

The Evaluation of Microwave-Assisted and Conventional Heating in the Acid-Catalyzed Synthesis of Biodiesel from Vegetable Oil

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Abstract: Microwave-assisted and conventional heating methods were evaluated in the transesterification acid-catalyzed reaction of vegetable oil with methanol into the methyl ester using a variety of solid acid catalysts, *p*-toluenesulfonic acid and Nafion NR 50 and the liquid catalyst sulfuric acid. Both heating methods gave excellent yields of product (<85%); however the microwave-assisted synthesis was completed in shorter reaction times, 1 h compared to more than 24 h. The heats of combustion for the biodiesel product were found to be between 38.75 and 42.05kJ/g, similar to literature values; however they are lower than the heat of combustion value for commercial petroleum diesel of 45.52kJ/g.

Keywords: Biodiesel, microwave-assisted, solid catalysis

1. INTRODUCTION

The rapid consumption of petroleum fuels and their increasing prices have come to worldwide attention due to their future environmental and economic.[1] This worldwide ecological and economical movement resulted in the search for alternative fuel sources.[2] Biodiesel is one of the fuels aimed at reducing the usage of petroleum fuels.[3] Unlike petroleum fuels, biodiesel fuels can be nontoxic and biodegradable.[2] Thus they offer lower potential environmental hazards in form of spills during transport compared to the petroleum fuels. Their production and consumption is a closed carbon cycle and CO₂ emissions may be reduced by as much as 78%.[4-5] Biodiesel is readily produced from waste vegetable oil and consists of fatty acids esters of various lengths (**Figure 1**).[6-8]

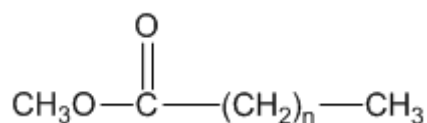


Figure 1. Structure of a fatty acid methyl ester (FAME) in biodiesel where $n = 13-17$ and 0-3 double bonds.

The esters are obtained by the transesterification of various glycerides with alcohols such as methanol or ethanol. The product esters are fatty acids methyl ester (FAME) or fatty acids ethyl esters (FAEE), depending on which alcohol was used in their synthesis.[2] Their synthesis is controlled by the acid and base catalyzed equilibrium shown in **Figure 2**. To increase the formation of the fatty acid ester an excess of the alcohol is used.[9]

In the commercial production of biodiesel two catalytic approaches are used; acid catalysts such as sulfuric acid (H₂SO₄) or *p*-toluenesulfonic acid (PTSA) and base catalysts such as sodium/potassium hydroxide (NaOH/KOH). One of the shortcomings from using alkali base catalysts is these tend to cause equipment deterioration and undesired side reactions whereas acidic reaction conditions do not cause similar equipment deterioration.[2] Also, by using acid catalysts oils with high free-acid and water content can be more easily processed. Waste vegetable oil tends to have higher free-acid content and more water than its virgin counterpart, and therefore acid-catalyzed transesterification is better suited for these reaction conditions.[1] There are several well-known solid-state supported acid catalysts: sulfated zirconia, sulfated Mn/Fe zirconia, Amberlyst-15 (macroporous resin with sulfonic acid functionality), SZ, Nafion NR 50 (perfluorinated resin) and WZ.[7,8,10] Biodiesel has also been synthesized using a non-catalytic approach from supercritical methanol.[11] These reactions were

completed in very short times (2-4 min) and high conversion rates.[12] Such short reaction times can be achieved because methanol and oil exist in a single phase.[11]

The field of microwave assisted synthesis of biodiesel is rapidly expanding. Advantages of using microwave heating over conventional heating are energy conservation and shorter reaction times.[13] A shorter reaction time offers the opportunity to develop a flow system, which could increase efficiency from not having to synthesize biodiesel in multiple individual batches.[14] A flow system was shown to produce high yields of biodiesel using 1:6 oil: alcohol ratio.[14] This ratio of oil to alcohol used far less alcohol than previous reports where ratios as high as 1:30 oil: alcohol were needed.[9,13] Microwave synthesis not only conserves energy by shorter reaction times but also reduces the need for large quantities of alcohol and thus decreases reaction waste.

2. MATERIALS AND METHODS

2.1. Materials and Equipment

All transesterification trials were carried out using commercially available catalysts. Nafion NR 50 (Fluka), sulfuric acid (Fisher), magnesium sulfate (Fisher), DOWEX 50W (Fisher), Amberlyst (Fisher), *p*-toluenesulfonic acid (Aldrich) and methanol (Aldrich) were used as received. A Milestone START microwave labstation was used for the microwave-assisted reactions. The synthesized biodiesel product was identified and characterized by GC-MS spectrometry, FTIR, and ¹H NMR spectroscopy using standard literature methods.[15-18] Percent conversions were determined by ¹H NMR.[18] The GC-MS was an Agilent 5977A Extractor XL MSD with a chemical ionization detector. Split injections with a 100:1 split ratio. The GC was fitted with an HP-5 (5% phenyl: 95% methyl silicone) column (dimensions: 30m x 0.32 mm; flow rate: 1.64mL/min; Injector temperature: 250 °C; Oven temperature: 150 °C; Detector temperature: 290 °C). FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR equipped with a universal ATR using a 9-bounce, liquid sampling top-plate. ¹H NMR spectra were recorded on a JEOL 400 MHz spectrometer in acetone-d₆. A Parr Instruments 1341 Oxygen Bomb Calorimeter with an 1108 Oxygen Combustion Bomb was used to measure the heats of combustion for the synthesized biodiesel and the commercially available petroleum diesel. Temperature changes were measured and recorded using a stainless steel temperature probe connected to a Vernier LabPro interface running LoggerPro v3.6.

2.2. General Procedures

Reaction Solutions: All reactions were done in a 200mL round bottom flask equipped with a teflon coated magnetic stir bar and a reflux condenser. The solution was refluxed by setting the heating temperature to 75 °C. Each reaction solution was prepared using 15mL vegetable oil, 30mmol of acid catalyst, and 25mL of methanol.

Catalyst: The solid-state catalysts were either *p*-toluenesulfonic acid, magnesium oxide, lauric acid, DOWEX 50W-X2, DOWEX 50W-X8, Amberlyst 15 or Nafion NR 50. The liquid catalyst was concentrated sulfuric acid.

2.3. Conventional Heating

The temperature of the heating mantle was set to 75 °C and the solution refluxed with stirring for the specified reaction time (1-180 h).

2.4. Microwave Heating

The microwave heating method was conducted for reaction times varying between 1-24h. In the microwave heating method the reaction solution temperature was set to 75 °C (5 min ramp, 600 W) and heated for the specified reaction time.

2.5. Phase Separation of the Biodiesel and Glycerol

After completion of the reaction, the mixture was allowed to cool and separated into two layers. The top layer, lighter in color, was the biodiesel; and the bottom layer, darker in color, was the glycerol. The methanol was removed *in vacuo* by rotary evaporation. Each layer was characterized by ¹H NMR and FTIR spectroscopy.

2.6. Purification of the Biodiesel

Into the biodiesel fraction 25 g of magnesium sulfate and 100mL of ice-cold methanol were added. The suspension was swirled occasionally and kept on ice for an additional 5 minutes. The solid

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magnesium sulfate was removed by vacuum filtration and the methanol was removed *in vacuo* by rotary evaporation. The biodiesel was neutral to litmus and used as is in the combustion analysis.

2.7. ^1H NMR and FTIR Identification and Characterization of the Biodiesel Product

The formation of the biodiesel was confirmed using ^1H NMR spectroscopy where a characteristic absorbance at 3.50ppm that corresponds to the methoxy protons (CH_3O -) appears.[13,18] The starting vegetable oil possesses characteristic multiplets around 4.35 and 4.15ppm which are absent in the biodiesel product. To determine the percent yield of the biodiesel product, NMR analysis of the product ester peak areas at 3.50ppm were compared of the peak areas of an internal standard (toluene). FTIR spectra displayed the characteristic ester carbonyl absorptions at or near 1745 cm^{-1} indicating that the starting vegetable oil fatty acids have been converted into the fatty acid methyl ester products. [17]

2.8. Heats of Combustion

Temperature was recorded during the calorimetry runs two readings per second over a typical 1000 second run. After calibration of the stainless steel temperature probe and calibration of the bomb calorimeter with benzoic acid, 1.0 g samples of synthesized biodiesel fuel (or commercially purchased diesel fuel) were combusted. A minimum of five trials for each sample were done.

3. RESULTS

3.1. Synthesis

Table 1. Summary of yields of biodiesel in the transesterification reaction of vegetable oil with methanol for *p*-toluenesulfonic acid (PTSA), sulfuric acid (H_2SO_4) and Nafion NR 50 catalysts using conventional and microwave heating methods and their heats of combustion.

Acid	Heating Method	Time, h	% Yield	Heat of Combustion ($\Delta\text{H}_\text{C}^0$) ^a , kJ/g	Energy Used ^b , kJ
PTSA	Microwave	2	90	40.56	1.26e3
PTSA	Conventional	2	7	40.25	1.94e3
PTSA	Conventional	168	89	40.43	1.63e5
H_2SO_4	Microwave	1	92	38.75	6.30e2
H_2SO_4	Conventional	1	5	37.25	9.70e2
H_2SO_4	Microwave	2	87	39.39	1.26e3
H_2SO_4	Conventional	2	12	38.45	1.94e3
H_2SO_4	Microwave	3	90	40.34	1.89e3
H_2SO_4	Conventional	3	21	38.65	2.97e3
H_2SO_4	Microwave	24	90	39.78	1.51e4
H_2SO_4	Conventional	24	88	41.15	2.33e4
Nafion NR 50	Microwave	3	0	---	---
Nafion NR 50	Microwave	24	0	---	---
Nafion NR 50	Conventional	3	20	38.75	6.48e3
Nafion NR 50	Conventional	120	90	42.05	1.17e5
Nafion NR 50	Conventional	168	86	40.95	1.63e5
Diesel Fuel	Commercially available			45.52	

^aReported as the average of 5-6 trails. ^bCalculated as $\text{Watt} \times \text{time (sec)}$. For the conventional heating the mantle was rated at 270 W. The microwave reactor used 600 Watts (maximum) for heating and averaged 175 Watts for the entire reaction. This latter value was used to calculate the energy used.

Eight catalysts were examined using both conventional and microwave heating methods for various reaction times and the results of only the catalysts were successful in producing biodiesel are summarized in **Table 1**. The catalysts magnesium oxide, lauric acid, DOWEX 50W-X2, DOWEX 50W-X8 and Amberlyst 15 did not produce any or insignificant amounts of biodiesel and were considered to be ineffective as catalysts. Nafion NR 50 produced biodiesel in 90% yield after 120

hours of conventional heating. Heating for 168 hours showed approximately the same percent yield, 86%, as 120 hours. Interestingly, no biodiesel was produced using this catalyst even after 24 hours of microwave heating. The catalyst *p*-toluenesulfonic acid successfully produced biodiesel by both conventional and microwave heating in good yields. Conventional heating for 168 hours gave an 89% yield compared to a 90% yield after 2 hours of microwave heating. Sulfuric acid gave an 88% yield after 24 hours of conventional heating and 90% yield by microwave heating for 1 hour with no increase for longer reaction times. This catalyst gave comparable yields for both heating methods. However, the use of microwave heating required significantly reduced reaction times to obtain approximately the same yield (1 h vs. 24 h) and much less energy consumption (6.30e2 vs. 2.33e4 kJ).

3.2. Neutralization

Biodiesel is acidic in nature and neutralization is necessary for commercial use. Several purification methods were explored: water washes, aqueous sodium chloride washes and the addition of magnesium sulfate with cold methanol. The latter was found to be the most convenient method to neutralize the acidic biodiesel. It produced the fewest emulsions and thus took less time to isolate the biodiesel layer and separated the greatest quantity of biodiesel from the other layer primarily consisting of methanol and glycerol. This method was used for all synthesis biodiesel samples.

3.3. Combustion

Bomb calorimetry is a destructive technique that measures the total amount of energy released upon combustion of a sample. This technique is a complementary method to ^1H NMR to determine the purity of a biodiesel sample. The process of combustion simulates its effectiveness in an engine. It was of interest to see if the reaction conditions affect the overall quality of produced fuel. The transesterification reaction is controlled by the acid or base catalyzed equilibrium shown in **Figure 2**. We attempted to quantify the difference in quality of the biodiesel products and as well as compare to a commercially available petroleum diesel sample. Calorimetric combustion studies of biodiesel were found to be between 38.75-42.05 kJ/g and are similar to those reported in the literature (Lang et al., 2001).[15] These values are 8-15% lower than the heat of combustion for a commercial petroleum diesel sample (45.52 kJ/g).

Comparison of conventional and microwave heating showed that usually the two heating methods yielded similar combustion values when the same catalyst was used. However, conventional heating reactions took significantly longer than for the microwave reaction to obtain approximately the same yield.

4. DISCUSSION

The solid-state catalysts magnesium oxide, lauric acid, DOWEX 50W-X2, DOWEX 50W-X8 and Amberlyst 15 gave none or low yields of biodiesel are considered to be ineffective as catalysts. The solid-state catalyst *p*-toluenesulfonic acid produced biodiesel in approximately 90% yield in both conventional and microwave heating reactions. However, the reaction times were dramatically different for heating methods, 120 hours for conventional heating compared to 2 hours for microwave heating. Also, the amount of power used for the microwave method was more than 100-fold less than for conventional heating, 1.26e3 kJ to 1.63e5 kJ. The liquid catalyst sulfuric acid gave about between 88-90% yield, again by both conventional and microwave heating. Again conventional heating took significantly longer than microwave heating to obtain these percent yields. Longer reaction times for both methods did not increase biodiesel yields and 90% conversion seems to be the maximum for the equilibrium reaction shown in **Figure 2**. These yields are similar to the results reported in the literature.[13,14] The solid catalyst Nafion NR 50 was found to be unreactive using microwave heating, most likely due to catalyst degradation of the polymer backbone.[19-21] Curiously, yields of approximately 90% were obtained using conventional heating for this catalyst.

Calorimetric studies of biodiesel gave combustion values of 40.25-40.56 kJ/g for *p*-toluenesulfonic acid and 37.25-41.15 kJ/g for sulfuric acid and 38.75-42.05 kJ/g for Nafion NR 50; comparable to literature values.[15,18] All biodiesel samples gave slightly lower heats of combustion than the commercial petroleum diesel fuel (45.52 kJ/g). However, the method of microwave heating using the solid catalyst *p*-toluenesulfonic acid produced the highest yield of biodiesel in the shortest time and is considered to be the most efficient method under our conditions.

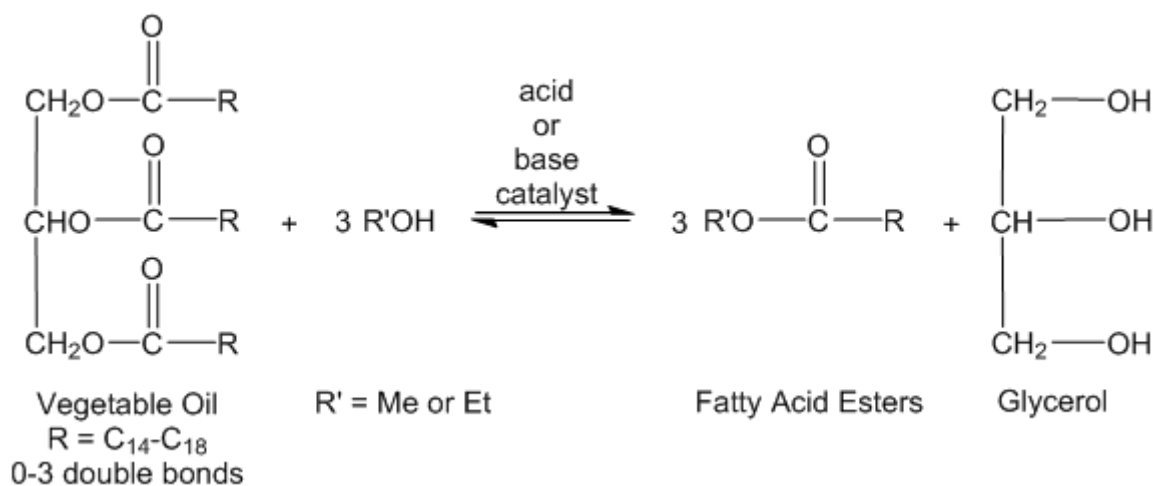


Figure2. General synthesis of biodiesel under acidic or basic conditions.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation (CHE-0643709).

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