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Conversion of Secondary Pulp and Paper Sludge to Glucose by Hydrothermal Treatment

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Abstract

Secondary pulp/paper sludge is residue from water treatment process of the paper industry. Main components of secondary pulp/paper sludge are cellulose, hemicelluose, lignin and calcium carbonate ($CaCO_3$). The cellulose and hemicellulose could be converted to glucose by hydrothermal treatment in a stainless steel tubular batch reactor. It was found that dried powder of secondary pulp/paper sludge with nominal size in a range of 595 to 840 µm contains different content of $CaCO_3$. Therefore, effect of $CaCO_3$ content on glucose yields was examined under designated temperature of 200-260 ºC and treating time of 0-40 minutes. Identification and quantification of glucose and other derivatives in aqueous phase was performed with high-performance liquid chromatography. Plausible reaction pathway of cellulose subject to hydrothermal treatment with the presence of $CaCO_3$ was proposed and discussed. The highest glucose yield could be obtained from secondary sludge at 220°C with 20 min holding time. It was found that $CaCO_3$ must be separated before hydrothermal treatment to again higher cellulose conversion.

Key words : Hydrothermal Treatment, Pulp/paper sludge, Glucose

Introduction

In many countries, the consumption of paper is still increasing annually, resulting in an increase in amount of waste of many forms including pulp/paper sludge. There are two kinds of sludge,namely primary and secondary sludge.(1) The primary pulp/paper sludge mainly consists of fibers, fine fiber and chemcial fillers. Meanwhile, the secondary pulp/paper sludge (secondary sludge, in short) is waste generated from biological treatment subject to aerobic digestion. In general, the secondary sludge is a liquid suspension with high solid content. It contains biodegradable organic compounds and inorganic compounds including a certain amount of heavy metals. The estimated amount of secondary sludge in 1999 in Japan was much more than 1.7 Mt/y . In North America, it is reported that 4 kg of secondary sludge is produced from 100 kg of paper. In general such sludge could be disposed by landfilling or incinerating with some disadvantages, such as high operating cost because of requirement of dewatering or energy loss due to evaporation in prior to its feeding into incineration process.

In Thailand, an estimated amount of secondary sludge is around 0.95 million tones/y with an increasing trend because of an increase in paper consumption per capita. It is reported that the sludge disposal/ management costs would go up to 60% of the total wastewater treatment operating costs.(2) Nevertheless, such secondary sludge can also be considered as waste biomass which could be subject to biological or thermo-chemical treatment processes for producing other useful products, such as hydrogen or ethalnol. Utilization of such secondary sludge would help decrease the fossil fuel consumption which in turn reduce the greenhouse gas emission.(3,4)

In general, hydrothermal processes are operated at relatively mild conditions without usage of auxilarly chemicals. Such processes are free from costly treatment. Hydrothermal treatment of sludge in one-step processes has been of interest for many researcher teams. For instance, Torii et al. investigated a hydrothermal treatment process of paper sludge in a tube bomb reactor to hydrolyze cellulose to glucose.(5) Zhang et al. investigated of hydrothermal on secondary sludge and sewage sludge to convert it to biooil.(6)

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In this work, a one-step hydrothermal treatment of secondary sludge was examined with a purpose for converting cellulose and hemicellulose in secondary sludge to glucose. Effect of calcium carbonate on the cellulose conversion was systematically examined and discussed.

Materials and Experimental Procedures

Material

Secondary sludge was supplied Norske Skog Thailand Co. Ltd., Singburi, Thailand. Major components of secondary sludge were analyzed based on the United States Department of Agriculture method (TAPPI's method) and summarized in dried weight basis in Table 1. Figure 1. shows SEM micrograph of typical sample of pulp and secondary sludge which were subject to hydrothermal treatment under the same condition.

Table 1. Compositions of screened pulp and secondary pulp and paper sludge (>840 μm, 595-840 μm, <595 μm) by TAPPI

	Pulp	Sludge		
		>840	595-840	595
Cellulose	0.48	0.40	0.33	0.20
Hemicellulose	0.22	0.23	0.25	0.27
Lignin	0.18	0.18	0.20	0.19
$CaCO_3$	0.07	0.17	0.21	0.32
	P	S1	S2	S3

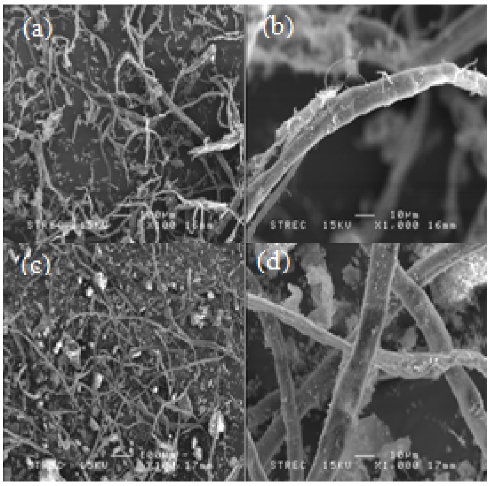

Figure 1. SEM micrographs of (a) pulp with 100-time magnification (b) Pulp with 1000-time magnification, (c) secondary sludge with 100 time magnification and (d) secondary sludge with 1000 time magnification

Experimental Method

Hydrothermal treatment was carried out in a SUS-316 stainless steel tube reactor (Swagelok Co.) with 1-inch O.D. and effective internal volume of 100 cm^3 illustrated schematically in Figure 2. It was heated up to targeted temperature using an electric furnace connected with a digital controller to detect the temperature every 1 minute. Treating temperature was controlled in a range of 200 - 260°C with holding time ranged from 10 to 40 min.(5) Table 2 summarizes the composition of each secondary sludge feedstock which was classified by screening process. S1 powder sample is secondary sludge with a nominal size larger than 840 μm, S2 with nominal size in a range of 595 to 840 μm and S3 with nominal size smaller than 595 μm. Pulp was a standard pulp sample taken from the pulp production process of the same supplier.

Table 2. Composition of each secondary sludge employed for hydrothermal treatment

Raw Material	Composition (g)				Total Initial Mass (g)	DI water, (g)
	Cellulose	Hemicellulose	Lignin	$CaCO_3$		
Pulp	0.66	0.32	0.27	0.08	1.35	80
S1	0.66	0.38	0.30	0.30	1.65	80
S2	0.66	0.50	0.40	0.42	2.00	80
S3	0.66	0.89	0.63	1.06	3.25	80

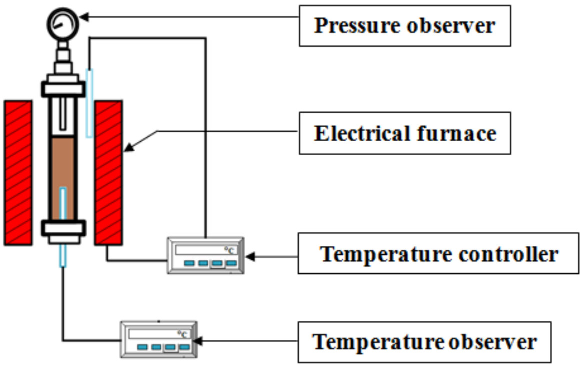

Figure 2. Schmatic diagram of tubular reactor

Analytical method

Identification and quantification of organic compounds and liquid products in the aqueous phase were performed using a high-performance liquid chromatography (HPLC, Varian, Prostar) equipped with 250x4.6 mm carbonyl column with a reflextive index (RI) detector. 69% acetonitrile: 31% H_2O was used as mobile phase for detecting saccharide content. Standardized sample size was 50 µl. The amount of each saccharide was determined from calibration curves obtained by analyzing standard saccharide solution with known content. The saccharide yields were calculated by the following equation :

$$\text{Each saccharide yield (\%)} = 100\left(\frac{\text{Gram of saccharide in liquid product}}{\text{Gram of cellulose in feedstock}}\right) \quad (1)$$

Results and Discussion

Effect of Treating Temperature

Effect of treating temperature in a range of 200-260ºC on production yields of glucose and fructose is shown in Figure 3. It was found that an increase in the treating temperature resulted in a gradual decrease in glucose yiled (Figure 3(a)). However, Figure 3(b) shows that the prodcution yield of fructose became higher with the treating temperature increased from 200 to 240ºC. A further increase in the treating temperature to 240ºC would result in a lower yield of fructose. Regarding to characteristics of each classified secondary sludge, similar tendency was observed. These results would be ascribed to the competitive rate of conversion of cellulose to polysaccharides againts decomposition of polysacharides. Jing and Lu as well as Khajavi et al. reported that glucose would be decomposed by thermal treatment of cellulose in a temperature range of 180-220ºC and 180-260ºC respectively.(7,8) The decomposition rate was increased with the higher reaction temperature. Similar trend was also observed with respect to every saccharide product. However, within the reaction temperature range of 200-220ºC, amount of fructose converted from cellulose was comparatively faster than its decomposition, leading to the increasing yield of fructose. In addition, there is also possibility that glucose would be transformed to fructose. Further investigation on stability of glucose and fructose under the hydrothermal treatment would be required for this confirmation. However, it would be reasonable to imply that treating temperature would exert significant effect on the conversion of cellulose in secondary sludge to saccharides regardless of the classified size in a range of 595 to 840 µm.

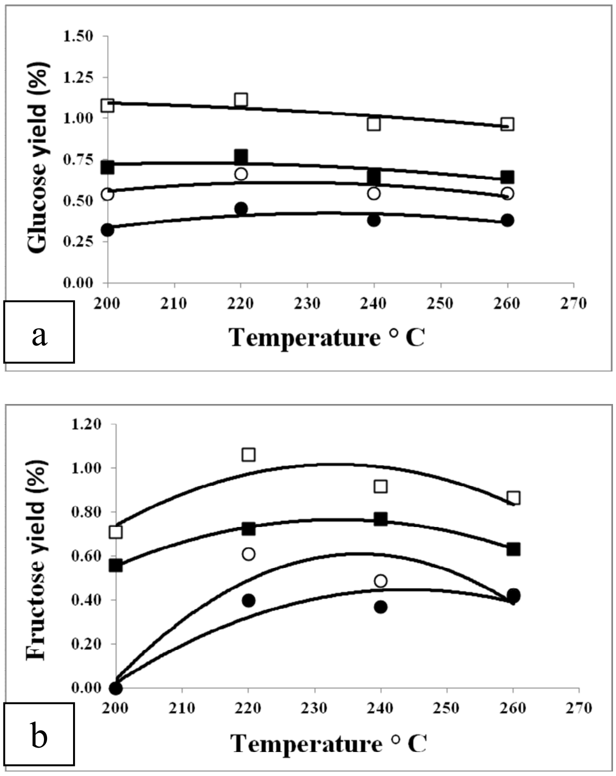

Figure 3. Effect of treating temperature on production yield of glucose and fructose obtained from hydrothermal treatment of different feedstock; □ Pulp, ■ Sludge S1, ○ Sludge S2, ● Sludge S3

Effect of Holding Time

Figure 4 shows the dependence of glucose and fructose yield on the holding time when each feedstock was kept at the targeted temperature. It could be clearly observed that with a holding time shorter than 20 min, the maximal yield of glucose and fructose could be obtained. A decrease in production yield of every monosaccharide with a longer holding time would be attributed to the higher decomposition of polysaccharides to other derivatives with smaller molecular size. Sasaki et al. reported that glucose decomposition rate which is faster than the hydrolysis rate of cellulose would become dominant with longer contacting time.(9) Therefore, hydrolyzed products would be converted or decomposed to other small compounds. Nevertheless, it should also be noted that for S3 feedstock production yield of all saccharides was significantly lower than any other cases. Without holding time, S3 feedstock could not provide yield both glucose and fructose. Theses results would be ascribed to the presence of calcium carbonate in the feedstock, which would be discussed further in the next section.

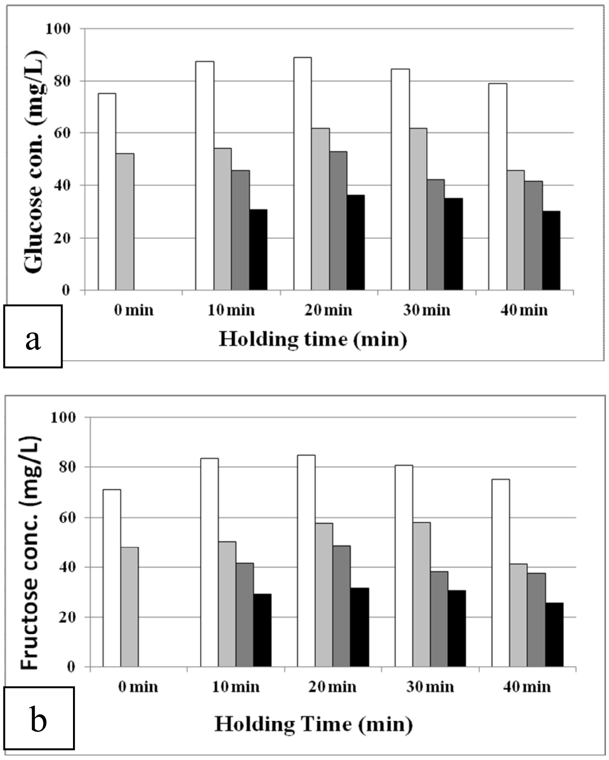

Figure 4. Effect of holding time on production yield of glucose and fructose converted from different feedstock; □ Pulp, ▨ Sludge S1, ▨ Sludge S2, ■ Sludge S3

Effect of Calcium Carbonate ($CaCO_3$)

The presence of calcium carbonate in secondary sludge would be anticipated to exert an affect on the conversion of cellulose by hydrothermal treatment because it would be dissociated to provide alkaline ions. Figure 5. reveals the dependence of glucose yield on the type of secondary sludge in comparison with the pulp feedstock. It could be clearly observed that secondary sludge which contained different amount of calcium carbonate would provide significantly lower yield of glucose. The higher the content of calcium carbonate, the lower the glucose yield. In general, hydrolysis reaction involves with H^+ which would break glycosidic bond in cellulose chain.[10)] Ragarding to reactions (2) to (5), calcium carbonate react with water, resulting in formation of CO_3^{2-}, HCO_3^-. Therefore, it is reasonably anticipated that those anions generated from calcium carbonate would react with proton ion, resulting in hindrance of hydrolysis of cellulose. As a result, formation of saccharide products would be obstructed due to the decrease in H+ ions consumed by those alkaline anions. This result is in good agreemnet with the previous report of Torii et al. focusing on conversion of pulp fibers to glucose, which was significantly suppressed by the presence of calcium carbonate added into the pulp suspension in form or Kaolin or Talc.(5)

$$2H_2O \longleftrightarrow H_3O^+ + OH^- \qquad (2)$$

$$CaCO_3 \longleftrightarrow Ca^{2+} + CO_3^{\ 2-} \qquad (3)$$

$$CO_3^{\ 2-} + H_3O^+ \longleftrightarrow HCO_3^{\ -} + H_2O \qquad (4)$$

$$CaCO_3 + H_3O^+ \longleftrightarrow Ca(OH)_2 + CO_2 + H_2O \qquad (5)$$

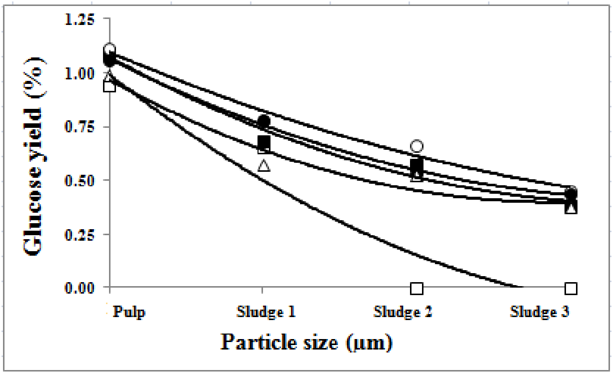

Figure 5. Dependence of glucose yield on type of secomndary sludge subject to hydrothermal treatment with different holding time : 0 min, ■ 10 min, ○ 20 min, ● 30 min, △ 40 min

Conclusion

Effect of treating temperature, holding time and calcium carbonate content on saccharide yield produced from hydrothermal treatment of secondary sludge was experimentally examined in a stainless tube reactor. Hydrolysis of cellulose is strongly dependent on the treating temperature and holding time. However, decomposition of saccharides generated from hydrothermal treatment of secondary sludge would also be enhanced by the increased temperature, resulting in a significant decrease in saccharides yield. It was also experimentally found that an optimal holding time of shorter than 20 min would provide the best saccharide production yield. Calcium carbonate would probably exhibit inhibiting effect on hydrothermal treatment of secondary sludge, suggesting that separation of calcium carbonate from the sludge should be taken into account before hydrothermal treatment of secondary sludge. The highest glucose yield obtained from hydrothermal treatment of secondary sludge could be achieved at treating temperature of 220ºC for 20 min holding time.

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