CH_3); 23.13 (CH_2); 23.23 (CH_2); 25.38 (CH_2); 26.05 (CH_2); 26.17 (CH_2); 27.73 (CH_2); 29.66 (CH_2); 29.76 (CH_2); 29.90 (CH_2); 30.12 (CH_2); 30.26 (CH_2); 30.32 (CH_2); 32.09 (CH_2); 32.49 (CH_2); 34.43 (CH_2); 34.59 (CH_2); 62.54 (CH_2 -O); 69.53 (CH-O); 128.44 (CH=); 128.60 (CH=); 130.13 (CH=); 130.31 (CH=); 130.41 (CH=); 130.51 (CH=); 132.26 (CH=); 172.85 (CO_2CH); 173.21 (CO_2CH_2).

Biodiesel: using pure canola oil (wt =97%); with used vegetable oil (wt =94%); and with animal fat (wt =78%)

^1H NMR (90 MHz CDCl_3) δ : 0.81-0.94 (m, CH_3); 1.26-1.61 (m, CH_2); 1.98-2.02 (m, CH_2); 2.21 (t, CH_2CO); 2.30-2.38 (m, CH_2); 3.65 (s, CH_3 -O); 5.34 (t, CH=).

^{13}C NMR (90MHz CDCl_3) δ : 14.12 (CH_3); 22.75 (CH_2); 25.02 (CH_2); 26.97 (CH_2); 27.29 (CH_2); 28.80 (CH_2); 28.86 (CH_2); 29.18 (CH_2); 29.21 (CH_2); 29.36 (CH_2); 29.42 (CH_2); 29.56 (CH_2); 29.62 (CH_2); 29.76 (CH_2); 29.86 (CH_2); 31.62 (CH_2); 32.01 (CH_2); 34.13 (CH_2); 51.57 (CH_3 -O); 128.00 (CH=); 128.16 (CH=); 129.80 (CH=); 130.05

(CH=); 130.23 (CH=); 174.23 (CO₂CH₃);

Results and Discussion

Synthesis

The method described was successful using pure canola oil, used vegetable oil, and animal fat. In the case of used vegetable oil, the reaction time was increased to 36 hours, and an additional quantity of morpholine (2g of morpholine for 30g of oil) was added. The yield for used vegetable oil was slightly less than with pure canola oil (94% < 97%). Used vegetable oils contain a higher concentration of free fatty acids than found in virgin oils. Under the basic conditions of this method the free fatty acids do not fully convert to biodiesel which accounts for the lower conversion percentage.

The reactions using animal fat as the fuel stock had a yield that was lower than both those of pure canola oil and used vegetable oil (78% < 94% < 97%). The reaction product consisted of a solid and a liquid phase. The solid residue consisted of a mixture of methyl esters and glycerides. This residue can be recycled to produce additional liquid biodiesel (45%). The reactions with animal fat required additional time (40 hour reaction). The solid animal fat required more time because it did not mix with the other reagents as well as liquid triglycerides, causing a slower reaction. An additional amount of morpholine was added for each of the reactions with animal fat (7g for 30g of animal fat).

Attempts were made to improve the yield (7) of reactions with animal fat by using a mixture of animal fat and pure canola oil, or animal fat with used vegetable oil (Table 1.).

Table 1. Biodiesel synthesis using mixtures of oil and animal fat

Reaction #	pure canola : animal fat	Yield wt %	used vegetable : animal fat	Yield wt %
1	2:8	76%	2:8	66%
2	4:6	76%	4:6	76%
3	6:4	82%	6:4	78%
4	8:2	97%	8:2	91%

The yield of the reactions with pure canola oil as opposed to used vegetable oil was slightly higher. However there was only a slight improvement in the yield was noticed for mixtures containing relatively low concentrations of animal fat.

Using morpholine as a catalyst allowed the production of a cleaner fuel and cleaner glycerol. This simplifies the purification of the product (8). Purification of biodiesel was done using filtration over silica gel using hexane under vacuum. The recovery of morpholine post reaction by vacuum distillation was acceptable (52%). Recovery of the excess methanol was more successful by simple distillation (97%). Because the morpholine and methanol can be easily removed by evaporation under vacuum the purification is significantly simplified.

Commercially available polymer bound morpholine was used as an attempt as a heterogeneous catalyst. This attempted catalyst was unsuccessful. This could be attributed to the form of the catalyst. The basic nitrogen of morpholine was bound to the solid support polymer strand. A more successful catalyst could be made using a different atom on morpholine to attach to the solid support polymer strand.

Biodiesel Characterization

The biodiesel produced using morpholine as a catalyst was tested against pure canola oil using ^1H NMR. The spectra of pure canola oil contained a multiplet at 4.13-4.28 ppm. This multiplet corresponds to the hydrogen atoms of glycerol (CH-O , $\text{CH}_2\text{-O}$). In the spectra of the biodiesel this multiplet was absent and there was a singlet at 3.65 ppm corresponding to the methoxy bond ($\text{CH}_3\text{-O}$).

With the ^{13}C NMR the spectra for pure canola oil and biodiesel were also compared. There are two significant peaks, 62.54 and 69.53 ppm. These correspond to the carbon of the glycerol ($\text{CH}_2\text{-O}$); (CH-O). For biodiesel there is a peak at 51.57 ppm which is for the methoxy group ($\text{CH}_3\text{-O}$).

Table 2. Biodiesel test results

Test conducted	Actual	Limit
Moisture	760 ppm	n/a
Total Glycerin	0.712%	<0.24%
Acid number	0.03 mg KOH/g	<0.50 mg KOH/g
Kinematic viscosity	5.10 mm^2/sec	1.9-6.0

The biodiesel produced required testing to confirm the quality of the product. Piedmont Biofuels performed various characterization tests (Table 2.), they included test for the moisture content, glycerine content, acid number, and kinematics of the biodiesel.

Conclusion

The Described method presents advantages over the traditional method by using a less

corrosive catalyst and allowing the production of cleaner reaction products. The principle disadvantage is that it requires longer reaction times that consume additional energy. The method is successful with a wide variety of fuel stocks. The blending of animal fat with pure canola oil or used vegetable oil to increase yield does not result in significant improvement. Although the attempts to recover catalyst yielded only modest results these can be improved with a more efficient distillation apparatus. Our groups next focus will be on obtaining and testing morpholine resins that leave the active site of the catalyst free, which could prove to be a successful heterogeneous catalyst.

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