

Comparison of Various Feedstocks for the Microwave-Assisted Synthesis of Biodiesel

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Abstract The microwave-assisted acid catalyzed synthesis of biodiesel from various feedstocks are reported. The feedstocks consist of vegetable, canola, olive, avocado, corn, cottonseed and soybean oils and also were compared to a commercial biodiesel sample that was prepared from a mixture of varying oils by GC-MS. All oils gave biodiesel in excellent yields (<85%). Combustion analysis gave heats of combustion between 40.75 to 43.45 kJ/g, similar to literature values.

Keywords Microwave-Assisted Synthesis, Biodiesel

1. Introduction

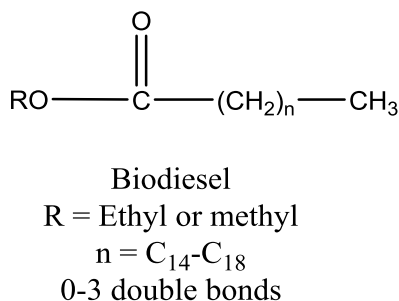


Figure 1. Structure of biodiesel

The rapid consumption of petroleum fuels and their increasing prices have come to worldwide attention. Due to their future environmental and economic impacts. [1] This worldwide ecological and economical movement has resulted in the search for alternative fuel sources. [2] Biodiesel is one potential fuel aimed at reducing the usage of petroleum fuels. [3] Unlike petroleum fuels, biodiesel fuels can be nontoxic and biodegradable. [2]. Their production and consumption is a closed carbon cycle and CO₂ emissions may be reduced by as much as 78%. [4-5] Biodiesel is commonly produced from waste vegetable oil and consists of fatty acid esters of various lengths (**Figure 1**), however other oils may be substituted in place of vegetable oil. [6-8]

The esters are synthesized in a transesterification reaction between various glycerides and 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 usually used. [9]

In the commercial production of biodiesel two catalytic approaches are used; acid catalysts such as sulfuric acid or *p*-toluenesulfonic acid and base catalysts such as sodium/potassium hydroxide. 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] In this work we used *p*-toluenesulfonic acid as the acid catalyst in all reactions. We chose this catalyst for its ease of use and high conversion (>95%) in the transesterification reaction. Some advantages of using microwave heating over conventional heating include energy conservation and shorter reaction times. [10] We have previously shown that the combination of *p*-toluenesulfonic acid and microwave heating produced biodiesel from vegetable oil in high yields. [11]

2. Materials and Methods

Materials and Equipment

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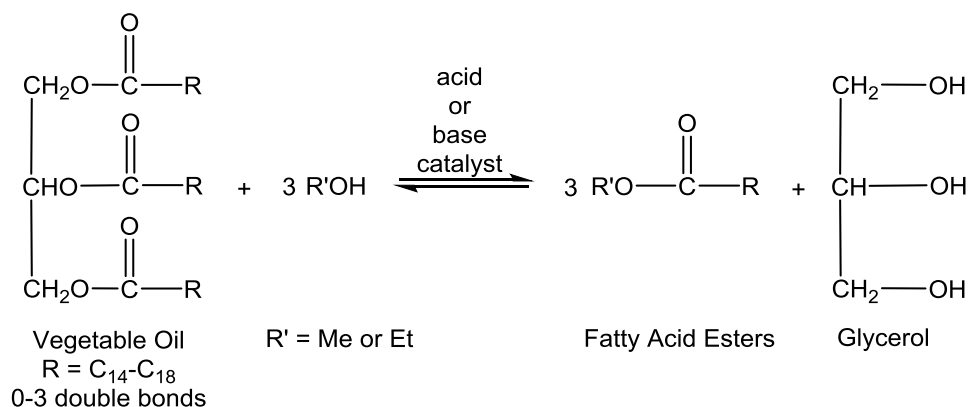


Figure 2. Reaction scheme for the synthesis of biodiesel from vegetable oil

All transesterification trials were carried out using *p*-toluenesulfonic acid (Fisher) and methanol (Fisher) and were used as received. A CEM Mars 6 microwave reactor was used for the microwave-assisted reactions. The synthesized biodiesel product was identified and characterized by GC-MS using standard literature methods. [12-15] Percent conversions were determined by GC-MS. [15] 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: 30 m x 0.32 mm; flow rate: 1.64 mL/min; Injector temperature: 250°C; Oven temperature: 150°C; Detector temperature: 290°C). 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 v3.10.1.

General Procedures

Reaction Solutions: All reactions were done in a 200 mL 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 65°C for 1 h. Each reaction solution was prepared using 15 mL oil, 5 g (30 mmol) of *p*-toluenesulfonic acid, and 25 mL of methanol.

Phase Separation of the Biodiesel and Glycerol

After completion of the reaction, the mixture was allowed to cool, gravity filtered through filter paper to remove the acid catalyst 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 biodiesel layer, which also contained some unreacted methanol, was collected and the methanol was removed *in vacuo* by rotary evaporation.

Purification of the Biodiesel

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

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

Heats of Combustion

The temperature was recorded during the calorimetry runs as 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 and Discussion

Bomb calorimetry was used 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 40.75 to 43.45 kJ/g (Table 1) and are similar to those reported in the literature. [12] These values are 5-10% lower than the heat of combustion for a commercial petroleum diesel sample (45.52 kJ/g). All oils gave a high % conversion, the lowest being for avocado oil (87%) and the highest for vegetable oil (97%).

Table 1. Summary of % conversion and combustion analysis for the various oils to biodiesel

Oil	% Conversion	Heat of Combustion (ΔH_c°), kJ/g
Avocado	87	40.75
Canola	91	41.50
Corn	92	42.23
Cottonseed	94	41.18
Olive	88	43.45
Soybean	90	42.95
Vegetable	97	42.25
Commercial	---	45.52

Table 2 lists the chemical composition of the biodiesel fractions produced from the various oils. They are

determined as percentages of the methyl ester product as determined by ratio from the integration of the peak areas in GC-MS. The three major components for all oils, except cottonseed, are methyl palmitate, methyl linoleate and methyl oleate. These methyl esters are derived from their

corresponding carboxylic acids after hydrolysis of the triglyceride. These compounds are what are listed as major components, either on their labels or from the USDA database.

Table 2. Summary of chemical composition of the biodiesel fractions from the various oils. Reported as percentages of the methyl ester product. [11,12]

Compound	Avocado	Canola	Corn	Cottonseed	Olive	Soybean	Vegetable
methyl hexadecanoate ^a	35.0	25.0	36.8	55.0	44.5	36.0	37.0
methyl (9Z,12Z)-9,12-octadecadienoate ^b	17.8	29.0	46.6	45.0	11.7	34.4	37.5
methyl (9Z)-9-octadecenoate ^c	41.5	39.1	16.6		32.5	14.9	17.8
methyl (9Z,12Z, 15Z)-9,12,15-octadecatrienoate ^d						0.9	
methyl octadecanoate ^e	5.7	6.9			11.3	13.8	7.7

^amethyl palmitate. ^bmethyl linoleate. ^cmethyl oleate. ^dmethyl linolenate. ^emethyl stearate.

4. Conclusions

We report the acid catalyzed microwave-assisted synthesis of biodiesel from various oils. We found no significant difference in the combustion analysis between the oils, but all were lower than that for commercial diesel. In the chemical composition of the different biodiesel products showed that all the oils contained the same three major components, with the exception of cottonseed oil. The source of oil for the production of biodiesel is shown to be wide ranging and not limited to exclusively vegetable oil.

ACKNOWLEDGEMENTS

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