World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:6, No:8, 2012

Open Science Index, Chemical and Molecular Engineering Vol:6, No:8, 2012 publications.waset.org/12500.pdf

Combined Microwaves and Microreactors Plant

Shigenori Togashi, Mitsuhiro Matsuzawa

Abstract**—**A pilot plant for continuous flow microwave-assisted chemical reaction combined with microreactors was developed and water heating tests were conducted for evaluation of the developed plant. We developed a microwave apparatus having a single microwave generator that can heat reaction solutions in four reaction fields simultaneously in order to increase throughput. We also designed a four-branch waveguide using electromagnetic simulation, and found that the transmission efficiency at 99%. Finally, we developed the pilot plant using the developed microwave apparatus and conducted water heating tests. The temperatures in the respective reaction fields were controlled within ±1.1 K at 353.2 K. Moreover, the energy absorption rates by the water were about 90% in the respective reaction fields, whereas the energy absorption rate was about 40% when 100 cm^3 of water was heated by a commercially available multimode microwave chemical reactor.

Keywords**—**Microwave, Microreactor, Heating, Electromagnetic Simulation

I. INTRODUCTION

CHEMICAL reaction processes using microwaves have attracted a great deal of attention. Numerous effects caused by microwaves in organic synthesis have been reported [1]–[3], e. g., reductions in chemical reaction times from hours to minutes, reductions in side reactions, and improvements in selectivity. Chemical-synthetic procedures using microwaves are expected to conserve energy, decrease the burden imposed on the environment, and simplify reaction processes.

Most chemical reactors that use microwaves are batch type reactors. However, one of the problems with these reactors is the difficulty in scaling them up from the laboratory to the production scale, because the depth that microwaves penetrate into absorbing materials is limited; e.g., the penetration depth generally used at 2.45 GHz is in the order of a few centimeters, depending on the dielectric properties of the absorbing materials. Consequently, when we try to scale these batch types up, microwaves are only absorbed at the surface of the batch reactors, and it is difficult to transmit microwaves inside them. In addition, the mixing efficiency of reaction solutions decreases when the batch type reactors are scaled up.

A continuous flow process is expected to be used to solve the penetration depth problem [4]. Namely, irradiating microwaves to a reaction solution flowing through a reaction tube without increasing the size of the tube is expected to solve the problem of the limited penetration depth of microwaves.

One example of the research on continuous flow processing using microwaves is the study conducted by He *et al.* on Suzuki-Miyaura coupling reactions using a micro-capillary tube through which reaction solution flowed and was irradiated by microwaves [5],[6]. They reported that they obtained a 70% yield of the product in less than 60 s. Organ *et al.* conducted microscale organic synthesis using microwaves and reported that excellent conversion was observed in a variety of cross-coupling and ring-closing metathesis reactions [7],[8]. However, the microwave-assisted chemical reactors used in these studies were commercially available ones that were not designed especially for continuous flow processing, so the energy absorption rate was not high, and the throughput was limited to laboratory scale, e.g., the throughputs were about several dozen mm^3/min.

Accordingly, the objective was to increase the throughput. To accomplish this objective, we developed a pilot plant of a continuous flow microwave-assisted chemical reactor using the concept of numbering-up, in which microwaves generated from a single microwave generator were divided into multiple reaction fields, and a reaction solution can be irradiated simultaneously in each reaction field by microwaves. Therefore, it was necessary to develop a branch waveguide by which microwaves could be divided uniformly and without losing energy in order to irradiate in multiple reaction fields uniformly and simultaneously. Therefore, we optimized the configuration of a waveguide using an electromagnetic simulation.

II. COMBINED MICROWAVES AND MICROREACTORS PLANT

A. Design of waveguide

Next, we developed a pilot plant for continuous flow microwave-assisted chemical reaction combined with microreactors using the concept of numbering-up, in which microwaves generated from a single microwave generator were divided into multiple reaction fields, and a reaction solution was simultaneously irradiated in the respective reaction fields by microwaves. We assumed Suzuki-Miyaura coupling reaction, Sonogashira coupling reaction, synthesis of silver nanoparticle, synthesis of biodiesel fuel and so on as typical reactions using the developed plant. For example, it was assumed that N,N-dimethylformamide was used as a solvent, phenylboronic acid and p-bromotoluene were used as solutes, $Pd(PPh_3)_4$ was used as a catalyst and 4-methylbiphenyl was produced by Suzuki-Miyaura coupling reaction.

The configuration of the waveguide needed to be designed so that it would be able to heat the reaction solutions efficiently in the multiple reaction fields using a single microwave generator. Accordingly, a branch waveguide was designed using electromagnetic simulation in this study.

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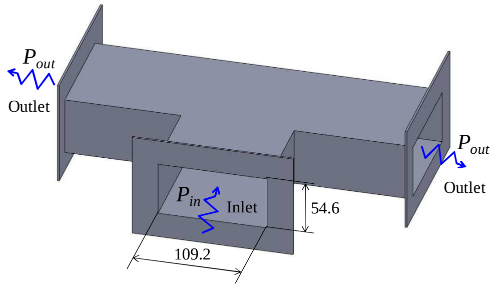
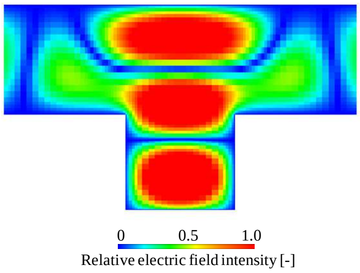


(a) Overview



(b) Relative electric field intensity distribution

Fig. 1 T-branch waveguide (Model 1)

We investigated a configuration of the branch waveguide in which incident waves were divided into two directions uniformly and without losing energy. First, we calculated the electric field intensity of a simple T-branch waveguide (Model 1) as shown in Fig. 1 (a). Fig. 1 (b) shows the relative electric field intensity distribution. We found that most of the incident waves were reflected and did not transmit up to the outlet of the waveguide. Here, transmission efficiency is defined as the ratio of all of the output microwave energy from the waveguide P_{out} to the input microwave energy into the waveguide P_{in} as shown in Figs. 1 and 2. The simulation results indicated that the transmission efficiency was 32% in this case, and it was difficult to transmit microwaves efficiently. Thus, a different design was needed for the branch waveguide. As a result of our investigation, we found that a waveguide with a 45-degree inclined plane (Model 2), as shown in Fig. 2, could transmit microwaves efficiently.

In this waveguide, the incident waves are halved along the X axis, and the divided waves transmit to each outlet. We optimized the length of C as shown in Fig. 2 using electromagnetic simulation. Fig. 3 plots the calculation results of the reflection coefficient when the length of C was changed. The reflection coefficient describes the intensity of a reflected wave relative to an incident wave, and the transmission efficiency increases when the reflection coefficient decreases.

The results show that the reflection coefficient was smallest when the length of C was 64 mm. Fig. 4 shows the relative electric field intensity distribution, and Fig. 5 shows the transmission efficiency of model 1 and model 2. The transmission efficiency of Model 2 was 99% due to the simulation.

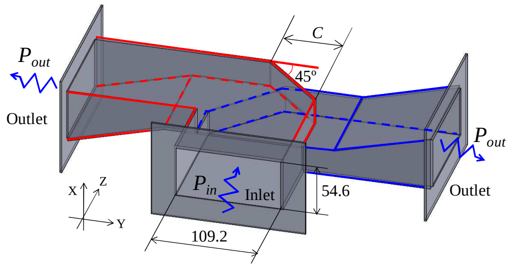


Fig. 2 Overview of branch waveguide (Model 2)

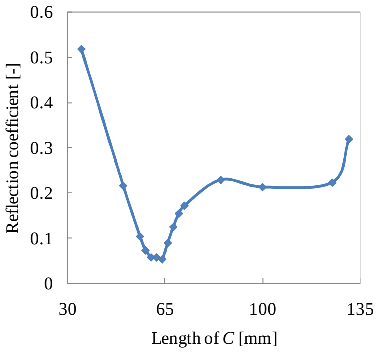


Fig. 3 Reflection coefficient when length of C was changed

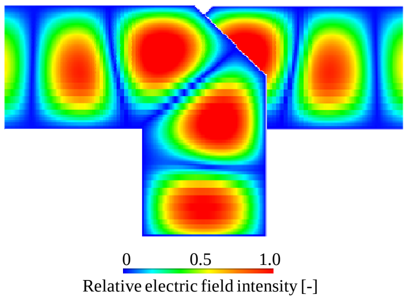


Fig. 4 Relative electric field intensity distribution

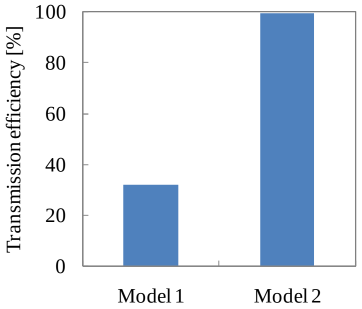


Fig. 5 Calculated results of transmission efficiency

We also investigated a four-branch waveguide configuration that was based on the above two-branch waveguide design. This configuration was designed to increase throughput by heating the reaction solution in four reaction fields simultaneously. Fig. 6 shows the schematic of the four-branch waveguide. It consists of three two-branch waveguides. Two of the two-branch waveguides are connected to an outlet of each branch of the

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third waveguide. Fig.7 (a) shows the relative electric field intensity distribution in the four-branch waveguide using the two-branch waveguides designed above, and Fig. 7 (b) also shows the relative electric field intensity distribution in the four-branch waveguide using simple T-branch waveguides (Fig. 1, model 1). These figures show that microwaves transmitted to the outlets of the waveguides efficiently when the designed two-branch waveguides were used. The results of calculating the transmission efficiency (Fig. 8) indicated that the transmission efficiency was 99% when the designed two-branch waveguides were used, and about 7% when the simple T-waveguides were used. Based on the four-branch waveguide, we developed a microwave apparatus by which the reaction solutions could be heated simultaneously by microwaves in the four reaction fields using a single microwave generator.

B. Configuration of the Pilot Plant

Based on the microwave apparatus with four-branch waveguide as shown in Fig. 6, we developed a pilot plant for continuous flow microwave-assisted chemical reaction combined with microreactors. Fig. 9 shows an overview of the plant. It consists of a flow control unit, the microwave apparatus, four microreactors, a control system, and a monitoring system. Two reagents flow into the microreactors and are mixed there; then they flow into the reaction tube in the applicator of the microwave apparatus, and the reaction solutions are microwave-irradiated and heated. The flow control unit consists of two nonpulsatile pumps (Nihon Seimitsu Kagaku, Ltd.). Pressure sensors were set in the upstream of the microreactors, and fiber optic probes for measuring temperatures were set at the inlets and outlets of the reaction tubes in the applicator. Flow sensors were positioned at the downstream of the reaction tubes. These components make it is possible to monitor the temperatures, pressures, and flow rates during reactions.

C. Experimental Evaluation

Water heating tests were conducted to evaluate the temperature control ability of the pilot plant. Water flowed at 10 cm^3/min in the respective reaction fields, and microwaves at 168 W were irradiated (i.e., microwaves at 42 W were irradiated in each of the respective reaction fields), and the reaction solution temperatures of the inlets and the outlets of the respective reaction tubes were measured by the fiber optic probes. Additionally, Fig. 10 plots the results of the energy absorption rates, which were about 90% in the respective reaction fields, whereas the energy absorption rate was about 40% when 100cm^3 of water was heated by a commercially available multimode microwave chemical reactor. The evaluation test demonstrated that the reaction solution was able to absorb microwaves efficiently, and the plant was able to control the reaction solution temperatures uniformly as designed by the simulation.

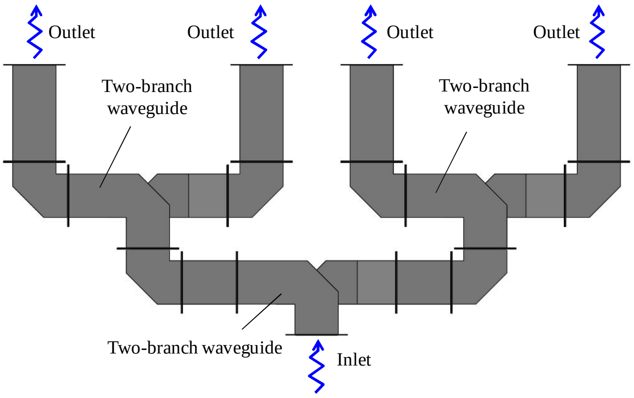
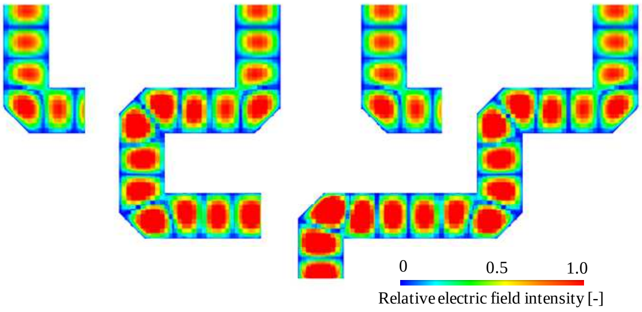
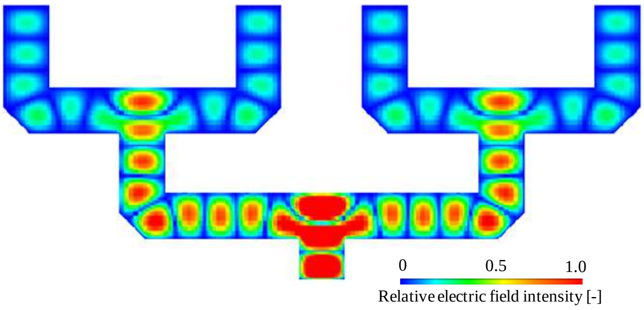


Fig. 6 Schematic of four-branch waveguide



(a) Relative electric field intensity distribution when the designed two-branch waveguides were used



(b) Relative electric field intensity distribution when the simple T-waveguides were used

Fig. 7 Relative electric field intensity distribution in the four-branch waveguide

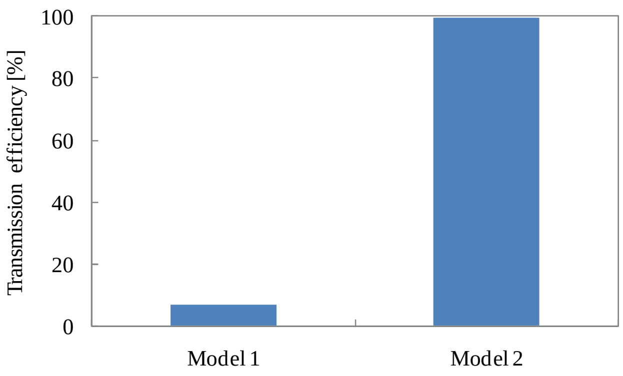


Fig. 8 Calculated results of transmission efficiency

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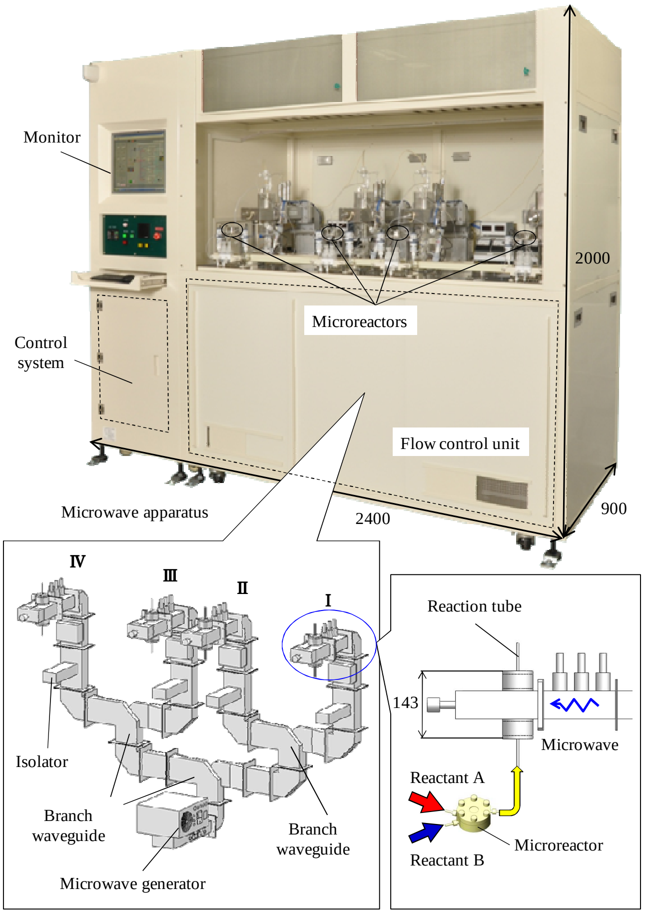

Fig. 9 Overview of Combined Microwaves and Microreactors Plant

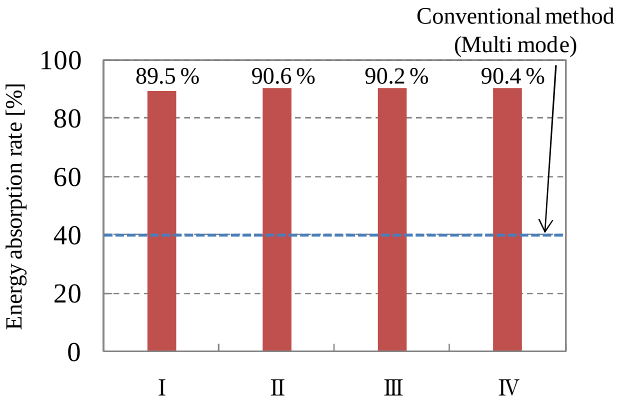

Fig. 10 Energy absorption rate by water in four reaction fields

III. CONCLUSION

A pilot plant for continuous flow microwave-assisted chemical reaction combined with microreactors was developed and water heating tests were conducted for evaluation test of the developed plant. We developed a microwave apparatus having a single microwave generator that can heat reaction solutions in four reaction fields simultaneously in order to increase throughput. We also designed a four-branch waveguide using electromagnetic simulation, and found that the transmission efficiency at 99%.

Finally, we developed the pilot plant using the developed microwave apparatus and conducted water heating tests. The temperatures in the respective reaction fields were controlled within ±1.1 K at 353.2 K when microwaves at 168 W were irradiated. Moreover, the energy absorption rates by the water were about 90% in the respective reaction fields, whereas the energy absorption rate was about 40% when 100 cm^3 of water was heated by a commercially available multimode microwave chemical reactor.

ACKNOWLEDGMENT

This research was financially supported by the Project “Development of Microspace and Nanospace Reaction Environment Technology for Functional Materials” of the New Energy and Industrial Technology Development Organization (NEDO), Japan.

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