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Energy efficiency of a scaled-up microwave-assisted transesterification for biodiesel production

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Abstract−We propose a scalable and energy-efficient microwave-assisted chemical reactor for biodiesel production, which is composed of a partially modified conventional 10-L stainless steel vessel and a microwave coupler to enable an optimized microwave injection of 99% power efficiency. The microwave power applied via a waveguide can be directly injected into the reaction vessel using a coupling rod clamped to a pressured microwave window, giving convenience of scale-up of the reactor volume because a conventional microwave transparent vessel like glass is not need. Microwave-assisted transesterification of triglycerides with potassium hydroxide catalyst achieved an accelerated conversion of 95% in 5 min. The precisely measured microwave energy consumption was only 87% of the calculated heat requirement for both the reactant and the vessel. Computer simulation studies indicated that the cause of the energy efficiency for microwave heating was the relatively low temperature of the vessel due to a reverse temperature gradient, in contrast to those done with conventional hot wall heating.

Keywords: Microwave, Scale-up, Energy Efficiency, Transesterification, Microwave Coupler

INTRODUCTION

During the past three decades, significant attention has been given to the use of microwave radiation instead of conventional external heating in chemical reactions [1-4]. Although the nature of microwave effects is still not completely understood [5-10], microwave-assisted chemical processes have demonstrated significant accelerations, higher yields, and higher product purities under milder reaction conditions in laboratory-scale work [4,11-13]. Recently, the scale up of microwave-assisted chemistry has become a field of increasing research interest [14-17]. However, large-scale experiments of microwave-assisted chemistry were demonstrated using laboratory-scale glassware, which have limited volumes due to the strength of glass and the space available in microwave cavities. These glassware-based microwave reactors inside the cavity structure are physically not feasible for scale up to commercially available levels in tons.

Moreover, scale-up may also lead to energy inefficiency as microwave-promoted reactions may be masked by an excessive energy supply from the microwave source. This issue may reduce or eliminate the beneficial microwave effects in production-scale reactions. In addition, energy efficiency by internal heating may be negated by the loss of energy during conversion of electrical energy to microwave energy. Critical discussions on the microwave effects and energy efficiency in the context of scaling up [14] have suggested that microwave chemistry can be efficient if the microwave heating system is optimized. The origin of the microwave energy efficiency in accelerated reactions with small-scale glassware was elucidated by precise microwave measurements performed on an optimized microwave system for a heterogeneous reaction [18]. Large-scale microwave reactors with glassware inside the microwave cavity have reported high energy efficiency in accelerated reactions [15,16,19]; however, it is difficult to estimate the energy efficiency in production-scale reactors because large-scale microwave reactors could not be scaled-down models of production-scale microwave reactors. More studies on scale-up microwave reactors are needed to prove the industrial feasibility of microwave-assisted chemical reactors.

On the other hand, significant environmental and energy concerns have led to demand for alternative fuels, such as biodiesel, which are derived from various bio-resources. Biodiesel is an immediately available alternative energy source of petroleum-based diesel. However, the cost of the available feedstock for biodiesel has increased abruptly due to global increase in the consumption of these feedstock materials, resulting in demand for alternative inexpensive feedstock [20] and more efficient processing methods such as the microwave heating [18,21-24], the use of supercritical methanol [25,26], combinations of these approaches [27], and ultrasonic sonochemistry [28,29].

Here, we propose a scalable and energy-efficient microwave-assisted reactor for biodiesel production, which is based on a partially modified conventional stainless steel vessel and a microwave coupler with optimized microwave injection efficiency. The energy efficiency of microwave-accelerated reactions at low temperatures is demonstrated by comparing the microwave energy consump-

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tion measurements and the calculated heat requirements. A rational explanation for the origin of the energy efficiency of microwave volumetric heating is given based on the results of thermal simulations.

MATERIALS AND METHODS

1. Transesterification

Soybean oil (triglycerides) was purchased from a local grocery store. For transesterification, methanol (99.5% purity) and KOH catalyst were used. The transesterification of soybean oil (3680 g) with 1 wt% (36.8 g) KOH catalyst was carried out with an oil/methanol molar ratio of 1 : 6 at 60 °C at atmospheric pressure. The agitation speed was 200 rpm. The reaction was started at room temperature. The microwave heating and agitation were initiated simultaneously to enable an exact reaction time measurement because the transesterification occurs at the beginning of the agitation. The reaction product was sampled during the reaction process without stopping the microwave irradiation. For the microwave energy consumption measurement, another reaction process was performed without the intermittent sampling. The content of fatty acid methyl esters (FAMEs) was determined by gas chromatography analysis using an Agilent 6890 system based on the EN-14103 standard method.

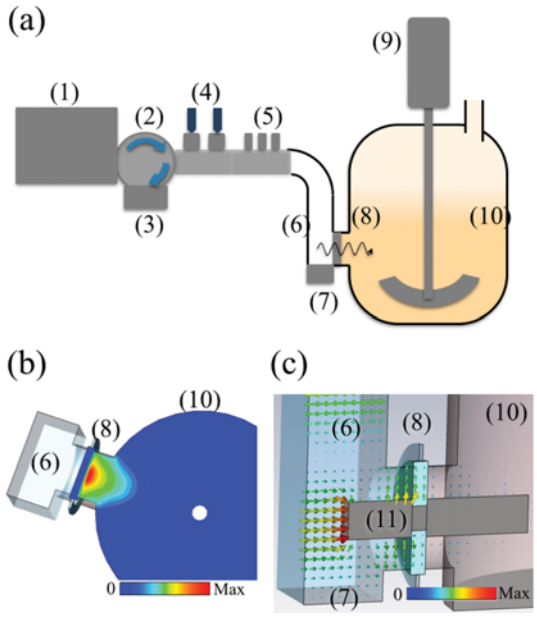

Fig. 1. Scaled-up microwave reactor.

(a) Experimental apparatus:

(1) Magnetron head, including high-voltage power supply
(2) Circulator
(3) Water load
(4) Microwave power sensors positioned at the forward and backward directional couplers
(5) 3-Stub tuner
(6) Bent waveguide
(7) Adjustable matcher
(8) Microwave coupler
(9) Mechanical stirrer
(10) 10-L stainless steel open vessel with temperature sensor located inside

(b) Cross-sectional view of the microwave power dissipation (absorption) distribution: the supplied microwave power is absorbed by the reactant and decays before reaching the center of the reactor.

(c) Electric field pattern of the 2.45 GHz microwave around the microwave coupler: coupling rod (11) collects the microwave from the rectangular waveguide into the coaxial-like waveguide structure, and transfers the microwave power to the inside of the vessel (10).

2. Microwave Apparatus

An experimental setup of a microwave heating system with a stainless steel reactor having a volume of 10 L is shown in Fig. 1(a). A 2,450 MHz microwave generator (Richardson Electronics) having a maximum power of 6 kW was used for our scaled-up reaction. To prevent any malfunction of the magnetron from unpredicted strong reflected microwave power, a circulator and a matched water load were attached to the microwave generator. Forward and backward directional couplers with microwave power sensors (Richardson Electronics) were used to observe both the forward and backward propagation of (supplied and reflected) microwave power, which are able to measure the microwave energy efficiency of the system. To enable efficient microwave power transfer between the standard rectangular waveguide and the reaction vessel, a coupling rod was clamped to the pressured window using an alumina plate. A three-stub tuner and an adjustable matcher are the tools used to optimize the microwave transfer efficiency from the waveguide to the conventional reactor. These tools can enable the impedance match between the magnetron and the reactor, thereby removing microwave energy loss in the microwave heating system. A conventional stainless steel reactor with an overhead stirrer was modified slightly to allow microwave power to enter the reaction vessel via the microwave coupler comprised of the pressured microwave window and the microwave coupling rod. The temperature of the reactor was measured using a thermocouple sensor that is located far from the microwave coupler to avoid any effects due to the microwaves. The temperature sensor and meter (WEST Instruments) have an accuracy of less than ±0.5 °C. The measured temperature was used as feedback for the computer to control the reaction temperature to within ±0.5 °C by adjusting the microwave power.

3. Computer Simulations

A three-dimensional microwave simulation (Fig. 1(b), 1(c)) was performed using the finite-element method with the Microwave Studio software. The simulation model is comprised of the waveguide, sliding short, microwave coupler, stainless steel reactor, and reactant inside, with the same dimensions as those of the experimental apparatus. The detailed dimensions of the microwave coupler and other microwave components were designed by parametric simulation studies for lossless microwave transfer. The simulation model has a single port with a fundamental microwave mode excited at the standard rectangular waveguide (WR-340). The complex dielectric constant of the mixed reactant was given by 6.614+j3.056, which is obtained from a calculation using the relevant mixed volume ratio.

Time-transient and axis-symmetric two-dimensional thermal simulations of the reactor were performed based on the finite-element method using the COMSOL Multiphysics software. The dimensions of the experimental reactor and the volume of the mixed reactant were used in the simulation model. Because the stirring was strong, for simplicity, uniform heating power that matched the

average value of the absorbed microwave power was applied to the reactant. The heat energy spread to the stainless steel vessel, and then dissipated via natural convection [30] from the external wall of the vessel. Heat spread due to fluid convection by stirring was reflected by simply adding an effective thermal conductivity of 16 W/(m·K), which was calculated from a fluid simulation. For the conventional heating simulation with a heat jacket, an additional metallic structure with the thickness of 1 cm was attached to the outside of the original reactor. The heating power was adjusted to obtain the same reactant temperature as that in the case of the microwave heating.

4. Calculation of the Heat Requirement

To estimate the energy efficiency of our microwave heating reactor, a heat requirement was calculated using the heat capacities of the reactant and vessel. In the calculation, the specific heats of soybean oil, methanol, KOH catalyst, and the reactor vessel were set to 1.967, 2.542, 1.228, and 0.5 J/(g·K), respectively. Because we used 3,680 g of soybean oil, 803.9 g of methanol, 36.8 g of KOH, and 11.6 kg reactor vessel, the total heat capacity was 15.12 kJ/K. From this calculation, we obtained the heat requirement as a function of the reactant temperature. The temperature dependence of the specific heat was ignored here.

RESULTS AND DISCUSSION

1. Scale-up of Microwave Reactor

The microwave reactor in the microwave heating system, shown in Fig. 1(a), is feasible for use in the scale up of commercial reactions because it is a conventional circular reactor that is slightly modified to attach the microwave coupler. The microwave coupler was designed to transfer the microwave power from the standard waveguide to the reactor without reflection or insertion loss. Like the microwave simulation shown in Fig. 1(c), the coupling rod was positioned at a distance of one quarter of a wavelength of the microwave from the moving short (metal block), which results in the collection of the microwave power at the coupling rod. The coupling rod, the pressured window, and the metal neck between the standard waveguide and the reaction vessel comprise a coaxial-like waveguide that can effectively transfer the microwave power into the reaction vessel. The design of the microwave coupler allows for the attachment of the waveguide component to any conventional chemical reactor. Moreover, it is possible to add additional microwave couplers with additional microwave generators to the reactor. Hence, it is straightforward to increase the total microwave power supplied as the reactor volume increases. As a result, there is no space limitation due to the volume of the microwave cavity.

The scale up of the microwave-assisted reaction is feasible because the microwave is directly injected into the reactant without contacting the air (or gas) space, and thus cannot propagate to the other side of the reactor wall. Therefore, even if additional microwave couplers and sources are required on the other side of the reactor wall, the microwave sources can be prevented from interfering with each other due to the different phases of the microwaves coming from the other sources. Any cross-talk between the microwave sources will cause a malfunction of the entire system. The computer simulation (Fig. 1(b)) indicates that the injected microwave power immediately starts to decay due its absorption by the reactant after passing through the microwave window. The microwave power dissipation is at a maximum near the microwave window inside the reactor and extends out as far as the distance from the microwave window. The microwave power disappears before reaching the center of the reactor. According to the simulation, over 99% of the microwave power input in the waveguide was absorbed by the reactant in the reactor.

However, the microwave heating by this direct injection process is non-uniform in the reactor, as shown in Fig. 1(c). Stirring of the reactant could compensate for the heating non-uniformity. If the reactant is highly viscous, or if the uniformity of the microwave heating is important to obtain the desired reaction velocity and yield, the direct microwave injection method may not be suitable.

For the chemical reaction, the microwave power was automatically adjusted to maintain the reaction temperature at 60 °C, as shown in Fig. 2(a). A maximum microwave power of 6 kW was applied

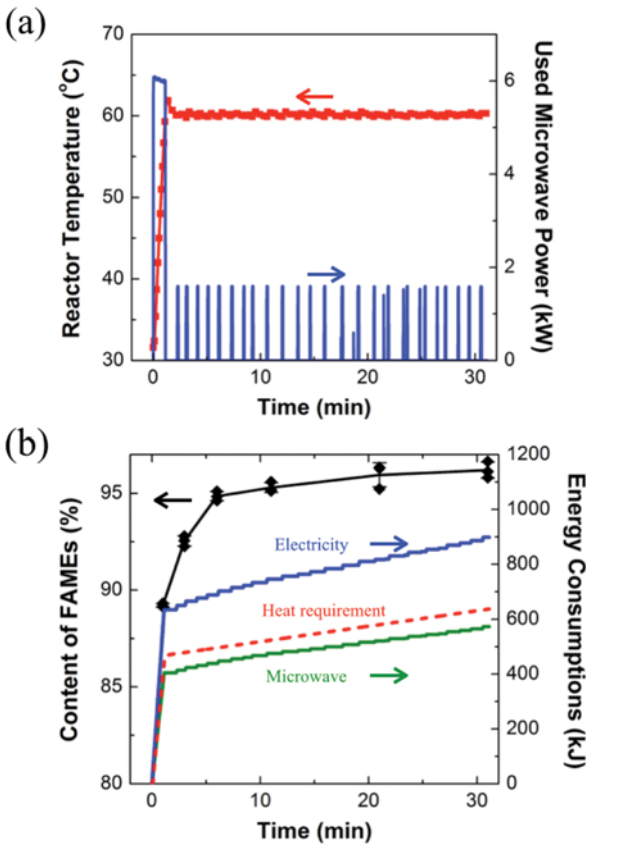

Fig. 2. (a) Temporal profiles of the reaction temperature (line and squares) and the microwave power used (line): the maximum microwave power of 6 kW was applied during the temperature rise over 67 s, and then mild microwave power of 1.5 kW was occasionally applied to maintain the reaction temperature of 60 °C. (b) Contents of FAMEs by transesterification in the scale-up microwave reactor (line and lozenges), energy consumptions of microwave and electricity during the reaction (solid line), and calculated heat requirement (dotted line). Transesterification was performed three times under the same conditions. Time in this graph includes the temperature rise over 67 s.

during the temperature rise for 67 s, and a mild microwave power of 1.5 kW was occasionally applied for temperature maintenance after 67 s. In the microwave heating system, 99% of the generated microwave power was used for heating the reactant, and the rest was reflected from the reactor and dumped at the water load.

The reaction velocity of the transesterification of triglycerides (vegetable oil) with KOH in this 5-L large-scale microwave reactor was similar to the results of previous studies in small-scale microwave reactors [31]. Fig. 2(b) shows that the content of FAMEs is three times that obtained by reactions done under the same conditions in small-scale microwave reactors. A conversion of 95% was obtained after 6.1 min (temperature maintaining time of 5.0 min), and the conversion was saturated at more than 96% due to the relatively low molar ratio of methanol to oil.

2. Energy Efficiency

Energy consumption was obtained from the microwave power applied, as measured with forward microwave directional couplers. The measured microwave energy consumption plot (Fig. 2(b)) shows that 404 kJ of energy was used for the temperature rise from 31.6 °C to 62.2 °C over 67 s. After completing the temperature rise, the energy consumption was slowly increased over time, until 572 kJ of microwave energy was used after 31 min. The electrical energy consumption for microwave generation was 634 kJ during the temperature rise and 898 kJ total after 31 min. To obtain electricity energy efficiency, electricity to microwave conversion efficiency of 63.7% was used in this system, which includes 91% efficiency of the high-voltage power supply and 70% efficiency of the magnetron. Other power consumption, for example, for the cooling fan, was ignored because it was small compared with the main power consumption. If the reaction was stopped at 6.1 min to obtain 95% conversion, the values of microwave and electrical energy were 436 kJ and 684 kJ, respectively. The microwave and electrical energy consumption per mole of synthesized FAMEs was 36.3 kJ/mol and 57.0 kJ/mol, respectively.

As shown in Fig. 2(b), the calculated heat requirement of the reactor, including the reactant and vessel heated to the reaction temperature, was 15% greater than the microwave energy consumption. This result implies that the microwave volumetric (internal) heating is more energy efficient than the conventional wall (external) heating. In previous studies [14], it was thought that microwave volumetric heating causes a reverse temperature gradient due to heat transfer from the reactant to the vessel wall. The reason that the microwave energy consumption was lower than the heat requirement in our experiment is thought to be due to the relatively low temperature of the vessel. However, the electrical energy consumption is still larger than the heat requirement, which is due to the heat requirement calculation being far from what actually occurs for wall heating devices. Unfortunately, the comparison of the energy efficiencies for the two heating methods is not easy due to various existing external heating methods corresponding to various environments, such as those in reactor scale and production processes.

Instead of a direct experimental comparison of the energy efficiency, we propose a fundamental and theoretical perspective for determining the energy efficiency using a thermal simulation study done with the COMSOL Multiphysics software. As shown in Fig. 3(a), when identical amounts of heating energy as used in the experiment were applied to the reactant over 1.1 min, the average reactant temperature was found to slightly overshoot to 62 °C, and then stabilized at 60 °C at approximately 2.0 min, similar to the experimental result. However, the average vessel temperature was lower and slowly increased compared with the reactant temperature. The vessel temperature was only 44 °C at 1.1 min and 48 °C at 2.0 min. The temperature distributions at 1.1 min and 2.1 min shown in the insert of Fig. 3(a) clearly show a reverse temperature gradient due to volumetric heating caused by the absorption of the microwaves. As a result, the microwave energy consumption in the experiment was less than the heat requirement due to the relatively low temperature of the vessel. This result agrees with the general expectation of previous studies.

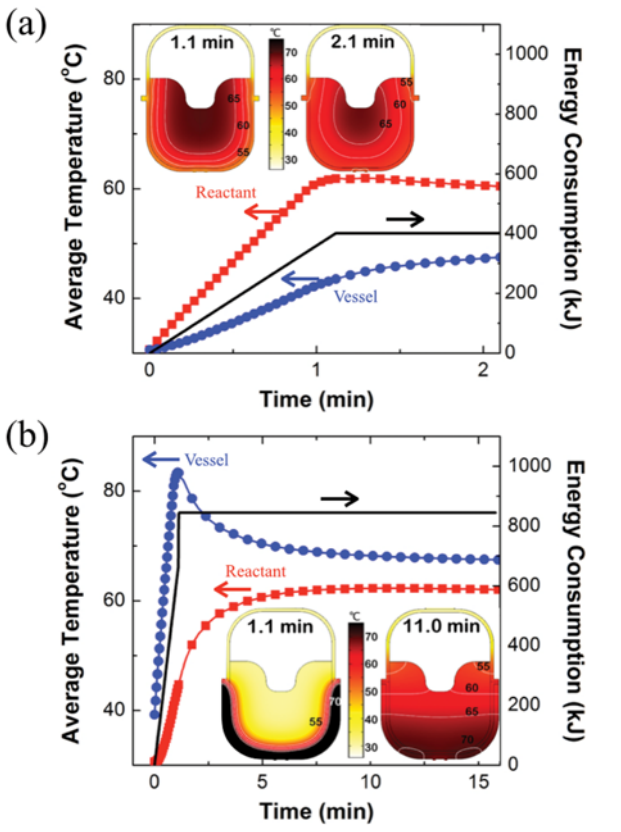

Fig. 3. Thermal simulation results: averaged temperatures of the reactant and the stainless vessel, and the temperature distribution at specific times (insert). (a) For microwave heating, the vessel temperature is lower than one of the reactants due to internal heating. (b) For conventional wall heating, the vessel temperature is higher than one of the reactants due to the hot wall.

However, when heat is supplied from a heat jacket outside the vessel, more heat energy is required. For comparison with the microwave heating in the simulation, heating power was applied to the heat jacket to obtain the same reactant temperature. As shown in Fig. 3(b), the average vessel temperature increased to 83 °C after 1.1 min, and the average reactant temperature was only 45 °C at that time. After completing the application of heat, the temperature difference between the reactant and the vessel slowly decreased. To obtain the reactant temperature of 60 °C, heat energy of 845 kJ was required, which is 209% and 133% of the energy consump-

tion of the microwave and of the electrical energy for the microwave, respectively, over the same time. The temperature distribution just after completing the heating for 1.1 min reveals a significant temperature gradient, which is assumed to be due to the inefficiency in the conventional external heating method.

The degree of energy efficiency of the microwave heating and the inefficiency of the conventional heating may vary, depending on the production process and reactor shape. Nevertheless, the energy consumption difference between the microwave and conventional heating will definitely increase as the scale of the reactor increases, because the temperature gradient via wall heating will be more significant, as indicated by the simulation results. Although there is energy loss in the conversion from electrical power to microwave power, microwave heating for chemical reactions could be an energy-saving alternative heating method in production-scale processes.

CONCLUSIONS

We have demonstrated that an easily scalable and energy-efficient microwave-assisted chemical reactor composed of a partially modified 10-L conventional stainless steel vessel and a microwave coupler enabled an optimized microwave injection of 99% energy. The results of computer simulations show that the microwave power applied via a waveguide can be directly injected into the reaction vessel using a coupling rod clamped to a pressured microwave window, giving convenience of scale-up of the reactor volume because a conventional microwave transparent vessel like glass is not needed. Microwave-assisted transesterification of triglycerides with potassium hydroxide catalyst achieved an accelerated conversion of 95% in 5 min. The precisely measured microwave energy consumption was 87% of the calculated heat requirement for both the reactant and the vessel. Thermal computer simulation studies clearly indicated that the cause of the energy efficiency of microwave heating is the relatively low temperature of the vessel, owing to the reverse temperature gradient in contrast to higher temperatures used in conventional hot wall heating.

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