

A Study of Alternative Catalysts and Analysis Methods for Biodiesel Production

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Abstract

This project aims to develop a cost efficient process for biodiesel production and can be divided in three main components: 1) production of biodiesel from a variety of fuel stocks using liquid morpholine as catalyst; 2) production of biodiesel using a homogeneous phase transfer catalyst; and 3) development of a method for using Infrared Spectroscopy (IR) to determine the extent of conversion of oil to biodiesel. The production of biodiesel from various fuel stocks in the presence of methanol using liquid morpholine as catalyst reduces the problems related to purification of the biodiesel since morpholine can be recovered by distillation. Furthermore the use of two homogeneous phase transfer catalyst, tetramethylammonium hydroxide (TMAH) and choline hydroxide (CH), was evaluated. The advantage of using these catalysts is that it allows for a better separation between the fuel and glycerin, thus additionally simplifying the purification procedure. Finally, this project endeavored to develop a way to use FT-IR to determine the purity of biodiesel samples obtained since FT-IR is faster and more readily available than the standard method of gas chromatographic analysis. For educational applications, a calibration curve was created by comparing data on the purity of biodiesel samples obtained from the GC-FID analysis to the ratio of the absorbances at 1197 cm^{-1} to 1166 cm^{-1} from the FT-IR spectrum. For field application, a similar method was developed using a portable IR spectrometer. The data collected gave a good linear fit for % purity of the samples versus absorbance ratio.

Keywords: Biodiesel, homogeneous catalysis, FT-IR analysis, fuel stock, transesterification

Introduction

Biodiesel is produced in a transesterification reaction between oil, an alcohol such as methanol and a catalyst (Figure 1). In industry, the catalyst of choice is potassium hydroxide (KOH) (1,2); however, it has been previously shown to be both caustic and corrosive making other alternatives attractive.

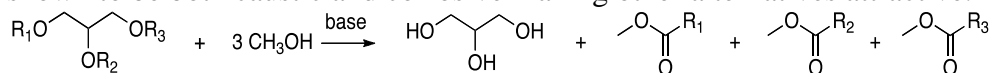


Fig. 1: Biodiesel synthesis reaction

Furthermore, these standard hydroxide catalysts require the use of additional catalyst and alcohol when inexpensive feedstock, for example waste oil, containing high levels of free fatty acids (FFAs) are used in the reaction. In addition, a titration must be performed to determine the concentration of FFAs prior to reaction which increases the time and expertise required.

Organic liquid amines such as morpholine are not as corrosive as the commonly used hydroxide bases and allow for the synthesis of biodiesel without the production of the soapy water byproduct which is generated during purification and which must be disposed of. Although the literature describes the production of biodiesel using low boiling amines (3-6), these examples are rare, take place at subcritical methanol temperature and the catalysts are not routinely recovered due to their high volatility. The study described herein examined biodiesel production using the less volatile (129°C) liquid amine base morpholine as a catalyst which allowed for its separation and recovery by distillation. In addition, a series of commercially available resins containing morpholine were examined as potential heterogeneous catalysts.

An additional goal of this project was to use a homogeneous phase transfer catalyst to facilitate biodiesel production. Choline hydroxide (7) and TMAH (8, 9) are reported to be far less corrosive than the traditional KOH but are equally effective. The main disadvantage of these compounds is the cost. Previous studies have described methods that use the two catalysts separately but these methods are not used extensively. The present work aims to develop an efficient method using one or both of these catalysts in combination in order to reduce the amount of catalyst required thereby reducing the cost of the fuel produced.

The final goal of this work was to develop a simplified method for the analysis of biodiesel. Typically, the purity of the biodiesel is measured via GC-FID analysis, but this method is a time consuming, and requires specialized and expensive instrumentation. A correlation between the quantitative GC-FID data and the qualitative FT-IR data was shown to provide

an alternative method of purity determination for students, faculty and others involved in biodiesel production. FT-IR has been used for functional group characterization (10-16) or in order to monitor the progress of a reaction (17-19) but to our knowledge there is no description of a method that uses the FT-IR for the estimation of the conversion of oil to biodiesel. A simple, portable IR spectrometer, the InfraSpec™ VFA-IR, is available for field-testing for those who wish to produce small quantities of biodiesel for their own use. This instrument presents the advantage of being smaller and therefore more portable and simple enough for a layperson to use. Use of the InfraSpec™ VFA-IR spectrometer in order to estimate the extent to which the conversion of oil to biodiesel has been achieved has not been described previously. Because different types of oils contain differing amounts for various fatty acid and therefore present different ratios between the IR peaks used in the analysis, calibration curves were prepared for the most common types of oils: soybean, canola and corn oil using either an FT-IR or the Infracpec™.

Experimental Section

Reagents

Methanol and Morpholine were purchased from Fisher Scientific (Atlanta, Ga). Methanol was dried over 4Å molecular sieves prior to use. Choline hydroxide was purchased from Sigma Aldrich as a 45% by weight solution in methanol.

Three oils which are readily available and commonly used to produce biodiesel, pure soybean, canola oil and corn oil, were purchased from Wal-Mart, and used vegetable oil and animal fat were donated by local restaurants.

Raw materials characterization.

Prior to the reaction, a titration of the used 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 10 mL 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

In the case of the morpholine catalyzed synthesis, the only pretreatment of the fuel stock necessary was filtration of the used vegetable oil and animal fat to remove any solid residue. In the case of phase transfer catalyzed reactions (CH, TMAH), because the catalyst is water-sensitive, the pure oil, was dried by filtration over silica gel.

Synthesis of biodiesel; morpholine catalyzed procedure

A round bottom flask (250 mL), containing 30.g of oil or animal fat, methanol and morpholine was used as the 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 0.027g of morpholine per gram of oil and per mL of KOH solution (1g/L) required in the titration of the waste oil. An additional 0.14g 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).

The reactions were followed by NMR. 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 by 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 removed *in vacuo*. The organic layer was then purified by filtration through silica gel using hexane as the eluent. (In the case of animal fat, a solid residue was isolated after the filtration of biodiesel using ethyl acetate as eluent. This residue is a mixture of methyl esters, FFA and glycerides.)

The yield was calculated with the formula:

$$\text{weight \%} = (\text{mass of biodiesel}/\text{mass of triglyceride}) \times 100. \quad (1)$$

Synthesis of biodiesel; phase transfer (CH or TMAH) catalyzed procedure

A round bottom flask equipped with a distillation head and a condenser, immersed in an oil bath, was used as the reactor. The reaction mixture was heated at reflux for one hour. When the reaction is complete, the excess methanol is recovered by distillation. Following methanol recovery the reaction mixture is injected with water; 5% of the mass of oil used in the reaction.

The reaction mixture is transferred into a separatory funnel and then the glycerol layer is separated. The organic layer is filtered over silica gel to eliminate the polar impurities. The samples are analyzed by NMR, GC-FID, InfraSpecTM VFA-IR and FT-IR instruments.

Analysis method; Biodiesel Characterization

The biodiesel production was confirmed by NMR. In ¹H NMR the spectra of pure vegetable oil has a multiplet at 4.13-4.28ppm that corresponds to the hydrogen atoms of the glycerol fragment (CH-O; CH₂-O). This peak is

not present in the ^1H NMR of the biodiesel but a singlet at 3.65ppm corresponding to the methoxy group ($\text{CH}_3\text{-O}$) is present instead.

Similarly in ^{13}C NMR for the pure canola oil, two peaks can be observed at 62.54 and 69.53 ppm corresponding to the carbon of the glycerol fragment ($\text{CH}_2\text{-O}$); (CH-O). Instead, for the biodiesel, only one peak is observed at 51.57 ppm corresponding to the methoxy group ($\text{CH}_3\text{-O}$).

Analysis by ^1H and ^{13}C NMR (Anasazi 90 MHz FT NMR).

Pure canola oil: ^1H NMR (90 MHz CDCl_3): \square 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 ; $\text{CH}_2\text{-O}$); 5.32 (t, CH=).

^{13}C NMR (90 MHz CDCl_3): $\square\square$ 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 ($\text{CH}_2\text{-O}$); 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: from pure canola oil (wt=97%); from used vegetable oil (wt=94%); from animal fat (wt=78%)

^1H NMR (90 MHz CDCl_3): \square 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, $\text{CH}_3\text{-O}$); 5.34 (t, CH=).

^{13}C NMR (90 MHz CDCl_3): $\square\square$ 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 ($\text{CH}_3\text{-O}$); 128.00 (CH=); 128.16 (CH=); 129.80 (CH=); 130.05 (CH=); 130.23 (CH=); 174.23 (CO_2CH_3)

To confirm that our product has the required properties, determination of the moisture, total glycerin, acid number and kinematic viscosity were performed by Piedmont Biofuels (see Table I).

Table I. Biodiesel test results

Test conducted	Actual	Limit
Moisture	760 ppm	NA
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

Gas Chromatography (GC)

A Shimadzu GC with Biodiesel Package, On-Column Injector (OCI) and Flame Ionization Detector (FID) was used to determine the free and total glycerol content using the ASTM D-6584 method. Figures 1 and 2 show typical chromatograms for unreacted oil and biodiesel, respectively.

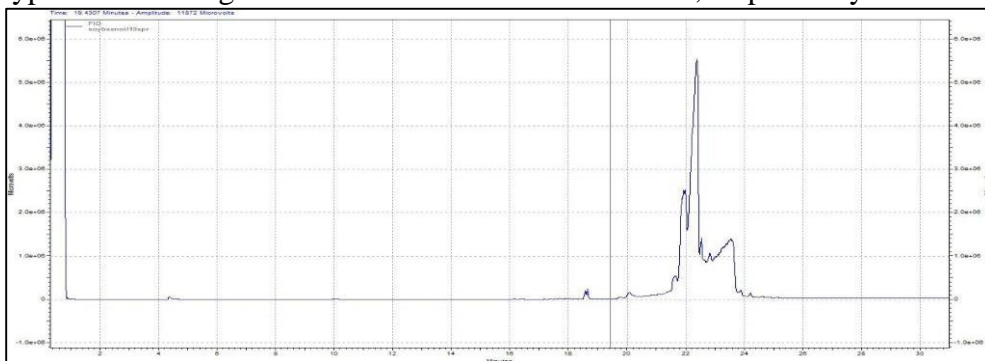


Figure 2: GC –FID of unreacted oil

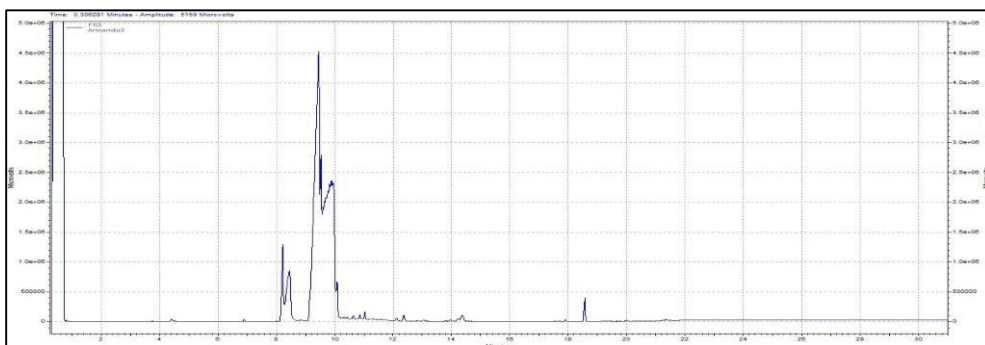


Figure 3: GC –FID of typical biodiesel sample

Fourier Transform Infrared (FTIR) Spectrometer

A Horizontal Attenuated Total Reflectance (HATR) Crystal (Perkin Elmer) with an angle of 45° composed of ZnSe was used. The instrument was configured to perform four scans from 2000.00 cm⁻¹ to 1000.00 cm⁻¹ with a resolution of 4.00 cm⁻¹. Figure 3 shows an overlay plot of the spectra for samples of varying % conversion in order to demonstrate the changes in the spectra which can be observed. A peak height ratio of 1197cm⁻¹ to 1166cm⁻¹ was chosen because it showed the best correlation to % conversion by GC.

The 1197cm^{-1} peak corresponds to absorbance by the O-CH₃ bond of the biodiesel and was observed to have the largest increase as the reaction proceeds.

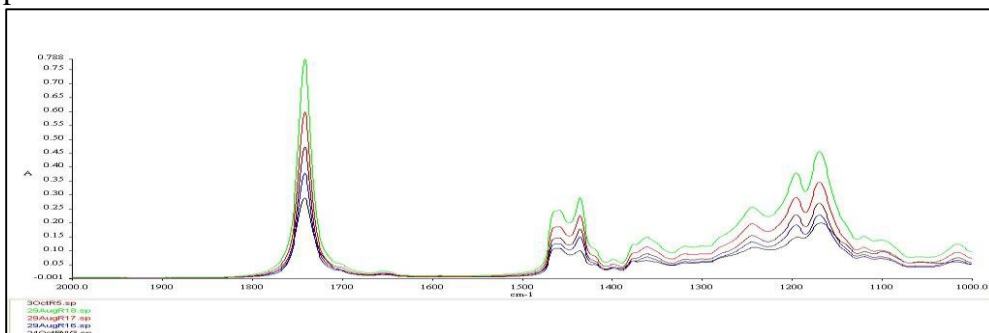


Figure 4: FT-IR spectra of samples of varying purity.

FT-IR and GC-FID analysis

In order to prepare the plot for the comparison of FT-IR and GC-FID analysis at peaks 1197 cm^{-1} and 1166 cm^{-1} various samples of biodiesel had to be produced. Time and temperature of reflux and catalyst amount were varied in order to get samples with a broad range of conversion results. After the biodiesel had been isolated, it was analyzed using the GC-FID. The ASTM D-6584 method determines the amount of glycerol present in the sample, however, this does not give the amount of biodiesel produced. To determine our % conversion, the “raw concentration” values for mono-, di-, triglycerides and free glycerol were summed and then subtracted from 100%. In addition, each sample was analyzed using the FT-IR. Five $1\text{ }\mu\text{L}$ drops were placed onto the ATR crystal. A spectrum was generated and the peak heights at 1197 cm^{-1} and 1166 cm^{-1} were recorded. Finally, % conversion was plotted versus the $1197/1166\text{ cm}^{-1}$ ratio in order to generate a calibration curve which can be used to determine the % conversion to biodiesel for a particular reaction. Figures 5, 6, and 7 show the results for the soybean oil, canola oil and corn oil, respectively.

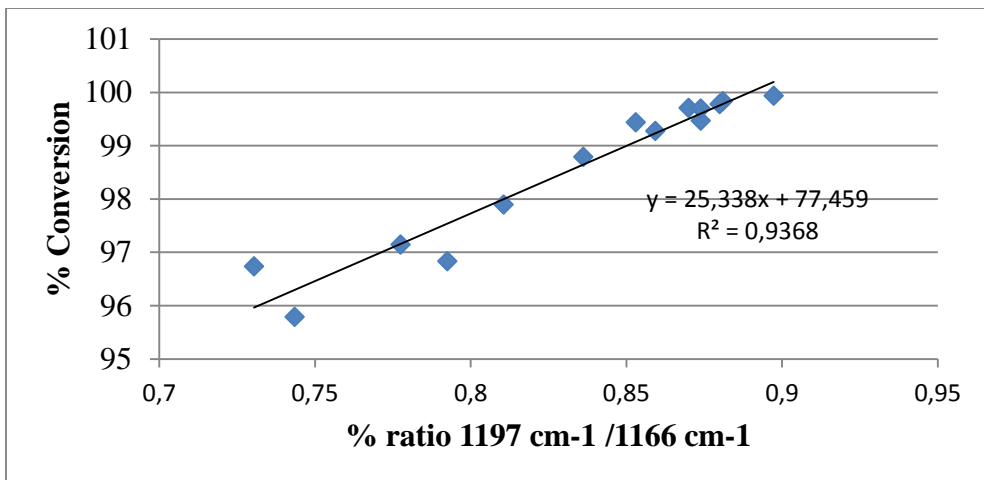


Figure 5: FT-IR curve for soybean oil.

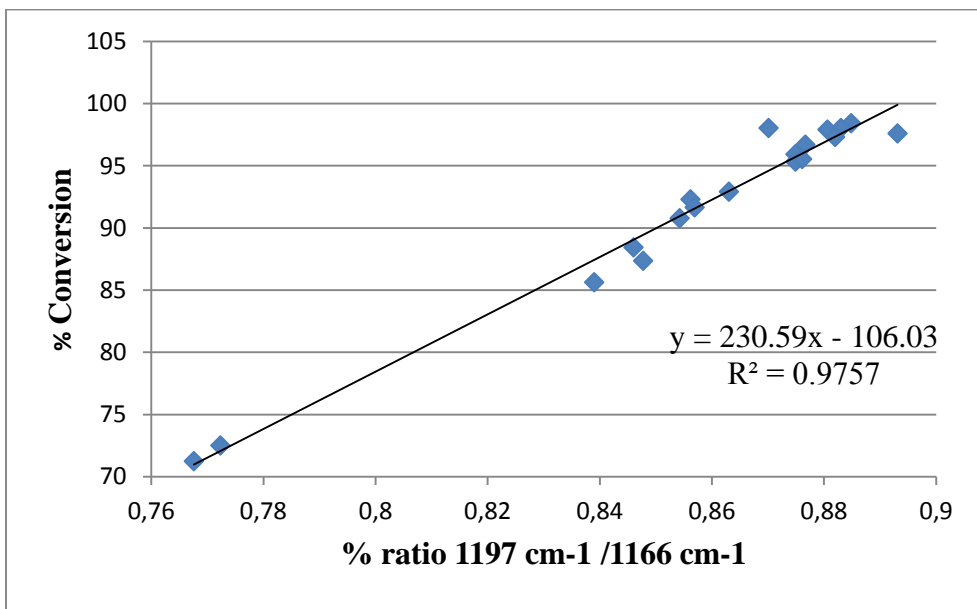


Figure 6: FT-IR curve for canola oil.

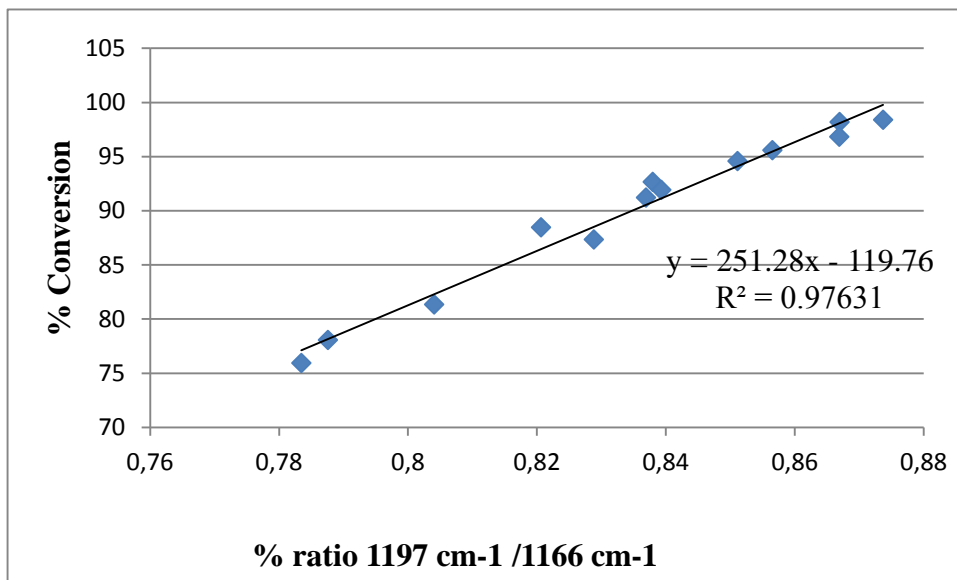


Figure 7: FT-IR curve for corn oil.

InfraSpec™ VFA-IR Spectrometer ES

An Attenuated Total Reflectance (ATR) Crystal (Sample Stage) with an angle of 45° composed of ZnSe was used. A Thin Film with CaF₂ Window was used for the source. The array type (Serial #: 2385) was Linear, 128 pixel, LiTaO₃. The instrument (Serial #: 391) was configured to perform four scans from 2000.00 cm⁻¹ to 1000.00 cm⁻¹ with a resolution of 43.00 cm⁻¹.

InfraSpec™ VFA-IR and GC-FID analysis

Each sample was additionally analyzed using the InfraSpec™ VFA-IR. The ATR crystal well was filled with the biodiesel sample. A spectrum was generated and the peak heights at 1197 cm⁻¹ and 1166 cm⁻¹ were recorded. The calibration curve generated can be used to determine the % conversion to biodiesel for a particular reaction. Figures 8 through 10 show the results for the soybean oil, canola oil, and corn oil, respectively.

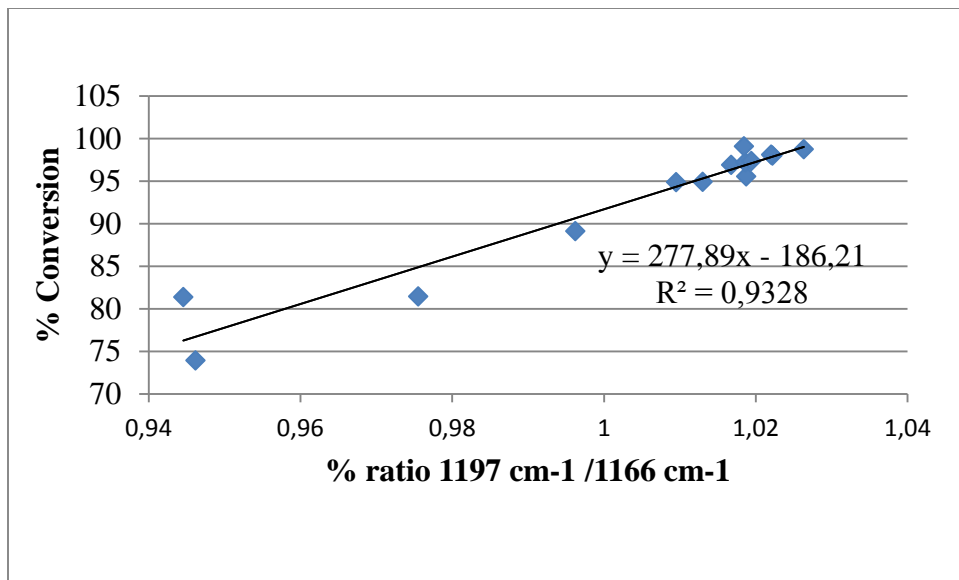


Figure 8: VFA-IR curve for soybean oil

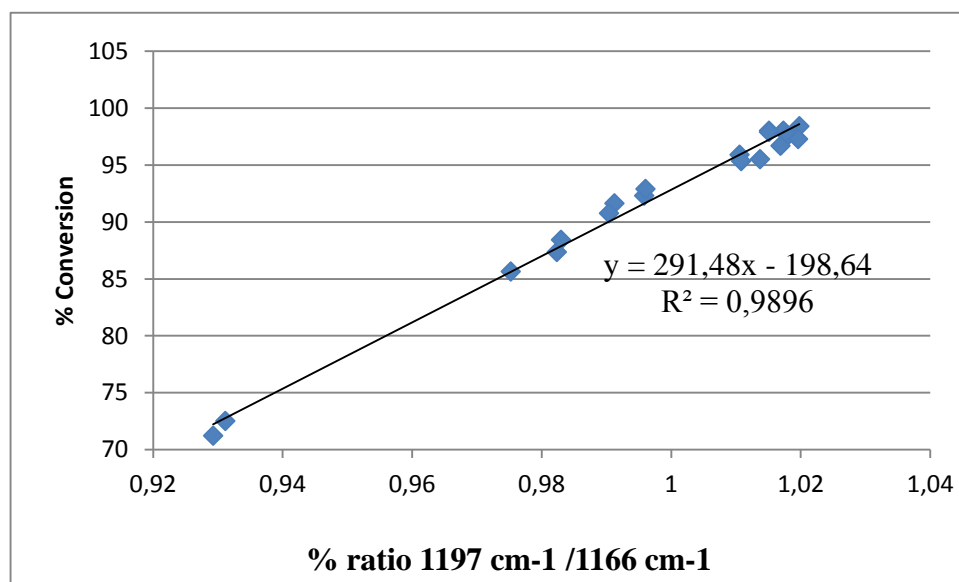


Figure 9: VFA-IR curve for canola oil

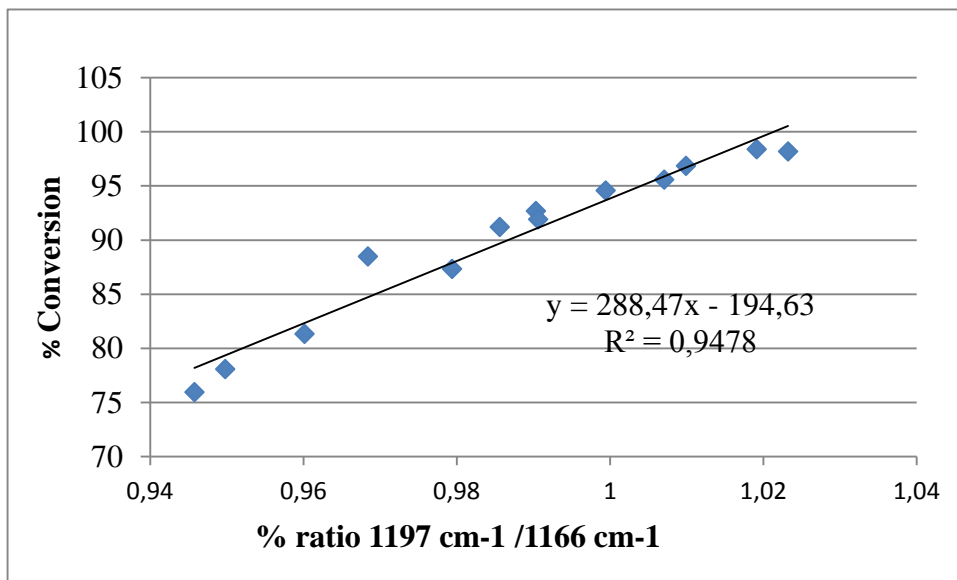


Figure 10: VFA-IR curve for corn oil.

Results and Discussion

Synthesis of biodiesel catalyzed by liquid morpholine

The method described herein was successful using pure canola oil, used vegetable oil, and animal fat. In the case of used vegetable oil the yield was more modest (94%), even though the reaction time was increased to 36h, and an additional quantity of morpholine (2g of morpholine for 30g of oil) was added. Waste vegetable oil has a higher concentration FFAs than virgin oil which under basic conditions can't be converted into biodiesel; the presence of FFA's in waste oil accounts for the lower % conversion.

For the animal fat, the yield was modest (78%). A solid residue containing a mixture of glycerides and methyl esters is recovered at the end of each reaction, indicating incomplete reaction and can be recycled to produce additional liquid biodiesel (45%). Since solid animal fat does not mix as easily with the reagents as the liquid triglycerides do, the rate of the reaction is slower and longer reaction times are required (40h). As a result, an additional quantity of morpholine was added (7g for 30g of animal fat).

In an attempt to improve the yield (20) when using animal fat, mixtures of animal fat with pure canola oil or used vegetable oil were used (see Table II).

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

Reaction No.	Mass of pure canola oil : animal fat	Yield wt %	Mass of used vegetable oil : 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%
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The yield of the reactions containing virgin vegetable oil were slightly higher than those using waste vegetable oil. However, only a modest improvement in the yield was noticed for the mixtures with a low concentration of animal fat.

The use of morpholine as a catalyst allowed the synthesis of cleaner fuel and glycerol, which simplified the purification process (1). The biodiesel was simply purified by filtration over silica gel using hexanes as eluent, followed by evaporation of the hexanes *in vacuo*. Recovery of the morpholine by vacuum distillation was moderately successful (52%). The excess methanol was easily recovered by distillation (97%). With respect to the glycerol by-product, the excess methanol or morpholine can be easily removed by evaporation under vacuum, thus simplifying significantly its purification.

Attempts to use commercially available polymer-bound morpholine as a heterogeneous catalyst for biodiesel synthesis were unsuccessful. This could be due to the fact that the basic nitrogen of the catalyst is the nitrogen atom which is connected to the solid support of the polymer and therefore more sterically hindered rendering it less basic.

Synthesis of biodiesel catalyzed by phase transfer catalyst (CH, TMAH)

Both CH and TMAH were found to be effective catalysts for the production of biodiesel from a variety of virgin and used oil stocks under a wide range of conditions. The reaction conditions for **Expt. 1** were developed in our lab. Despite the high % conversion, the use a large excess of methanol (28 equivalents) will increase the cost of the reaction due to the fact that the methanol distillation will consume significant energy and time. A more cost-effective procedure used an increased amount of catalyst, (**Expt. 2 and 3**) or less methanol (6 equivalents).

Table III. Reactions conditions and results

Expt.	Type of oil	Moles of oil ¹	Moles of MeOH	Catalyst used	Mole % catalyst ²	% Conversion (m/m%) ³	Percent Weight ⁴
1	Pure canola	0.27	7.5	TMAH	1%	99.15%	97%
2	Used vegetable	0.49	2.81	TMAH	4%	74.62%	92%
3	Used vegetable	0.49	2.81	CH	5%	83.20%	91%
4	Pure soybean	0.49	2.81	CH	17%	98.77%	94%
5	Pure vegetable	0.49	2.81	CH	10%	98.05%	89%
6	Pure vegetable	0.49	2.81	KOH	13%	99.2%	86%
7	Pure soybean	0.49	2.81	TMAH & CH	2% & 2%	79.85%	78%
8	Pure soybean	0.49	2.81	TMAH	3%	76.11%	89%
9	Pure soybean	0.49	2.81	CH	5%	85.98%	93%
10	Used vegetable	0.49	2.81	KOH & TMAH	4% & 1%	75.58%	90%
11	Used vegetable	0.49	2.81	KOH	13%	95.99%	99%

1. Moles of oil is approximate since different fatty acids will give different molar masses.
2. Relative to moles of oil.
3. From GC-FID data
4. % by mass biodiesel isolated to mass of oil reacted

A variation of **Expt. 4** was described in the literature (Weidner et al., 2011), and the large amount of catalyst necessary for the reaction raises the cost of the process, despite that the fact that no distillation of the excess methanol is necessary. **Expt. 5** demonstrates that significantly less catalyst can be used since this reaction has a high conversion rate, meeting the ASTM D6584 standard of containing less than 0.24% free and total glycerin while using substantially less catalyst than **Expt. 4**.

Expt. 6 is the standard procedure using KOH and was performed for the purpose of comparison. We can see that using pre-treated used vegetable oil (**Expt. 1 vs. 2**) requires the addition of a larger quantity of catalyst.

By comparing **Expts. 7-9**, we can determine that it is not an advantage to mix the two phase transfer catalysts. **Expt. 10** show that the same amount of KOH and phase transfer catalyst, in this case TMAH, can be used instead.

GC-FID, FT-IR and InfraSpecTM VFA-IR analysis

The analytical method developed based on the ratio of the 1197 cm^{-1} and 1166 cm^{-1} FT-IR peaks vs. GC-FID % conversion works nicely for organic chemistry laboratory experiments, especially since it allows students to analyze the product generated in a chemical reactions. For at-home biodiesel producers, a simplified IR spectrometer is available for field-testing. Despite the fact that the instrument has a lower resolution compared with the FT-IR, a good linear fit can be observed at similar conversions. The highest variance is observed for biodiesel derived from soybean oil. In this case, the InfraSpecTM VFA-IR spectrometer analysis provides a curve with a better linear fit for conversions lower than 95%.

Overall, it appears that this method works well for reactions in which least 70% of the fuel stock was converted to biodiesel.

Conclusion

With respect to the process catalyzed by liquid morpholine, the method described presents the advantage of using a less corrosive catalyst and producing cleaner reaction products. The main disadvantage of this method is the longer reaction times that consume additional energy. The method is successful with a wide variety of fuel stocks. Blending of the animal fat with pure vegetable oil or used vegetable oil in an attempt to produce higher yields, does not result in significant improvement. Recovery of the morpholine

through distillation was demonstrated which would allow for its reuse in subsequent reactions. While the morpholine resins investigated were unsuccessful at catalyzing the reaction, other derivatives of morpholine resins which leave the active site of the catalyst free could possibly be successful as a heterogeneous catalyst. This method, while not practical for large-scale production, can be improved and presents an alternative to the existing methods used in the laboratory.

Concerning the process catalyzed by the phase transfer catalysts, although the high cost of CH and TMAH catalysts compared to potassium hydroxide presently prevents the widespread use of the method described, possible increased demand for these compounds could lower their prices, thus making this method a viable alternative.

Finally with respect to the IR analysis, data was collected in order to obtain a calibration curve for each of the most commonly used oils: soybean, canola, and corn oil using both an FT-IR instrument as well as the InfraSpec™ VFA-IR spectrometer. Based on the parameters of the method for GC-FID analysis, this technique is most accurate for samples with higher conversion rates (>70%) than those with high levels of unconverted oil.

IR analysis can provide a fast and easy method for the determination of the degree of conversion of the vegetable oils to biodiesel. Although not suitable to replace the GC-FID analysis in the determination of fuel compliance with the ASTM standard, it can provide a good method for estimation of the oil conversion in lab and field, prior to a more complex analysis. This analytical method could also be used in a monitoring system to track the progress of the biodiesel preparation.

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Conference on Environmental Pollution and Remediation (ICEPR'13) in July 2013.

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