

Batch and Continuous-Flow Preparation of Biodiesel Derived from Butanol and Facilitated by Microwave Heating

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The batch and continuous-flow preparation of biodiesel derived from vegetable oil and 1-butanol using a commercially available scientific microwave apparatus is reported. The methodology allows for the reaction to be run under atmospheric conditions and, in continuous-flow mode, can be performed at flow rates up to 2.3 L/min using a 4 L reaction vessel. It can be utilized with new or used vegetable oil with 1-butanol and a 1:6 molar ratio of oil to alcohol. Sulfuric acid or potassium hydroxide can be used as the catalyst.

Introduction

Research focused around the manufacture of biodiesels is increasing at a very fast rate.¹ This is driven, at least in part, by the fact that biodiesels are an immediately applicable replacement for diesel fuel and can also be used as heating oil.^{2,3} Other alternative energy technologies such as fuel cells,^{4,5} solar energy,⁶ and wind power⁷ have exciting potential but are still developing and costs are high in many cases.⁸ Biodiesel is the product of a transesterification reaction between vegetable oils or animal fats and an alcohol using an acid or base catalyst.^{9–12} Looking in the literature, the alcohol used in the reaction is almost always methanol and the word biodiesel is synonymous

with methyl ester products. Methyl esters are the most popular esters for a number of reasons, perhaps the most influential being the price point of methanol compared to other alcohols. Also, from a chemistry perspective, the transesterification between vegetable oil and methanol is faster than with other aliphatic alcohols. However, while vegetable oil is a biorenewable resource, methanol is predominantly not. It is commonly produced synthetically from natural gas by a multistep process. In 2006, DuPont and BP announced that they had created a partnership directed toward the preparation of biobutanol—1-butanol generated from the same agricultural feedstocks as ethanol (i.e., corn, wheat, sugar beet, sorghum, cassava, and sugarcane)—with the aim of producing it by the end of 2007.^{13–15} One of their major motivations for this comes from the fact that it can be used as an additive for conventional gasoline. It has an energy content closer to that of gasoline than ethanol, so consumers face less of a compromise on fuel economy and also can be blended at higher concentrations than bioethanol for use in standard vehicle engines. However, we believe that this is only one application of biobutanol and its addition to gasoline only sugars the pill rather than opening up avenues for a totally biorenewable fuel. Spurred by the development of biobutanol, we wanted to develop a process for the rapid, easy preparation of biodiesel derived from vegetable oil and butanol, both of which would now be biorenewable feedstocks and

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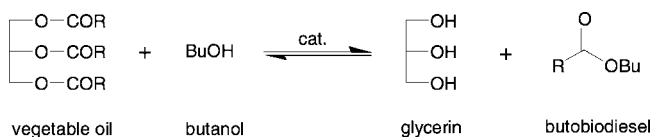
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Scheme 1



which, for the purposes of clarification, we term in this paper “butobiodiesel” (Scheme 1).

There have been previous efforts directed at preparing biodiesels using 1-butanol as the alcohol component. However, the relative rate of reaction of butanol as compared to methanol makes it a more difficult prospect. We have recently reported the use of microwave heating as a tool for generating fatty acid methyl esters from vegetable oil and methanol^{16,17} and wanted to see if we could expand this to the preparation of the corresponding butyl esters. Microwave heating offers a unique advantage over conventional heating methodologies. Conventional thermal heating relies on conduction currents within the sample to provide an overall rise in temperature. By definition, this is a relatively slow process. Microwave irradiation allows for direct transfer of energy into the sample and it is possible to accomplish chemical reactions in seconds or minutes, instead of the hours or days it can take using conventional heating.¹⁸ We wanted to see if the issues associated with the slow transesterification reaction between butanol and vegetable oil could be overcome by using microwave heating. Our results are presented here.

Results and Discussion

To initiate our study, we decided to attempt the preparation of butobiodiesel using the same optimal methodology we developed for the generation of biodiesel. Our conditions for batch processing required heating a mixture of vegetable oil and methanol (~1:6 stoichiometric ratio) containing potassium hydroxide (1 wt %) to 50 °C and holding it at this temperature for 1 min using an open round-bottom flask. This gave us a quantitative conversion to biodiesel. It is not necessary to heat the reaction mixture to above this temperature. Using 1 L vegetable oil, we performed the same reaction but using 1-butanol in the place of methanol with the aim of forming butobiodiesel. While a range of analytical methods have been developed for analysts of biodiesel, this is not the case for butobiodiesel. Therefore, we had to find a suitable technique that would allow us to obtain conversion values. We decided to use ¹H NMR (nuclear magnetic resonance) spectroscopy since that has been shown to be a reliable alternative to GC (gas chromatography) as a method for analyzing total conversion in the case of biodiesel (although it does not allow for more detailed analysis of the constituent parts).^{19–23} Quantification

Table 1. Base-Catalyzed Preparation of Butobiodiesel^a

entry	reaction conditions ^b	conversion (%)
1	oil:butanol ratio of 1:6; 1 wt % KOH; 50 °C for 1 min	80
2	oil:butanol ratio of 1:3 ; 1 wt % KOH; 50 °C for 1 min	63
3	oil:butanol ratio of 1:6; 1 wt % KOH; 50 °C for 15 min	86
4	oil:butanol ratio of 1:6; 1 wt % KOH; 120 °C for 1 min	93

^a Reactions were performed in a 3 L reaction vessel using 1 L of vegetable oil. The reaction mixtures were stirred using a magnetic stir bar and were heated to the target temperature using a microwave power of 1600 W. Once at temperature, the reaction mixture was held for the time noted. ^b Conditions changed from entry 1 are highlighted in bold.

of conversion in the case of biodiesel can be made by building an analytical curve or by using an internal standard. However, the simplest method is by applying a simple equation, relating the normalized integral of the signal due to the α -acyl methylenic protons in soybean oil plus alkyl esters (2.2–2.4 ppm) and the integral of the singlet due to the protons on the OCH₃ group in biodiesel (3.6–3.7 ppm). When moving from methanol to ethanol a problem arises due to a superimposition of the glyceryl methylenic hydrogens in soybean oil and the -OCH₂ group in the ethyl ester biodiesel product. While this problem has been overcome by a number of methods,²⁴ it concerned us when thinking about quantifying our conversion with butanol by applying NMR spectroscopy. However, fortunately, in the case of butobiodiesel, the triplet due to the -OCH₂ group in the butyl ester chain is centered at 4.05 ppm and the signals due to the glyceryl methylenic hydrogens in soybean oil start at 4.10 ppm. Using a 300 MHz spectrometer, it is possible to integrate the butyl ester triplet without incorporating part of the oil signal and so the same equation can be used for butobiodiesel as for regular biodiesel, the only change being the normalization factor. For methanol, the integral of the signal due to the protons on the OCH₃ group equates to three protons and that for the α -acyl methylenic protons in soybean oil plus alkyl esters corresponds to two protons. Thus, we need to multiply the integral value for the -OCH₃ group by 2 and the integral value of the α -acyl methylenic protons by 3 to normalize them. In the case of *n*-butanol, since the integrals of the signals for the -OCH₂ group in the butyl ester chain and the α -acyl methylenic protons both equate to two protons, we do not need to apply this same normalization step. By using this method, we found we had obtained an 80% conversion to butobiodiesel in our initial reaction (Table 1, entry 1). With this result in hand, we wanted to probe the effect of varying the reaction parameters. Not unexpectedly, reducing the oil to butanol ratio from 1:6 to 1:3 had a deleterious effect on the outcome of the reaction with a 63% conversion to butobiodiesel being obtained (Table 1, entry 2). Working with an oil to butanol ratio of 1:6 but extending the reaction time from 1 to 15 min had only a marginal effect on the product conversion (Table 1, entry 3). Increasing the temperature, however, did lead to an increase in conversion even at the short 1 min reaction time. Performing the reaction at 120 °C gave a 93% conversion to butobiodiesel. With operationally viable conditions in hand, we wanted to turn our attention to

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addressing a further challenge, namely developing an acid-catalyzed analog of the reaction.^{12,25,26}

In the biodiesel industry, it is well-known that base-catalyzed processes suffer from some serious limitations that can translate into high production costs for biodiesel. Feedstock specifications are a significant issue; in particular, the free fatty acid (FFA) content generally must not exceed 0.5 wt %. If it does, soap formation can be a problem, this leading to issues inside the reactor and greatly increasing the costs associated with product separation. In addition, the oil, alcohol, and catalyst must be essentially anhydrous. This is required because any water in the reaction mixture will hydrolyze the fatty acid alkyl esters to free fatty acids and thus again generate soap. As a consequence, biodiesel manufactured using a base-catalyzed route generally requires refined vegetable oils and other less expensive sources of triglyceride feedstocks require pretreatment thus adding to costs. An alternative is to use an acid catalyst. However, there are disadvantages here too. The base-catalyzed preparation of biodiesel is known to be significantly faster than that using an acid catalyst. This means that the acid-catalyzed route can be significantly more time consuming. It was our objective to see if the reaction rate of the acid-catalyzed route could be accelerated using microwave irradiation, thus expanding the range of possible feedstocks that could be processed. To start this work we decided to focus on the acid-catalyzed preparation of fatty acid methyl esters (i.e., biodiesel). We decided to initiate these studies by working on a small scale. Starting with 2 g of vegetable oil and performing the reaction at 50 °C using a 1:6 oil to methanol ratio and 1 wt % sulfuric acid yielded none of the desired methyl ester products after 10 min (Table 2, entry 1). Increasing the catalyst loading to 5 wt % and then the oil to methanol ratio to 1:30 still did not lead to product conversion (Table 2, entries 2 and 3). However, these changes, together with increasing the temperature to 150 °C and performing the reaction in a sealed tube led to promising results, a 57% conversion being obtained. Extending the reaction time to 15 min led to an increase in conversion to 93% (Table 2, entry 4). From these initial results, it seemed clear that, when using an acid catalyst, elevated temperatures were required and, as a result, sealed vessel processing was essential. We then moved to the acid-catalyzed preparation of butobiodiesel. When using the optimized conditions for the biodiesel experiments, still working in a sealed tube but replacing methanol by butanol, significant decomposition was observed (Table 2, entry 5). Lowering of the reaction temperature to 100 °C and the oil:butanol ratio to 1:6, we obtained an 80% conversion to butobiodiesel (Table 2, entry 6). We wanted to develop a process that worked at atmospheric pressure, mainly for operational reasons and because one of our aims was to move to continuous-flow processing. Performing the reaction at 100 °C in an open vessel using butanol as a reagent would be feasible unlike the case of methanol where its boiling point is 65 °C. Working in an open vessel and starting with 1 L of vegetable oil, we obtained an almost identical conversion to butobiodiesel as in the sealed tube if we performed the reaction for 15 min (Table 2, entry 7). However, we noticed the onset of decomposition, a very dark brown coloration being observed. We wanted to reduce the reaction time as much as possible. By increasing the temperature to 120 °C, we could reduce the time from 15 to 2 min and obtain an excellent conversion to butobiodiesel

Table 2. Acid-Catalyzed Preparation of Biodiesel and Butobiodiesel^a

entry	reaction conditions ^b	conversion (%)
1	oil:methanol ratio of 1:6; 1 wt % H ₂ SO ₄ ; 50 °C for 10 min, sealed vessel	0
2	oil:methanol ratio of 1:6; 5 wt % H₂SO₄ ; 50 °C for 10 min, sealed vessel	0
3	oil:methanol ratio of 1:30; 5 wt % H₂SO₄ ; 50 °C for 10 min, sealed vessel	0
4	oil:methanol ratio of 1:30; 5 wt % H₂SO₄ ; 150 °C for 10 min, sealed vessel	93
5	oil:butanol ratio of 1:30; 5 wt % H ₂ SO ₄ ; 150 °C for 10 min, sealed vessel	decomposition
6	oil:butanol ratio of 1:6; 5 wt % H₂SO₄ ; 100 °C for 10 min, sealed vessel	80
7	oil:butanol ratio of 1:6; 5 wt % H ₂ SO ₄ ; 100 °C for 15 min, open vessel	76
8	oil:butanol ratio of 1:6; 5 wt % H₂SO₄ ; 120 °C for 2 min , open vessel	93
9	oil:butanol ratio of 1:6; 1 wt % H₂SO₄ ; 120 °C for 2 min , open vessel	25
10	oil:butanol ratio of 1:6; 2 wt % H₂SO₄ ; 120 °C for 2 min , open vessel	33
11	oil:butanol ratio of 1:6; 3 wt % H₂SO₄ ; 120 °C for 2 min , open vessel	52
12	oil:butanol ratio of 1:6; 4 wt % H₂SO₄ ; 120 °C for 2 min , open vessel	66
13	oil:butanol ratio of 1:3; 5 wt % H₂SO₄ ; 120 °C for 2 min , open vessel	59
14	oil:butanol ratio of 1:4.5; 5 wt % H₂SO₄ ; 120 °C for 2 min , open vessel	62

^a Reactions were performed either in a 3 L reaction vessel using 1 L of vegetable oil or in a sealed tube of 10 mL capacity using 2 g of oil. The reaction mixtures were stirred using a magnetic stir bar and were heated to the target temperature using the maximum microwave power. Once at temperature, the reaction mixture was held for the time noted.

^b Conditions changed from entries 1 (in the case of methanol) and 5 (in the case of butanol) are highlighted in bold.

(Table 2, entry 8). Decreasing either the catalyst loading or the oil to butanol ratio had a deleterious effect on the reaction (Table 2, entries 9–14). Thus, our optimal conditions were a vegetable oil:butanol ratio of 1:6 and 5 wt % sulfuric acid, heating the reaction mixture to 120 °C in an open vessel, and holding at this temperature for 2 min.

To probe the energy consumption during the course of the reaction, we monitored the power consumption using a power meter. As with our biodiesel experiments we found that, with the microwave running with a continuous output of 1600 W, approximately 2500 W power was being drawn. When preparing biodiesel we undertook a series of calculations to determine the energy efficiency of the process. For the conventional process we used figures from the joint US Department of Agriculture and US Department of Energy 1998 study into the life cycle inventory of biodiesel and petroleum diesel for use in an urban bus.²⁷ Their assumptions for reactor conditions were based on a review of the literature. Our microwave process compared favorably with the conventional method. By using a power meter, for our process of preparing butobiodiesel we found that with the microwave running with a continuous output of 1600 W, approximately 2500 W power was being drawn. This is comparable to the power used in the preparation of biodiesel. However, the flow rate is significantly different. For the biodiesel reactions we were able to flow at 7.2 L/min as opposed to the 2.3 L/min in the preparation of butobiodiesel. Also, because of its increased molecular weight, the volume of butanol required is higher than that of methanol for the reaction. This reduces the relative volume of biodiesel prepared

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per unit time. This would suggest that the process to generate butobiodiesel is not as energy efficient as that to generate biodiesel. However, there are no figures available for the conventional preparation of butobiodiesel to perform a complete comparison.

Putting the work in context, in addition to our previous reports for the preparation of biodiesel using microwave heating, there has been a report of the use of a domestic microwave for the reaction between methanol and seed oils in a batch process.²⁸ A scientific microwave apparatus has been used for transesterification of triglycerides to fatty acid methyl esters and involves use of 10 wt % of a zeolite catalyst, heating to 170 °C for 2 h in a sealed vessel with only moderate conversions being obtained.²⁹ A small scale batch and stop-flow methodology has recently been reported using a scientific microwave unit. The reaction is performed using methyl *tert*-butyl ether (MTBE) as a solvent.³⁰ After submission of this paper, a report of the preparation of biodiesel from butanol under supercritical conditions using microwave heating appeared.³¹ This method requires the use of silicon carbide passive heating elements and optimal conditions involve heating at 310 °C for 4 h. The method allows for processing 10 mL of oil in a sealed vessel. Three patent applications have been filed on the use of microwave heating in biofuel manufacture. All three use specially designed large microwave apparatus rather than readily available commercial scientific models.^{32–34}

Summary

In summary, we report here a methodology for the preparation of biodiesel derived from vegetable oil and 1-butanol, for convenience termed here as butobiodiesel. The method involves the use of microwave heating. Both batch and continuous flow processing have been studied as well as base and acid catalysis of the reaction.

Experimental Section

General. Reactions at atmospheric pressure were performed in either a 50 mL or a 3 L round-bottom flask or a 4 L flow cell under atmospheric pressure in the presence of air. Sealed vessel reactions were performed in sealed 10 mL tubes. ¹H NMR spectra were recorded at 293 K on a 300 or 400 MHz spectrometer (Bruker Avance); chemical shifts being referenced to the residual peaks of CHCl₃ in CDCl₃ (ppm). Laboratory-grade methanol, butanol, sulfuric acid, and potassium hydroxide were used as purchased without any further purification. New (soybean) oil was purchased from a local grocery store. Used vegetable oil was collected from local restaurants. Reactions were performed using a commercially available microwave apparatus. Small scale reactions were performed in a CEM Discover. The machine consists of a continuous focused microwave power delivery system with operator selectable power output from 0 to 300 W. The temperature of the contents of the vessels was monitored using an IR sensor located underneath the reaction vessel. The contents of the vessel were stirred by means of a rotating magnetic plate located below the floor of the microwave cavity and a Teflon-coated magnetic stir bar in the vessel. In the case of sealed vessels, the tubes were sealed with a septum and the pressure monitored directly using a load cell. Temperature, pressure, and power profiles were monitored using commercially available software provided by the microwave

manufacturer. Larger scale batch experiments and continuous-flow runs were performed in a CEM MARS unit. The machine consists of a continuous microwave power delivery system with operator selectable power output from 0 to 1600 W. Reactions were performed in either a 3 L round-bottom flask or 4 L flow-through reactor vessel. For continuous-flow experiments a Teflon inlet tube (9.53 mm i.d.) was placed 2.5 cm from the bottom of the reactor and a Teflon outlet tube (9.53 mm i.d.) placed 2.5 cm from the top of the reactor. The temperature of the contents of the vessel was monitored using a fiber optic probe inserted directly into the reaction mixture by means of a Teflon thermowell. The contents of the vessel were stirred by means of a rotating magnetic plate located below the floor of the microwave cavity and a Teflon-coated magnetic stir bar in the reactor vessel. Variac devices were used both for monitoring power consumption of the microwave unit (built in-house using a variac from Superior Electric, monitoring power output using a standard watt meter, all installed inside a 19 in. rack panel cabinet) and varying pump speed (Staco Energy Products Co., 120 V input: 50/60 Hz, 120/140 V output: 10 A, 1.4 kVA).

Typical Batch Reaction Procedure. To a 3 L two-neck round-bottomed flask equipped with a stirring bar were added soybean oil (1 kg) and a solution of sulfuric acid (5 wt %, 27 mL) in butanol (630 mL). The reaction mixture was placed into the microwave cavity, an immersion well placed into one of the necks of the flask and a glass connector (linking the flask inside the cavity with a reflux condenser outside the cavity) into the other. A fiber optic probe was placed into the immersion well. The reaction mixture was heated from room temperature to 120 °C using an initial microwave power of 1600 W and then held at this temperature for 2 min. Upon cooling to room temperature the reaction vessel was removed from the microwave cavity and the contents were decanted into a settling vessel. The material was washed with water and then brine. The extent of transesterification of soybean oil was determined by solution ¹H NMR spectroscopy. The relevant signals chosen for integration were those of the -OCH₂ group in the butyl ester chain and those of the α -methylene protons present in all triglyceride derivatives (2.3 ppm, triplet) of the soybean oil. The conversion was calculated directly from the integrated areas of these signals.

Continuous-Flow Reaction Procedure. A stock solution of 1-butanol (20 L) and sulfuric acid (660 mL) was prepared. To a 50 L polypropylene container equipped with an overhead paddle stirrer were added unused vegetable oil (10 L) and butanol/sulfuric acid stock solution (6.75 L). A portion of this feedstock mixture was then pumped into the 4 L reactor until full. The flow was stopped and microwave power of 1600 W used to heat the contents of the vessel from room temperature to 120 °C, this taking approximately 3 min. The mixture was then held at this temperature for 2 min before the feedstock flow was restarted and material passed through the reactor at a rate of 2.3 L/min, during which a microwave power of 1600 W was used to heat the contents of the vessel. As the holding vessel was reaching empty, 10 L of used oil (FFA 1.4) and a further 6.25 L of butanol/sulfuric acid stock solution was added and processed without stopping the flow. Again, as the holding vessel was reaching empty, 10 L of used oil (FFA 6.5) and a further 6.25 L of butanol/sulfuric acid stock solution was added and processed without stopping the flow. After processing this, the pump was stopped. Throughout the run, the product stream was collected in a second 50 L polypropylene container and aliquots were collected from the stream over time. Each of these aliquots were placed into glass vessels and allowed to settle. After careful washing with water, the extent of transesterification was determined by solution ¹H NMR spectroscopy.

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