Preparation of 5-hydroxymethylfurfural by hydrothermal treatment of palm kernel shell residues

P. Tongrod[1]*, R. Tuanpusa*[2]*, N. Suankaew*[3]*, T. Samanmulya*[4]*, B. Kongsombat*[5]
and T. Charinpanitkul[6]

Abstract

Hydrothermal treatment of biomass is one of the most promising technologies for converting biomass into a higher value-added form. In the past decade, it is well recognized that palm oil production is one of the major industries in Thailand, which generates many residues of palm kernel shell. This work focuses on utilizing hydrothermal treatment of cellulose in palm kernel shell residues for 5-hydroxymethyl-furfural (5-HMF) production. Because the palm kernel shell residues mainly contain cellulose of 60 wt%, it would possibly provide a high yield of sugar products. Palm kernel shells residues were treated by alkali solutions before adding into a batch-type tubular reactor. A series of systematic experiments were performed in a reaction temperature range of 200 to 300 °C, heating rate ranging from 5 to 10 °C/min, concentration of palm kernel shell residues (feedstock) at 10 and 20 wt%, and lignin content in a range of 3-10%. Moreover, effect of adding of 2-butanol as extracting solvent was also investigated in order to increase the 5-HMF yield in liquid product. It was found that the 5-HMF yield was dependent on the reaction temperature, heating rate, concentration of feedstock and lignin content. Furthermore, the experimental results showed that 2-butanol was a good selective solvents for the production of 5-HMF in the hydrothermal treatment process. In addition, liquid product obtained from the hydrothermal treatment consisted of 1,3-dihydroxyacetone dimer, formic acid, acetaldehyde, acetic acid and furfural.

Keyword: Hydrothermal, Palm kernel shell, 5-hydroxymethylfurfural

---

[1] *Center of Excellence in Particle Technology, Faculty of Engineering, Chulalongkorn University*

[2] *Center of Excellence in Particle Technology, Faculty of Engineering, Chulalongkorn University*

[3] *Center of Excellence in Particle Technology, Faculty of Engineering, Chulalongkorn University*

[4] *Center of Excellence in Particle Technology, Faculty of Engineering, Chulalongkorn University*

[5] *Center of Excellence in Particle Technology, Faculty of Engineering, Chulalongkorn University*

[6] *Center of Excellence in Particle Technology, Faculty of Engineering, Chulalongkorn University*

1.Introduction

In recent years, the emission of green house gases has been mentioned as the main cause of global warming. For example, carbon dioxide (CO_2) is one of the greenhouse gases generated with a large amount each year from the burning of fossil fuels to produce energy. To reduce the demand for fossil fuels, many researchers have paid their attention to other sources of clean energy such as solar, wind, wave and geothermal but biomass would be the best candidates which have been employing a lot attention. Biomass is an organic compound which is a major source of energy in the world. Many researchers have proven its viability for large scale production. Moreover, biomass energy generation will cause lower green house effect due to the recycling process of the plant rotation [1]. Particularly, there are various biomass materials available in Thailand. Agricultural waste, such as corn, cob, husk, bagasse, sawdust, coconut and palm kernel shell, could be used as promising alternatives of renewable energy sources which are abundant and inexpensive. Palm oil production is one of the major industries in the south of Thailand. Palm oil mills in the region generate 386,930 tons/yr, 165,830 tons/yr and 110,550 tons/yr of empty fruit bunches, palm press fibers and palm kernel shells, respectively [2]. It could be implied that there are plenty of palm oil wastes production in each year. Component of the palm oil biomass residues that can be employed are empty fruit bunch, mesocarp fibers, palm kernel shells, palm tree trunks and fronds [3]. Palm oil biomass consists of cellulose, hemicellulose, lignin and ash.

Cellulose is a valuable renewable energy resource which store in biomass, and also glucose and its derivatives which can be obtained by the hydrolysis of cellulose are expected to be valuable chemicals, food and feed stock [4]. Many technologies have been developed for the pre-treatment and hydrolysis of cellulose, including such technologies as hydrothermal treatment, acid treatment, steam explosion and enzymatic hydrolysis [5-7]. In addition to these approaches, subcritical and supercritical water treatments have also been investigated and have shown some particular advantages, such as high reaction rate, no catalyst requirement and no product inhibition [8].

Transformations of cellulose hydrolysis in subcritical and supercritical water have been investigated. When cellulose aqueous is hydrothermally treated at high temperature, the glycosidic bond of cellulose chains would be hydrolyzed. Cellulose could be converted into water-soluble oligosaccharides, including cellobiose, cellotriose, cellotetraose and cellopentaose, were called olimers. Thereafter, original cellulose would be converted into glucose, fructose and fragmentation products such as 1,6-anhydroglucose, erythrose and 5-hydroxymethylfurfural (5-HMF) [9]. One promising chemical transformation of biomass is 5-hydroxymethylfurfural (5-HMF), which is suitable for alternative liquid bio-fuels. 5-HMF is a versatile chemical platform that can be used to integrate a wide range of chemicals derived from petroleum, particularly in 2,5-dimethylfuran (DMF). DMF has been proposed as a replacement of ethanol for the production of liquid bio-fuel, it has an energy density 40% greater than ethanol [10-11].

Specially, it could be noted that there is no clear evidence of reported results of preparation of 5-HMF from palm kernel shell via hydrothermal treatment process. Therefore, the aim of this study is to investigate condition for preparing 5-HMF from palm kernel shell residues in subcritical water.

2.Material

Palm kernel shell residues were supplied as a supportive material from Thai Hybrid Energy Co., Ltd. (Bangkok, Thailand). The residues and de-ionized water were used as the feedstock for hydrolysis process. The chemical reagents used for degumming of palm kernel shell residues and preparation of 5-HMF were sodium hydroxide (NaOH; Suksapan), sodium sulfide ($Na_2S{\cdot}xH_2O$; Panreac), sodium chlorite ($NaClO_2$; Ajax Chemicals), acetic acid (CH_3COOH; QREC). and 2-butanol (C_4H_9OH; Carlo Erba Reagents). All chemicals were analytical (A.R.) grade and used as received.

3.Experimental

The palm kernel shell residues were initially ground and sieved to a powder with a particle size around 0.8 mm. Then, the ground residues were dried at 90 ^{o}C for 10 minutes to remove the volatile matter. After that, cellulose was extracted from the palm kernel shell residues by the following steps. Briefly, the residues were pretreated by soaking into 1 w/v% NaOH solution at 80 °C for 2 h, followed by washing with adequate distilled water to remove the epidermis. The pretreated residues were treated further in a mixture of 1 w/v% NaOH solution and 1 w/v% Na_2S with a volumetric ratio of 1:30 at 80 °C for 1.5 h to obtain cellulose fibers. The cellulose fibers were then bleached by a mixture of 0.7 v/v% sodium chlorite ($NaClO_4$) aqueous solution and an acetate buffer at 80 °C for 1.5 h to remove the lignin residues [12]. The acetate buffer was prepared by dissolving 2.7 g of NaOH solid in a solution of 7.5 ml of glacial acetate acid in 100 ml of distilled water. The bleached fibers were washed repeatedly by distilled water and subsequently dried in oven at 90 °C for 10 min.

A series of experiment of hydrothermal treatment of palm kernel shell residues were conducted in a batch-type tubular reactor system. The system consists of a tubular reactor with a vertical-tubular electrical furnace incorporated with a temperature controller as shown in Fig.1. The reactor was made of stainless steel having an outside diameter of 19.05 mm, a wall thickness of 1.65 mm and a corresponding internal volume of 24.70 ml.

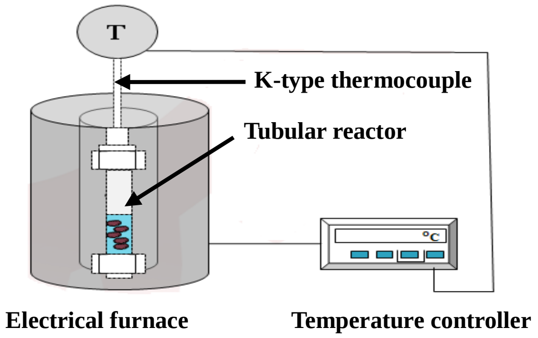

Fig. 1 Experimental apparatus

At the beginning of experiment, the reactor was loaded at 10 wt% of biomass by placing 1 g of the pretreated palm kernel shell residues and 9 g of de-ionized water into the reactor, and then heated to a designated temperature at a designated heating rate. The temperature and heating rate were varied from 200 to 300 °C and 5 to 10 °C/min, respectively. The volumetric ratio of space to the total volume is 75%. After the end of the hydrothermal treatment period, the reactor was immediately cooled down by quenching in water to stop the hydrothermal process. Each sample contains both liquid and solid parts. The liquid part was taken for the determination of 5-HMF and other hydrolyzed products by using High Performance Liquid Chromatography (HPLC; Varian, Prostar) analyzer equipped with a fluorescent detector and an Octadecyl Silane (ODS) C18 column. The amount of 5-HMF contained in the solid part was negligible since 5-HMF is a highly water-soluble substance.

4.Results and Discussion

Effect of reaction temperature. Effect of each operating parameters on 5-HMF concentration was examined experimentally. Among these parameters, reaction temperatures which are defined as a maximum temperature within the reactor, which could be achieved by a constant heating rate of 5 °C/min.

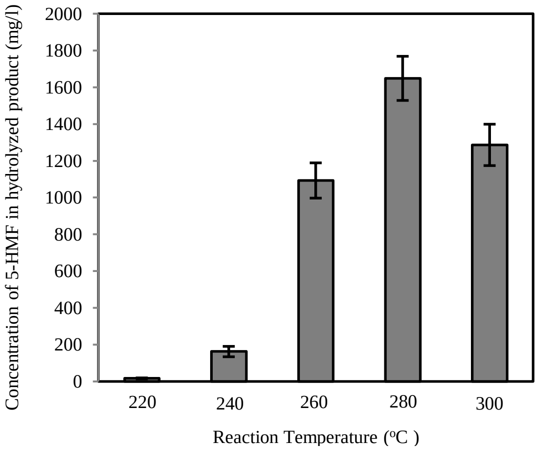

Fig.2 Reaction-temperature dependence on concentration of 5-HMF at a heating rate of 5 °C/min

Fig.2 shows the effect of reaction temperature within the range of 200 to 300 °C on the concentration of 5-HMF. The results indicate that the concentration of 5-HMF increases with increasing temperature due to the continuous increase in decomposition of glucose with temperature. The increase in the 5-HMF concentration reaches a maximum at the reaction temperature ranging between 280-300 °C. This observation is consistent with the result reported in a previous study on the decomposition of 5-HMF in the hydrothermal process above 300 °C [13].

Effect of heating rate. Dried palm kernel shell residues were hydrothermally treated under conditions of reaction temperature from 220 to 300 °C with heating rate at 5, 7.5 and 10 °C/min.

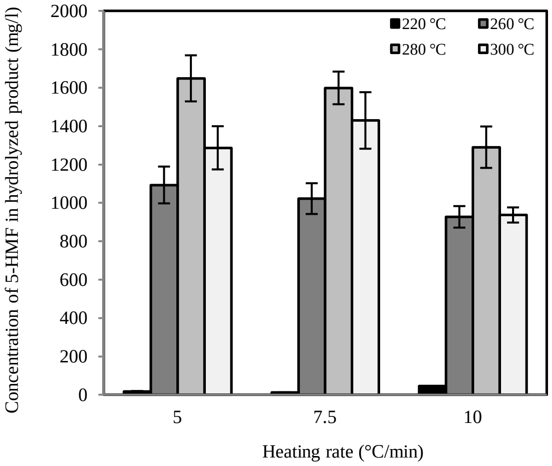

Fig.3 Heating-rate dependence on concentration of 5-HMF at difference reaction temperatures

Fig.3 shows the dependence of 5-HMF concentration on the heating rate. At the beginning with the lowest of the reaction temperatures of 220 °C, glucose is the main component in the liquid product, which was indicated in the previous study meanwhile 5-HMF will be converted from glucose therefore yield of 5-HMF can cause to the lowest concentration accordingly. At the reaction temperatures of 260 °C, the yield of 5-HMF became lower when the heating rate was increased. This result suggests that with a lower heating rate the palm kernel shell was subjected to water vapor with a longer contact time, resulting in a larger amount of cellulose converted to 5-HMF. Finally a corresponding result was observed at the higher reaction temperature of 280 °C and above when the heating rate was increased from 5 to 7.5 °C/min. On the other hand, at the highest of heating rate, the contact time with water vapor was too short to allow the conversion of cellulose into 5-HMF sufficiently. This leads to a decrease in concentration of 5-HMF at all reaction temperature. This experimental result is accordance with the previous work which they concluded that the yield of 5-HMF steadily decreases when the heating rate was increased [14].

Effect of concentration of feedstock. In this study, we employed the concentration of feedstock at 10 and 20 wt% with the optimal reaction temperature at 280 °C and heating rate at 5, 7.5 and 10 °C/min. As shown in Fig. 4, when we changed the initial concentration of feedstock from 10 to 20 wt% at several of heating rate, it could be observed that the concentration of 5-HMF was obviously increased due to the fact that the larger surface area of feedstock could be caused the higher rate of reaction. This experimental result is consistent with the previous work, It could be noted that the change in the initial concentration of feedstock from 10 to 30 wt% was significantly increased in the concentration of 5-HMF in liquid product [15].

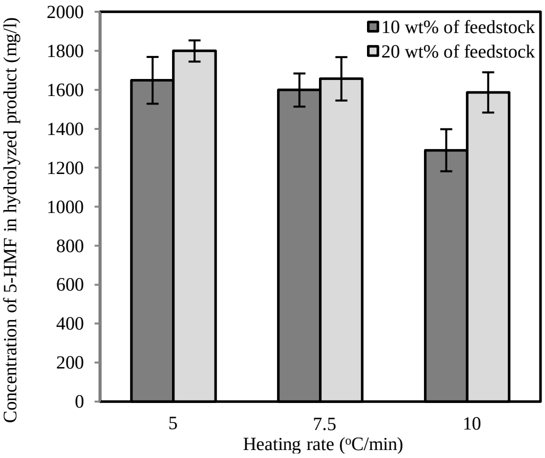

Fig.4 Concentration of feedstock dependence on concentration of 5-HMF at difference heating rate

Effect of lignin content. This study investigates the effect of lignin content of palm kernel shell residues on the hydrothermal treatment process with the optimal experimental condition at 280 °C and 5 °C/min, respectively. As shown in Table 1, it was not clear about how to control the lignin content in feedstock and how much its composition might be varied.

Table 1 The lignin content in several physical properties of feedstock

Chemical component	wt%			
	Sample A	Sample B	Sample C	Sample D
Lignin	3.59	5.78	6.93	9.98

Sample A = Raw material residues treated with alkali solution for 3 hrs.

Sample B = Raw material residues treated with alkali solution for 1.5 hrs.

Sample C = Original raw material residues without alkali treatment and sift with size 800 µm.

Sample D = Original raw material residues without alkali treatment and sift with size 250 µm.

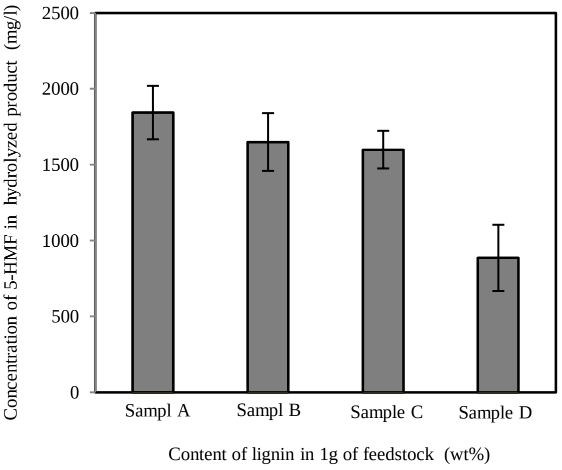

Fig.5 Lignin content dependence on concentration of 5-HMF at optimal experimental condition

As shown in Fig. 5, this experimental result indicated that the influence of lignin content led to decrease the concentration of 5-HMF with an increase in lignin fraction. Furthermore, this study suggests that the amount of lignin content should be considered an important process parameter which affects the efficiency of hydrothermal treatment process. For the bio-energy industry, lignin is a barrier particularly in both saccharification process and hydrolysis process for production of liquid bio-fuel [16-17].

Effect of 2-butanol. In general, dehydration of palm kernel residues would be expected with the presence of 2-butanol. Fig. 6 shows the effects of adding of 2-butanol at 20, 30, 40, 50 and 60 v/v% on the concentration of 5-HMF which was obtained from the hydrothermal treatment of palm kernel residues. After dehydration, the liquid products consisted of portions of the aqueous phase and extracting phase. Each portion was separated and taken to determine the amount of 5-HMF using HPLC analysis. It could be seen that the total concentration of 5-HMF became higher with the increase in 2-butanol loading singlehandedly, in particular at 40 v/v% of 2-butanol. This is attributed to the extracting capability of 2-butanol which could suppress degradation reactions arising when 5-HMF came to contact with de-ionized water [15].

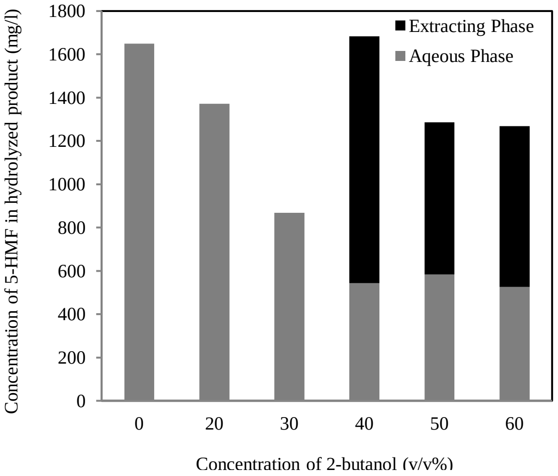

Fig.6 Effect of 2-butanol loading on concentration of 5-HMF at optimal experimental condition

In addition, when 2-butanol was loaded more than 40 v/v%, it decreased in portion of water used for the conversion of cellulose to 5-HMF, yield of 5-HMF could be decreased accordingly.

5.Conclusion

Palm kernel shell residues could be converted to liquefied products including 5-HMF within the tubular reactor operated under subcritical water conditions. The process parameters which could affect the concentration of 5-HMF are reaction temperature, heating rate, concentration of feedstock and lignin content. A relatively high yield of 5-HMF could be obtained at the reaction temperature between 280-300 °C. The increase in heating rate led to decrease in concentration of 5-HMF at all reaction temperatures because a contact time between water vapor and cellulose was depleted. Moreover, an increase in concentration of feedstock led to the increasing concentration of 5-HMF because the larger amount of palm kernel shell residues could be hydrolyzed. Furthermore, the component of lignin in feedstock has significant influence on the concentration of 5-HMF in liquid product. The larger amount of lignin content in feedstock reduced the concentration of 5-HMF because lignin is a striking barrier between cellulose and water vapor in the hydrolysis process. In addition, effect of adding of 2-butanol as extracting solvent to the hydrothermal treatment process could increase the total concentration of 5-HMF in liquid product when this result was compared with the previous study under the same experimental condition.

Acknowledgment

This research has been supported partially by the Centenary Fund of Chulalongkorn University to Center of Excellence in Particle Technology and Energy Research Institute of Chulalongkorn University.

References

[1] M.J. Antal, S.G. Allen, D. Schulman, X. Xu, Biomass gasification in supercritical water, Ind. Eng. Chem. Res. 39 (2000) 4044-4053.

[2] S. Prasertsan, P. Prasertsan, Biomass residues from palm oil mills in Thailand: An overview on quantity and potential usage, Biomass and Bioenergy 11 (1996) 387–395.

[3] S. Saka, Whole efficient utilization of oil palm to value-added products. In: Proceeding of JSPS-VCC Natural Resources & Energy Environment Seminar, Kyoto, Japan, 2005.

[4] M. Sasaki, B. Kabyemela, R. Malaluan, S. Hirose, N. Takeda, T. Adschiri, K. Arai, Cellulose hydrolysis in subcritical and supercritical water, J. Supercrit. Fluids 13 (1998) 261-268.

[5] B.C. Saha, L.B. Iten, M.A. Cotta, Y.V. Wu, Dilute acid pretreatment, enzymatic saccharification and fermentation of wheat straw to ethanol, Process Biochem. 40 (2005) 3693–3700.

[6] F. Xu, R. Sun, P. Fowler, M.S. Baird, Characteristics of degraded cellulose obtained from steam-exploded wheat straw, Carbohydr. Res. 340 (2005) 97–106.

[7] B. Yu, L. Qi, Research status of lignocellulosic materials for fuel ethanol, Ind. Eng. Chem. Res. 25 (2006) 244–249.

[8] Y. Zhao, W.J. Lu, H.T. Wang, Supercritical hydrolysis of cellulose for oligosaccharides production in combined technology, J. Chem. Eng. 150 (2009) 411–417.

[9] M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri, K. Arai. Dissolution and hydrolysis of cellulose in subcritical and supercritical water, Ind. Eng. Chem. Res. 39 (2000) 2883–2890.

[10] T.A. Werpy and G. Petersen, Top value added chemicals from biomass, Department of Energy (DOE), Golden, CO; DOE/GO-102004-1992 (2004) USA.

[11] G.W. Huber, J.N. Chheda, C.J. Barrett, J.A. Dumesic, Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates, Science 308 (2005) 1446–1450.

[12] R. Li, J. Fei, Y. Cai, Y. Li, J. Feng, J. Yao, Cellulose whiskers extracted from mulberry: A novel biomass production, Carbohydr. Polym. 76 (2009) 94–99.

[13] A. Chuntanapum, T.L.K. Yong, S. Miyake, Y. Matsumura, Behavior of 5-HMF in Subcritical and Supercritical Water, Ind. Eng. Chem. Res. 47 (2008) 2956-2962.

[14] Q. Bao, K. Qiao, D. Tomida C. Yokoyama, Preparation of 5-hydroymethylfurfural by dehydration of fructose in the presence of acidic ionic liquid, Catal. Commun. 9 (2008) 1383–1388.

[15] J.N. Chheda, Y.R. Leshkov J.A. Dumesic, Production of 5-hydroxymethylfurfural and furfural by dehydration ofbiomass-derived mono-and poly-saccharides, Green Chem. 9 (2007) 342–350.

[16] L. Li, Y. Zhou, X. Cheng, J. Son, J.M. Marita, J. Ralph, V.L. Chiang, Combinatorial modification of multiple lignin traits in trees through multigene cotransformation, Proc. Natl. Acad. Sci. 100 (2003) 4939–4944.

[17] F. Chen, R.A. Dixon, Lignin modification improves fermentable sugar yields for bio-fuel production. Nat. Biotechnol. 25 (2007) 759–761.