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Microwave-assisted Hydrothermal Hydrolysis of Maltose with Addition of Microwave Absorbing Agents

S. Tsubaki^{a,c,*}, A. Onda^b, K. Yanagisawa^b, J. Azuma^c^a*Oceanography Section, Science Research Center, Kochi University, Japan*^b*Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi, University Japan*^c*Division of Environmental Science and Technology, Graduate School of Agriculture, Kyoto University, Japan*

Abstract

Hydrolysis of polysaccharides is one of the important steps for biorefinery. This paper demonstrates effects of microwave heating on hydrothermal hydrolysis of carbohydrate by comparing microwave and induction ovens. Identical thermal history could be obtained by high heating rate of both methods. To have higher sensitivity for detection of microwave effects, maltose was used as the simplest substrate. Hydrothermal hydrolysis was conducted at heating temperatures at 180 °C to 220 °C for 0 - 30 min of heating time with 4 min of come-up time. These heating profiles were precisely traced by using PID-aided temperature control. Hydrothermal hydrolysis of maltose started above 180 °C. Higher saccharification rate was achieved at higher temperature, however, degradation of glucose became predominant at 220 °C. Highest saccharification rates were almost the same by both heating methods, however, glucose yield was relatively higher at severer condition in microwave heating showing higher stability of glucose under electromagnetic field. To improve the microwave-assisted hydrothermal hydrolysis, several kinds of microwave absorbing agents including salt, metal oxide and graphite were tested. From the screening, halide salts (LiCl, LiBr, NaCl, NaBr, KCl, KBr) improved the reaction and the highest saccharification rate attained around 70% at lower temperature (200 °C) with salt concentration of 1% w/w. There was no significant difference among kinds of halide salts with different alkali metals. Sulfate, metal oxides and graphite did not show good effect. By monitoring the microwave outputs, the additions of halide salts were also found effective for reducing the total energy consumption. Increase in heating temperature required higher energy consumption when the water was used for medium, however, addition of sodium chloride at 1% w/w decreased the total energy consumption down to 60 - 70%. The results suggested that assistance of salts may be effective to improve hydrothermal hydrolysis of biomass under electromagnetic field. This method may be usable for salt containing biomass such as marine biomass.

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* Corresponding author. Tel.: +81-88-844-8927; fax: +81-88-844-8927
E-mail address: stsubaki@kochi-u.ac.jp

1. Introduction

The concept of biorefinery is to produce fuels and chemicals from biomass which has been appreciated as the only source of renewable organic chemicals alternative to fossil resources. Separation and hydrolysis of biomass components are important steps for their chemical conversion into useful chemicals. Physicochemical and chemical pretreatments such as hydrothermal hydrolysis, steaming, steam explosion, acid hydrolysis, alkaline cooking, oxidative decomposition and solvolysis are the typical pretreatments of lignocelluloses. In most of the case, these pretreatments require high temperature reaction with usage of hazardous acid/alkaline/oxidative reagents, therefore, alternative method is required for establishment of more environmentally-friendly methods.

Microwave irradiation has been reported to be an effective pretreatment method for improvement of enzymatic susceptibility of lignocellulose [1,2] and also applicable for wide variety of plant/mushroom biomass (*e.g.* fruiting body of mushroom, soybean residue, tea residue, stones of Japanese apricot, fruit peels of *Citrus unshiu*, corn pericarp and cassava residue) [3-9]. Microwave is electromagnetic waves with frequencies between approximately 300 MHz and 300 GHz. These electromagnetic waves has been used for communication and radars, as well as heating sources for domestic cooking devices, vulcanization of rubbers, drying and sterilization of foods, calcination of metal oxides, processing of woods and medical cares. Microwave heating mechanism can be summarized as dipole rotations and vibration of ions under an electromagnetic field. Solid materials such as conductors and magnetic materials are also heated easily by joule heat generated by induction heating and magnetic loss. Combination of these heating mechanisms derives unique heating specific to microwaves. Advantages of microwave heating are fast heating rate and response, high heating efficiency, uniform/local heating and selective heating. Microwave heating is also interested for their specific effects to accelerate chemical reactions by increasing chemical reaction rate and improving selectivity of the product. Therefore, microwave heating is expected to improve biomass conversion reactions.

To evaluate the effects of microwave heating, we have employed induction heating as a conventional heating which can run hydrothermal reactions under the same heating rate as the microwave heating. Induction heating is based on electromagnetic induction which can heat metal quickly by joule heat generated by eddy current. Although biomass conversion process include several steps (*e.g.* separation of biomass components and depolymerization of macromolecules), this study focused on hydrolysis of disaccharides for higher sensitivity in detection of microwave effects in simplified system. Additionally, some microwave absorbing materials such as salt, metal oxide and graphites were screened to improve the hydrothermal hydrolysis of disaccharides by microwave heating.

2. Experiment

2.1. Materials

Maltose was purchased from Wako Pure Chemical Industries Ltd. The glucose C2 was also purchased from Wako Pure Chemical Industries Ltd. Other chemicals and reagents were all analytical grade.

2.2. Microwave irradiation and induction heating

Microwave irradiation was conducted by using START D microwave oven (Frequency; 2.45 GHz, max output; 1 kW, multimode oven, Milestone Inc., Shelton, CT, USA) and HPR-100 TFM reactor (100 mL closed reactor). The temperature inside the reactor was monitored by using thermocouple

thermometer. The 250 mg of substrate was dissolved in 10 mL of distilled water and microwaved at closed system. The reaction temperature was controlled by PID in a closed condition with temperature profile as follows; 4 min of come up time; 0 - 30 min of heating time at desired temperature and 180 °C, 200 °C and 220 °C of heating temperature under agitation using stirrer bar. In the case of additive screening, salts, metal oxides and graphites were added to the reaction media by 1% w/w. The concentration of glucose after hydrothermal hydrolysis of maltose was determined colorimetrically by using glucose C2 kit based on mutarotase-GOD method.

Induction heating was conducted by using SSN-400 (Shikokurika, Kochi, Japan) using hastelloy-C lined iron autoclave (50 mL). The temperature was measured by thermocouple thermometer and controlled by PID, tracing the same thermal history as conducted in microwave experiments. The reactant inside was mixed by rocking the whole induction coil unit and autoclave.

3. Results and Discussion

3.1. Comparison of microwave heating and induction heating

Hydrolysis of polysaccharide is an important step for sugar platform-based biorefinery. Previous hydrolytic methods require strong acid. Hydrothermal hydrolysis is one of the environmentally-friendly methods, because biomass can be hydrolyzed without any hazardous catalyst due to its increased ion product. Microwave heating has been reported to be an effective alternative heating source to conduct hydrothermal pretreatment [1,2]. To reveal detailed mechanisms of microwave effects, hydrothermal hydrolysis was conducted for saccharification of maltose, which is the simplest model compound of carbohydrate, by using both microwave heating and external heating (induction oven) at exactly the same thermal history.

The saccharification rate after both heating is shown in Figure 1. In both cases, heating above 180 °C was required to initiate hydrothermal hydrolysis of maltose. The behavior of saccharification rate was very similar at 180 °C. Highest saccharification rate were almost the same by both heating methods, however, higher glucose yield was obtained at severer conditions by using of microwave heating.

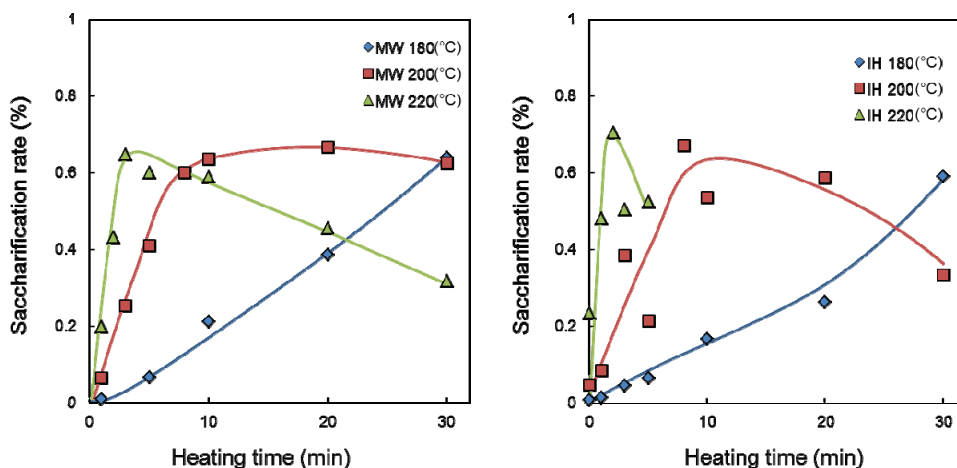


Fig. 1. Comparison of microwave heating and induction heating for hydrothermal hydrolysis of maltose

3.2. Screening microwave absorbing agent to improve maltose saccharification

Several salts (soluble and insoluble), metal oxides and graphite were screened to improve maltose hydrolysis under microwave irradiation. Figure 2 shows saccharification of maltose with addition of soluble salts (1%, w/w). All halide salts tested (LiCl, LiBr, NaCl, NaBr, KCl, KBr) were effective for improving saccharification rate at decreased reaction temperature with no clear difference among their compositions. On the other hand, sulfate had negative effect in this reaction.

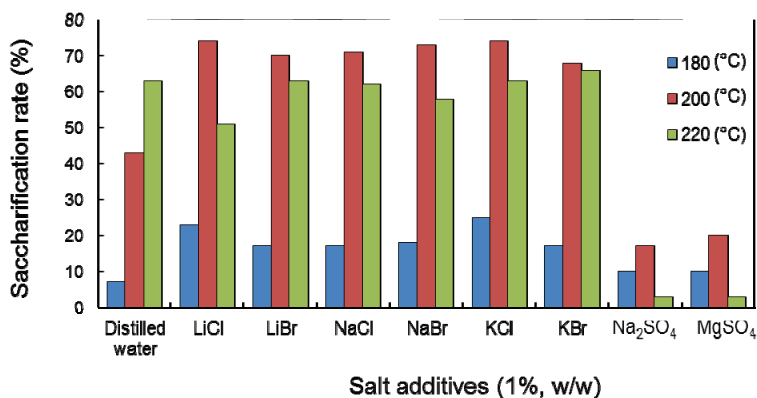


Fig. 2. Screening of soluble salts (1% w/w) to improve maltose hydrolysis by hydrothermal hydrolysis using microwave irradiation

Subsequently, solid materials were further screened for improvement of maltose hydrolysis using microwave energy. Salts with poor solubility to water had completely negative effect for hydrolysis. Metal oxides and graphite have been reported to absorb microwave energy, however, zinc oxide, alumina and graphite had no or negative effect on maltose hydrolysis (Figure 3). From this screening, halide salts were revealed to be effective to improve microwave assisted hydrothermal hydrolysis of maltose. Previously, the similar effect was observed for acid hydrolysis of starch and stones of Japanese apricot [10,11]. Addition of halide salt is also effective for hydrothermal hydrolysis which can be conducted without acid catalyst.

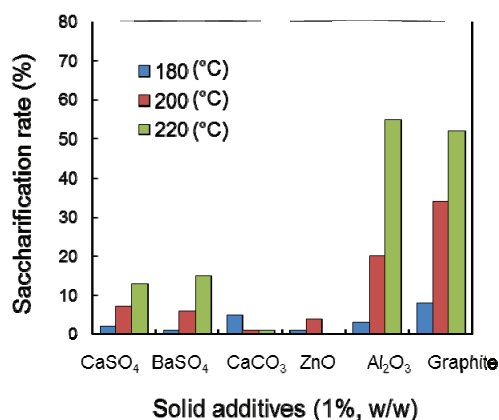


Fig. 3. Screening of solid salts, metal oxides and graphite (1%, w/w) to improve maltose hydrolysis by hydrothermal hydrolysis using microwave irradiation

3.3. Microwave output

Microwave absorbing property of the reaction media under hydrothermal condition was studied by measuring the microwave output. Hydrothermal hydrolysis with absent of sodium chloride required proportional microwave energy with increase in heating temperature. However, addition of salt improved the microwave absorption property of water and drastically reduced the microwave output especially at elevated temperature (200 °C and 220 °C) down to 60 - 70%.

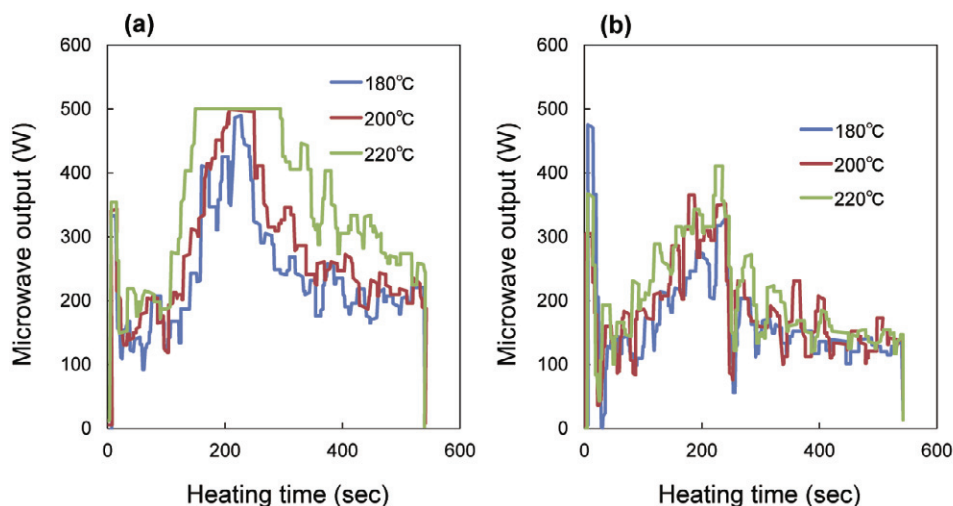


Fig. 4. Microwave output profile of hydrothermal hydrolysis by (a) distilled water and (b) saline solution containing 1% w/w sodium chloride. Come-up time; 240 sec, heating time; 300 sec

4. Conclusion

Hydrothermal hydrolysis of maltose was conducted by microwave and induction heating under completely the same thermal history to investigate the effects of microwave energy on hydrolysis of carbohydrates which is the main reaction required for sugar-platform biorefinery. Although the highest saccharification rates were almost the same by both heating, improved saccharification rate of maltose could be obtained by microwave irradiation at higher temperature and elongated reaction time than induction heating. Subsequently, microwave absorbing material was screened at the concentration of 1% w/w to further improve the microwave-assisted hydrothermal hydrolysis. Halide salts (chloride, bromide and iodide) had positive effect on hydrolysis while sulfate, solid salts, metal oxides and graphite had negative or no effects. Solution containing halide salts had high microwave absorbing properties, which could reduce the total microwave energy consumption especially at elevated temperatures.

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References

- [1] Azuma J., Tanaka F., Koshijima T., *Mokuzai Gakkaishi* 1984; **30**: 501-509.
- [2] Azuma J., Tanaka F., Koshijima T., *J. Ferment. Technol.* 1984; **62**: 377-384.
- [3] Ookushi Y., Sakamoto M., Azuma J., *J. Appl. Glycosci.* 2006; **53**: 267-272.
- [4] Tsubaki S., Nakauchi M., Ozaki Y., Azuma J., *Food Sci. Technol. Res.* 2009; **15**: 307-314.
- [5] Tsubaki S., Iida H., Sakamoto M., Azuma J., *J. Agric. Food Chem.* 2008; **56**: 11293-11299.
- [6] Tsubaki S., Sakamoto M., Azuma J., *Food Chem.* 2010; **123**: 1255-1258.
- [7] Inoue T., Tsubaki S., Ogawa K., Onishi K., Azuma J., *Food Chem.* 2010; **123**: 542-547.
- [8] Yoshida T., Tsubaki S., Teramoto Y., Azuma J., *Bioresour. Technol.* 2010; **101**: 7820-7826.
- [9] Hermiati E., Azuma J., Tsubaki S., Djumali M., Candra S.T., Ono S., Bambang P., *Carbohydr. Polym.* 2012; **87**: 939-942.
- [10] Kunlan L., Lixin X., Jun L., Jun P., Guoying C., Zuwei X., *Carbohydr. Res.* 2001; **331**: 9-12.
- [11] Tsubaki S., Ozaki Y., Azuma J., *J. Food Sci.* 2010; **75**: C152-C159.