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Continuous-Flow Preparation of Biodiesel Using Microwave Heating

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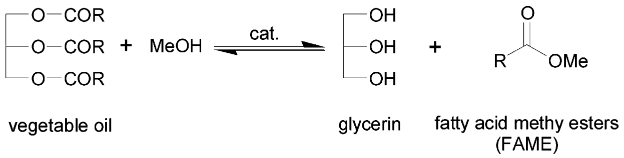
The continuous-flow preparation of biodiesel using a commercially available scientific microwave apparatus offers a fast, easy route to this valuable biofuel. The methodology allows for the reaction to be run under atmospheric conditions and performed at flow rates of up to 7.2 L/min using a 4 L reaction vessel. It can be utilized with new or used vegetable oil with methanol and a 1:6 molar ratio of oil/alcohol. Energy consumption calculations suggest that the continuous-flow microwave methodology for the transesterification reaction is more energy-efficient than using a conventional heated apparatus.

Introduction

There is increasing interest in developing alternative energy resources. An immediately applicable option is replacement of diesel fuel by biodiesel, which consists of the simple alkyl esters of fatty acids.[1,2] With little modification, diesel engine vehicles can use biodiesel fuels. They can also be used as heating oils. Biodiesels are biodegradable and nontoxic and have lower CO and hydrocarbon emissions than petroleum-based diesel when combusted.[3,4] Conversely, they do present other technical challenges, such as low cloud points and elevated NO_x emissions.[5] Biodiesel is generally made from vegetable oils or animal fats by transesterification with methanol using an acid or base catalyst (Scheme 1).[6,7] The products of the reaction are fatty acid methyl esters (FAMEs), which is the biodiesel, and glycerin, which also has numerous applications.[8] The most commonly used catalysts in transesterification reactions are NaOH, KOH, and H_2SO_4, although an area of recent research has been the development of solid acid catalysts for the reaction.[9] The starting oil and methanol are generally heated and stirred with the catalyst. In the case of the basic catalysts, the base is first dissolved in the methanol prior to the addition. With solid acid catalysts, the reagents can be passed over a catalyst bed. Both batch and continuous-flow technologies have been used to scale up the reaction.[10] Alongside the advances in chemistry, there have been assessments of the economics of biodiesel production.[11] Transesterification is not the only route to production of FAMEs. An alternative approach is to hydrolyze all triglycerides to free fatty acids and then directly esterify these fatty acids with methanol. However, transesterification is the process of choice in the majority, if not all, of the commercial biodiesel production facilities that have come on line.

Scheme 1



Recently, we reported the use of microwave heating as a fast, simple way to prepare biodiesel in a batch mode.[12] Because the preparation of FAME from oil and methanol is a simple

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transesterification,[13] we wanted to see whether, by using a commercially available scientific microwave apparatus, it was possible to prepare biodiesel rapidly and in good conversions. Using microwave heating for preparative chemistry, it is often possible to accelerate the rate of reactions and increase selectivity.[14,15] Our methodology allows for the preparation of biodiesel under atmospheric conditions, with the reaction being completed in a matter of a few minutes and performed on batch scales up to 3 kg of oil at a time. The procedure can be utilized with new or used vegetable oil and methanol or ethanol. The 1:6 molar ratio of oil/methanol used is lower than many reports when applying conventional heating, where a ratio from 1:9 up to 1:30 is more common. We now present here the extension of the microwave-heating methodology to continuous-flow processing.

Experimental Section

General Procedures. All reactions were performed under atmospheric pressure in the presence of air. ^1H nuclear magnetic resonance (NMR) spectra were recorded at 293 K on a 300 or 400 MHz spectrometer (Brucker Avance), with chemical shifts being referenced to the residual peaks of $CHCl_3$ in $CDCl_3$ (ppm). Laboratory-grade methanol, ethanol, 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 a restaurant.[16] Reactions were performed using a commercially available multimode microwave apparatus (CEM MARS). The machine consists of a continuous microwave power delivery system with an operator-selectable power output from 0 to 1600 W. Reactions were performed in either a 2 or 4 L reactor vessel. A polypropylene inlet tube (9.32 mm i.d.) was placed 2.5 cm from the bottom of the reactor, and a polypropylene outlet tube (9.32 mm i.d.) was 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 for both 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 Procedure. To a 50 L polypropylene container equipped with an overhead paddle stirrer were added vegetable oil (43 L), methanol (9.2 L, 7.28 kg, 227.4 mol), and potassium hydroxide (337 g, 6.0 mol). A portion of this feedstock mixture was then pumped into the 4 L reactor until it was full. The flow was stopped, and microwave power of 1600 W was used to heat the contents of the vessel from room temperature to 50 °C, with this taking approximately 3 min. The mixture was then held at this temperature for 1 min before the feedstock flow was restarted, and the material passed through the reactor at a rate of 7.2 L/min for a time of 6 min 10 s, during which a microwave power of 1600 W was used to heat the contents of the vessel. After this time, the pump was stopped. Throughout the process, the product stream was collected in a second 50 L polypropylene container. At the end of the process, a portion of the contents of the product vessel was decanted into a settling vessel. After the removal of glycerin, the biodiesel was washed with water and the extent of transesterification was determined by solution ^1H NMR spectroscopy and gas chromatography (GC) analysis. The relevant signals chosen for integration were those of methoxy groups in the FAME (3.66 ppm, singlet) and those of the α-methylene protons present in all triglyceride derivatives (2.3 ppm, triplet) of the soybean oil.[17] The conversion was calculated from the GC data obtained using an algorithm developed in-house based around the American Society for Testing and Materials (ASTM)[18] test method for determination of free and total glycerin.[19]

Figure 1. Prototype of the 2 L reaction vessel.

Results and Discussion

Our optimum conditions for the batch preparation of biodiesel using microwave heating involved using a 1:6 ratio of vegetable oil/methanol and 1 wt % KOH as a catalyst. The mixture was heated to 50 °C using an initial microwave power and holding at this temperature for 1 min. This resulted in a quantitative conversion to the transesterified products. We wanted to use these conditions as a guide for developing our continuous-flow approach and to use the same commercially available microwave unit. Our prototype reaction vessel, of approximately 2 L volume, is shown in Figure 1. This was placed inside the microwave cavity with tubing attached to the vessel, with the objective of passing material into the reactor at the bottom and out through the top. A thermowell was also inserted into the reactor through which a fiber-optic probe was placed, so that the temperature of the reaction mixture could be measured. The probe was located in the upper quadrant of the reactor. A 10 L mixture of vegetable oil, methanol, and catalyst was made (1:6 ratio of vegetable oil/methanol and 1 wt % KOH as a catalyst) and placed into a holding tank. A quantity of this mixture was pumped into the reaction vessel to fill it completely. The flow was then stopped, and the mixture was heated to 50 °C using an initial microwave power of 600 W. After 1 min at this temperature, the reagent stream was restarted and the remainder

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Figure 2. Flow-through reactor (2 L) inside the microwave cavity.

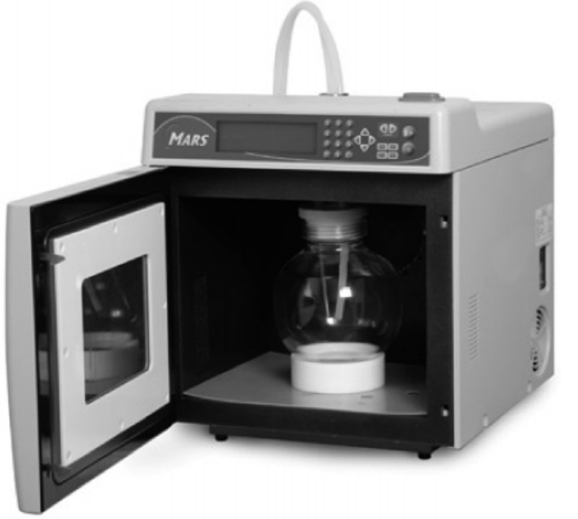

Figure 3. Flow-through reactor (4 L) inside the microwave cavity.

of the contents of the holding tank was pumped through the reactor at a rate of approximately 2 L/min. Analysis of the product stream showed that biodiesel was being formed. This was also evident by the build-up of a significant glycerin layer at the bottom of the reactor.

Because glycerin is denser than the biodiesel and without stirring, a problem that would arise is that over time the entire vessel would fill with glycerin. This could easily be overcome by stirring the reaction mixture constantly. To achieve this, we moved to an alternative 2 L volume reactor, shown in Figure 2. This commercially available reactor is more suited to continuous-flow chemistry. Similar to the prototype, reagents could be pumped in through a tube located near the bottom of the vessel and out at the top. Again, the temperature could be measured using a fiber-optic probe. The addition of a Teflon-coated magnetic stir bar allowed us to agitate the contents of the vessel by means of a rotating magnetic plate located below the floor of the microwave cavity. Using a similar methodology, we again pumped reagents from a holding tank into the reactor to fill it. After heating to 50 °C, with this time using an initial microwave power of 1600 W, and holding the mixture at this temperature for 1 min, we restarted the flow of feedstock. We ran the reaction for 10 min, passing material through the reactor at a rate of 2 L/min. Material was pumped through the vessel in a single pass. The microwave power was automatically controlled to hold the contents of the reactor at 50 °C. We analyzed the product formed using both NMR spectroscopy and GC. As illustrated by us and others, the extent of transesterification of soybean oil can easily be determined by solution ^{1}H NMR spectroscopy. The relevant signals chosen for integration were those of methoxy groups in the FAME (3.66 ppm, singlet) and those of the α-methylene protons present in all triglyceride derivatives (2.3 ppm, triplet) of the soybean oil.[20] The conversion of oil to biodiesel was calculated directly from the integrated areas of these signals. Using GC, it was possible to determine the quantity of glycerol, monolein, diolein, triolein, and biodiesel in the product stream (entry 1 in Table 1). From this data, we found that we had a conversion to biodiesel of 97%.

While being able to generate approximately 2 L of biodiesel/min, we were keen to test the limits of the microwave methodology. To do this, we moved to a 4 L reactor (Figure 3). Using an identical procedure, we first performed the reaction using a flow rate of 2 L/min, with this meaning that the feedstock was in the reactor for approximately 2 min. Again, the microwave power was automatically controlled to hold the contents of the reactor at 50 °C. On the basis of NMR and GC analysis, we obtained a 98% conversion to biodiesel (entry 2 in Table 1). We next performed the reaction using a flow rate of 7.2 L/min, the maximum possible with our pump. After filling the reactor with reagents, heating with a microwave power of 1600 W to 50 °C, holding for 1 min, and then commencing the flow of feedstock, we found that at the high rate used the microwave power was constant at 1600 W, while the temperature dropped over the period of the first 2 min to 37 °C, where it stabilized for the remainder of the 5 min run, during which time approximately 38 L of feedstock was processed. From NMR and GC analysis, we obtained a 99% conversion to biodiesel (entry 3 in Table 1) corresponding to approximately 6.1 L of biodiesel/min.

There are two mechanisms by which microwave energy can interact with a sample. If a molecule possesses a dipole moment, then, when it is exposed to microwave irradiation, the dipole tries to align with the applied electric field. Because the electric field is oscillating, the dipoles constantly try to realign to follow this. At 2.45 GHz, molecules have time to align with the electric field but not to follow the oscillating field exactly. This continual reorientation of the molecules results in friction and thus heat. If a molecule is charged, then the electric field component of the microwave irradiation moves the ions back and forth through the sample while also colliding them into each other. This movement again generates heat. Because the mixture of vegetable oil, methanol, and potassium hydroxide contains both polar and ionic components, rapid heating is observed upon microwave irradiation, and because the energy interacts with the sample on a molecular level, very efficient heating can be obtained. In addition, because the energy is interacting with the molecules at a very fast rate, the molecules do not have time to relax and the heat generated can be, for short times, much greater than the overall recorded temperature of the bulk reaction mixture. In essence, there will be instantaneous localized

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Table 1. Overall Conversion and Component Mass Percent Data for the Preparation of Biodiesel Using a Continuous-Flow Microwave Apparatus

entry	reaction conditions	overall conversion (%)	mass percent glycerin (%)	mass percent monolein (%)	mass percent diolein (%)	mass percent triolein (%)	mass percent biodiesel (%)
1	2 L/min in a 2 L vessel	97.9	0.13	0.36	0.43	1.13	95.25
2	2 L/min in a 4 L vessel	97.9	0.14	0.44	0.74	1.70	94.40
3	7.2 L/min in a 4 L vessel	98.9	0.19	0.28	0.14	0.4	94.60

superheating.[21] Thus, the bulk temperature may not be an accurate measure of the temperature at which the actual reaction is taking place. Microwave heating compares very favorably over conventional methods, where heating can be relatively slow and inefficient because transferring energy into a sample depends upon convection currents and the thermal conductivity of the reaction mixture.

To probe the energy consumption during the course of the reaction, we monitored the power consumption in the 7.2 L/min reaction using a power meter. We found that, with the microwave running with a continuous output of 1600 W, between 2500 and 2600 W power was being drawn. This indicates that the magnetron is approximately 60% efficient. The efficiency of a magnetron is always an issue when considering the overall energy consumption in a microwave-promoted reaction. However, we believe that the process is still efficient because almost all of the microwave energy, once generated, is absorbed by the reaction mixture in the cavity. It is hard to compare directly conventional and microwave-heating processes. However, a rudimentary calculation can be made by using figures from the joint U.S. Department of Agriculture and U.S. Department of Energy 1998 study into the life cycle inventory of biodiesel and petroleum diesel for use in an urban bus.[22] Their assumptions for reactor conditions were based on a review of the literature.[23] The model assumes a two-stage reactor scheme, in which 90% yields are achieved at each stage. This corresponds to an overall yield of 99%. Reported temperatures in the reactors vary from 50 to 120 °C. They selected a temperature of 60 °C because the lower end of the temperature range is typical of more modern commercial facilities. In their model, 10 455 kg of triglycerides/h enters the reactors and produces 10 397 kg of methyl esters/h. This corresponds exactly to a 99% yield of ester from triglyceride on a molar basis. They assume that no other losses of oil or product occur. They heat reaction mixtures in both processes using steam, and total steam requirements are 25 605.02 kcal/metric ton of biodiesel produced. This corresponds to 107 134 kJ/1000 kg. On the basis of a biodiesel density of 0.88 g/mL, 107 134 kJ/1136 L or 94.3 kJ/L of biodiesel prepared is given (entry 1 in Table 2). In our reactor, we produce approximately 6.1 L of biodiesel/min, during which time the microwave unit uses 156 kJ of energy (assuming a power consumption of 2600 W for 1 min; 1 W = 1 J s^{-1}). Thus, in our microwave process, we use 26.0 kJ/L of biodiesel prepared (entry 2 in Table 2), with this corresponding to approximately a quarter of the energy consumed in the model conventional study. While this calculation does not take into account the energy consumed in generating the steam and electricity to drive the conventional and microwave processes, respectively, it does show that the transesterification reaction itself is energy-efficient when using microwave heating.

Table 2. Energy Consumption Estimations for the Preparation of Biodiesel Using Conventional and Microwave Heating

entry	reaction conditions	energy consumption (kJ/L)[a]
1	conventional heating[b]	94.3
2	microwave, continuous flow at a 7.2 L/min feedstock flow	26.0
3	microwave, continuous flow at a 2 L/min feedstock flow[c]	60.3 (92.3)[d]
4[e]	microwave heating, 4.6 L batch reaction	90.1

[a] Normalized for energy consumed per liter of biodiesel prepared. [b] On the basis of values from the joint U.S. Department of Agriculture and U.S. Department of Energy 1998 study into the life cycle inventory of biodiesel and petroleum diesel for use in an urban bus. [c] Assuming a power consumption of 1700 W and a microwave input of 1045 W. [d] Assuming a power consumption of 2600 W and a microwave input of 1600 W. [e] Assuming a power consumption of 1300 W, a microwave input of 800 W, a time to reach 50 °C of 3.5 min, and a hold time at 50 °C of 1 min.

These rudimentary calculations can be extended to our original batch processes as well as our smaller continuous-flow runs. The results are summarized in Table 2. For 2 L continuous-flow conditions, the initial assumption was made that the microwave unit would operate at an average of 66% of maximum power (1100 W microwave input; power consumed 2600 W) as observed when the reaction was performed. On the basis of this, energy consumption would be 60.3 kJ/L of biodiesel prepared. If the microwave was operating at full power (1600 W; power consumed 2600 W), energy consumption would be 92.3 kJ/L of biodiesel prepared. For a batch process, we based our calculations on our previous observation that to heat a 4.6 L reaction mixture to the target temperature of 50 °C takes 3.5 min using a microwave power of 1300 W. With a hold time of 1 min at 50 °C, a total reaction time of 4.5 min is given. Assuming that the microwave power remains constant at 1300 W throughout means that the energy consumption would be 90.1 kJ/L of biodiesel prepared. In reality, the power drops once the target temperature is reached. Thus, this is an overestimation of energy consumption.

It is evident that, while the energy consumption of the batch process may be on the order of that of the conventional methodology, the continuous-flow processes are more energy-efficient. Also, the figures used for the conventional method are based on a well-refined, large-scale process. Thus, if we were to compare our batch results with those from conventional experiments using, for example, an electric hotplate, in all probability, the microwave process would be significantly more energy-efficient.

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When our results are placed in context, there has been a paper on the use of a domestic microwave for the reaction between methanol and seed oils in a batch process.[24] This is, however, limited because of the possible scale and the inherent reproducibility and safety issues concerned with using a home microwave apparatus for synthesis. A scientific microwave apparatus has been used for transesterification of triglycerides to FAMEs and involves the 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.[25] Three patent applications have been filed on the use of microwave heating in biofuel manufacture. All three use a specially designed large microwave apparatus rather than readily available commercial scientific models.[26−28] An advantage of our design is that, with the high throughput possible, a combination of several units in parallel has the potential for the production of significant quantities of biodiesel and can also offer redundancy. If one unit fails with the others used in parallel production, the process can still continue at a slightly lower output. However, if one large unit fails, the entire process is halted until repairs have been made. With four of our units, a theoretical throughput of 12 824 640 L (3 389 512 gallons) per year would be possible.

In summary, we have developed a continuous-flow approach for the preparation of biodiesel using microwave heating. A commercially available scientific microwave apparatus is used, and the methodology offers a fast, easy route to this valuable biofuel. The reaction is performed under atmospheric conditions and at flow rates up to 7.2 L/min using a 4 L reaction vessel. It can be utilized with new or used vegetable oil with methanol in a 1:6 molar ratio of oil/alcohol with, in our case, no observable differences in performance. Rudimentary energy consumption calculations suggest that the continuous-flow microwave methodology for the transesterification reaction is more energy-efficient than using a conventional heated apparatus.

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