

Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 79 (2015) 220 – 225

Energy

Procedia

2015 International Conference on Alternative Energy in Developing Countries and Emerging Economies

Delignification of Elephant Grass for Production of Cellulosic Intermediate

Jurarut Minmunin^{a*}, Paiboon Limpitipanich^b, Anucha Promwungkwa^a

^aDepartment of Mechanical Engineering, Chiang Mai University, 239 Huay Kaew Rd., Muang, Chiang Mai 50200, Thailand

^bDepartment of Mechanical Engineering, Burapha University, 169 Longhard-Bangsaen Rd., Muang, Chonburi 20131, Thailand

Abstract

In this work, elephant grass, a species of Napier grass (*P. purpureum* x *P. americanum* hybrid) which contains 60.20% cellulose, 23.80% hemicellulose and 8.20% lignin, was tested in laboratory for lignin remover or delignification. Two steps of delignification were combined. Alkali pretreatment was used for determining the best condition of the first delignification. Then, a pretreated material from the best condition was tested with ozonolysis process. Five concentrations of sodium hydroxide (NaOH) with vary from 0.5 to 10.5 wt.% were used for alkali pretreatment. Ozone flow rate of 5 liters per minute for time from 10 to 30 minutes were used. The best condition for the combined process was 5.5 wt.% NaOH solution and 30 minutes of ozone flow. With this condition, 93.78% of lignin was removed and 80.59% of cellulose and 63.57% of solid were recovered comparing with an untreated one. Furthermore, the ratio of lignin to cellulose was dramatically reduced from 0.1362 to 0.0105 which advantages for ethanol production.

© 2015 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the Organizing Committee of 2015 AEDCEE

Keywords: Napier grass; elephant grass; alkali pretreatment; ozone pretreatment; delignification

1. Introduction

Due to global energy crisis, an alternative energy has been developed. In Thailand, Ministry of Energy of Thailand implemented the Alternative Energy Development Plan. As addressed by the plan, 25% of total energy consumption in Thailand's economy in 2021 must be substituted by renewable and alternative energy [1]. In transport sector, ethanol which is used for mixing with gasoline must be

* Corresponding author. Tel.: +665-394-4146; fax: +665-394-4145.

E-mail address: jurarut@hotmail.com .

produced 9 million liters per day in 2021. In 2013, the capability of ethanol production was 4.2 million liters per day, but only 2.9 million liters per day was produced [2]. Now ethanol in Thailand is made from molasses, sugarcane and cassava which are biomass having recalcitrant lignocellulosic structure [2].

To produce ethanol from a lignocellulosic biomass feedstock, fermentable sugars can be yielded by fermentation using microorganisms. Ethanol fermentation can be produced by a two-step process [3-6]. The first stage is called delignification. The process eliminates lignin from biomass which yields a cellulosic intermediate. The intermediate is reactive to ethanol with an enzymatic hydrolysis in the second step. Several pretreatment technologies have been used to convert a lignocellulosic biomass into fermentable sugars [3, 7-9]. Alkaline pretreatment, for example, is a process which removes lignin from the biomass. It also removes acetyl and various uronic acid substitutions on hemicellulose that against the enzyme to access the hemicellulose and cellulose surfaces [6, 10]. Ozone is another well-known pretreatment method. It focuses on lignin degradation by attacking and cleavage of aromatic rings structures, but hemicellulose and cellulose are hardly decomposed [11].

Most tropical countries have high potential to grow cellulosic biomass due to their solar radiation, diversity of climatic zones and biodiversity [12]. One of the potential biomass is Napier grass. It is a high potential energy crop since it has high sugar content compared with others such as cassava, sugarcane and coconut. It yields high dry matter (about 49.1 tons/hectare/year) [13], but needs low fermentation. In this work, elephant grass, a species of Napier grass (*P. purpureum* x *P. americanum* hybrid), was experimental investigated in laboratory for delignification. Alkali and ozone pretreatments were studied. The best conditions of the pretreatments that advantage for production of cellulosic intermediate were studied.

2. Materials and methods

2.1. Materials

Elephant grass used in this study was from Amphoe Hang Chat, Lampang Province, Thailand. The farming area are around 1,200 rai. Its altitude is 1,200 meters above sea level. The grass is utilized for livestock feed at Thai Elephant Conservation Center with a capacity of 500 tons per year. Following TAPPI T 203 om-88, T 223 om-88 and T 222 om-88, the dry grass contains 60.2% cellulose, 23.8% hemicellulose and 8.2% lignin.

Elephant grass which a height of 3 – 4 meters was harvested from the plant. It was cut to a small size less than 1 cm. This grass was washed with distilled water and immediately dried in an air flow. After that, the material was grinded to a particle size less than 1 mm and dried again in an oven at 103°C for hours to achieve a moisture content of less than 10 wt.%. To keep the material for delignification, it was vacuum stored in a sealed plastic bag in desiccator as shown in Fig. 1(a).

2.2. Alkali pretreatment with sodium hydroxide

The first process to remove lignin from the material was alkali. Sodium hydroxide is one that yields the highest concentration of reducing sugar comparing with others such as dilute acid and steam explosion [12]. NaOH solutions with concentration of 0.5, 3.0, 5.5, 8.0 and 10.5 wt.% were used. 20.0 g of material was immersed in the solution and incubated at 70 °C for 2 hours. Then, it was washed with distilled water until neutral PH and dried at 103 – 105 °C for 10 hours. The material was characterized to determine its composition. All contents were expressed on a dry basis throughout this work. A sample of material after alkali pretreatment is shown in Fig. 1(b).



Fig. 1. (a) Untreated material; (b) Elephant grass after alkali pretreatment; (c) Elephant grass after ozonolysis process.

2.3. Ozone pretreatment

A material from alkali pretreatment which shows the lowest ratio of lignin to cellulose was selected for ozonolysis process. Biomass which has low lignin to cellulose ratio is high potential one for ethanol production. Percent cellulose recovery, solid recovery and lignin remover are also considered since cellulose can be decomposed with alkali solution.

Before delignification with ozone, a selected material was dried at 103 – 105 °C for 4 hours. 20.0 g of material was mixed with 160 g of distilled water in a reactor. 5 liters per minute of ozone was flowed into the reactor for 10, 20 and 30 minutes. The ozone was generator from ECONOWATT model OZG gas 1000 mg. Then, the materials were washed with distilled water and dried at 103 – 105 °C for 10 hours. The material was characterized to determine its composition. A sample of material after delignification is shown in Fig. 1(c).

3. Results and discussion

3.1. Composition of sample after alkali pretreatment

Table 1 lists the major compositions of untreated and alkali-pretreated materials. The major compositions are cellulose, hemicellulose and lignin. As seen in the table, cellulose steadily increases from 60.20% of untreated material to 68.50% for 10.5 wt.% solution, but lignin slightly decreases from 8.20% to 5.20% for 5.5 wt.% solution and then rises to 6.50% for 10.5 wt.% solution. Since the sample with 5.5 wt.% solution presents the lowest portion of lignin, it is selected to proceed with ozonolysis process. The corresponding characterization of the materials are presented in Table 2. Cellulose is listed with recovery portion, while how large of removed matter are presented for hemicellulose, lignin and other. It can be seen that alkali solution decomposes all compositions. For example, the untreated material is decreased in solid matter to 46.00% for 10.5 wt.% solution. Reduction in mass of cellulose and lignin as found in this study are in agreement with various alkaline pretreatments of lignocellulosic biomass, i.e., eucalyptus residue, *Larix leptolepis* and *Pinus rigida*, as did by Park and Kim [14].

3.2. Composition of sample after ozonolysis process

Table 3 lists the major compositions of alkali-pretreated materials with ozonolysis process. It can be seen that cellulose sharply increases and lignin dramatically decreases for large in amount of ozone time. Cellulose rises from 65.39% to 76.32% for 30 minutes of ozone flow. In contrast, lignin drops from

Table 1. Major compositions of untreated and pretreated materials with alkali pretreatment

NaOH solution (%)	Composition (wt.%, based on dry matter)			
	Cellulose	Hemicellulose	Lignin	Other
0.0	60.20	23.80	8.20	7.80
0.5	61.94	23.98	7.79	6.30
3.0	63.20	24.10	7.50	5.20
5.5	65.39	25.50	5.20	3.90
8.0	65.97	24.22	5.31	4.50
10.5	68.50	21.70	6.50	3.30

Table 2. Characterization of untreated and pretreated materials with alkali pretreatment

NaOH solution (wt.%)	Solid remaining (%)	Cellulose recovery (%)	Remover (%)		
			Hemicellulose	Lignin	Other
0.0	100.00	100.00	0.00	0.00	0.00
0.5	96.10	98.87	3.19	8.66	22.44
3.0	87.00	91.34	11.91	20.43	41.99
5.5	76.51	83.11	18.03	51.46	61.73
8.0	65.94	72.25	32.90	57.32	61.92
10.5	46.00	52.34	58.07	63.54	80.51

Table 3. Major compositions of alkali-pretreated materials with ozonolysis process

Time of ozone flow (minute)	Composition (wt.%, based on dry matter)			
	Cellulose	Hemicellulose	Lignin	Other
0	65.39	25.50	5.20	3.90
10	69.77	23.22	4.20	2.81
20	74.80	21.40	1.50	2.30
30	76.32	20.48	0.80	2.40

Table 4. Characterization of alkali-pretreated materials with ozonolysis process

Time of ozone flow (minute)	Solid remaining (%)	Cellulose recovery (%)	Remover (%)		
			Hemicellulose	Lignin	Other
0	76.51	83.11	18.03	51.46	61.73
10	70.93	82.20	30.80	63.66	74.49
20	65.50	81.39	41.11	87.99	80.71
30	63.57	80.59	45.29	93.78	80.45

5.20% to 0.80% accordingly. The corresponding characterization of the materials are listed in Table 4. Cellulose is presented with recovery portion, while how large of removed matter are shown for hemicellulose, lignin and other. As increasing of ozone time, cellulose is remain stable, but hemicellulose, lignin and other are significantly removed. Ozone does not decompose cellulose during delignification, but it changes hemicellulose and lignin to soluble compound as did by Sun and Cheng [11]

3.3. Optimum pretreatment conditions

Delignification with alkali makes the grass sample losing all solid materials which are cellulose, hemicellulose, lignin and other as shown in Table 2. In contrast, ozone decomposes lignin, hemicellulose and other, but it does not destroy cellulose as presented Table 4. The best delignification condition could be one which presents low lignin and high cellulose contents or low lignin to cellulose ratio. Other factors, i.e., lignin remover and solid and cellulose recoveries are considered.

Fig. 2(a) presents the percent of lignin to cellulose for various alkali and ozone pretreatment conditions, while Fig. 2(b) shows their major compositions in percent compared with that of an untreated material. As seen in Fig. 2(a), alkali pretreatment with 5.5 wt.% NaOH presents the least lignin to cellulose ratio of 0.0796 (or 7.96%). At this condition, 76.51% of solid and 83.11% of cellulose are recoveries which are much higher than those of pretreatment with 10.5 wt.% NaOH as shown in Table 2 and Fig. 2(b). Therefore, the best condition for alkali pretreatment is 5.5 wt.% NaOH. That is why it was selected to proceed with ozonolysis process.

Ozone changes hemicellulose and lignin to soluble compound, but it does not decompose cellulose during delignification as shown in Table 4. Long time period of ozone flow could be suitable for delignification. Because almost lignin is removed for delignification with 30 minutes, it is not necessary to use ozone more this period. Therefore, the best period time for ozone pretreatment is 30 minutes. The best combined process condition of alkali and ozone is 5.5 wt.% NaOH and 30 minutes of ozone flow. At this condition, the percent of lignin to cellulose is reduced from 13.62% to 1.05% (see Fig. 2(a)). Comparing with 100% in mass of the untreated material, the remaining solid or total composition is 63.57%, while cellulose and lignin contents are 48.52% and 0.99%, respectively, as presented in Fig. 2(b).

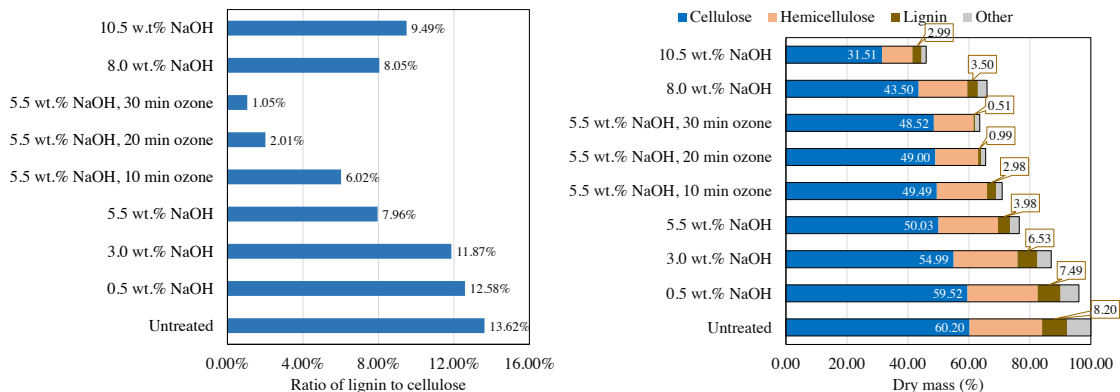


Fig. 2. (a) Ratio of lignin to cellulose of elephant grass after pretreatments; (b) Major compositions of untreated and pretreated materials which presented in dry mass compared with that of an untreated material.

4. Conclusion

Lignin in elephant grass was removed by two delignification processes: alkali and ozone. Pretreatment with NaOH solution decomposes both cellulose and lignin contents. The best concentration of alkali pretreatment is 5.5 wt.% NaOH by soaking the grass at 70 °C for 2 hours. Ozone can remove lignin and hemicellulose but it does not decompose cellulose. The best condition for the combined process was 5.5 wt.% alkali solution and 30 minutes of ozone flow. With this condition, 93.78% of lignin was removed, and 80.59% of cellulose and 63.57% of solid were recovered. The ratio of lignin to cellulose is 0.0105 which presents that almost lignin is removed from the elephant grass.

Acknowledgements

The authors would like to acknowledge the Energy Policy and Planning Office, Thailand's Ministry of Energy for their financial support. Special thanks to Northern Petroleum Development Center, Defense Energy Department, and Faculty of Engineering, Chiang Mai University.

References

- [1] Ministry of Energy, Thailand. The Renewable and Alternative Energy Development Plan for 25 Percent in 10 Years (AEDP 2012-2021). Available from: http://www4.dede.go.th/dede/images/stories/pdf/dede_aedp_2012_21.pdf; cited on April 21, 2015.
- [2] Bank of Thailand. Ethanol Situation Report 2013 and tendency to 2014. Available from: https://www.bot.or.th/Thai/MonetaryPolicy/NorthEastern/Doelib_CommodityYearly/Ethanol%20Yearly%202556.pdf; cited on April 21, 2015.
- [3] Tam-Anh D et.al. Pretreatment of rice straw with ammonia and ionic liquid for lignocellulose conversion to fermentable sugars. *Bioresource Technology* 2010; 101:7423–38.
- [4] Galbe, M., Liden, G., Zacchi, G. Production of ethanol from biomass – research in Sweden. *Journal of Scientific & Industrial Research* 2005; 64(11):905–919.
- [5] Oscar J. Sánchez, Carlos A. Cardona. Trends in biotechnological production of fuel ethanol from different feedstocks. *Bioresource Technology* 2008; 99(13):5270–95.
- [6] Ye Sun, Jiayang Cheng. Hydrolysis of lignocellulosic materials for ethanol production: a review, *Bioresource Technology* 2002; 83(1):1–11.
- [7] Chandra, R., Bura, R., Mabee, W.E., Berlin, A., Pan, X., Saddler, J.N. Substrate pretreatment: the key to effective enzymatic hydrolysis of lignocellulosics. In: Lisbeth, O. (Ed.). *Advances in Biochemical Engineering/Biotechnology–Biofuels* 2007;108, p. 368.
- [8] A.T.W.M. Hendriks, G. Zeeman. Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresource Technology* 2008; 100(1):10–8.
- [9] Nathan Mosier, Charles Wyman, Bruce Dale, Richard Elander, Y.Y. Lee, Mark Holtzapple et al. Features of promising technologies for pretreatment of lignocellulosic biomass, *Bioresource Technology* 2005; 96(6):673–86.
- [10] Chang V.S., Holtzapple M.T. Fundamental factors affecting biomass enzymatic reactivity. *Applied Biochemistry and Biotechnology - Part A. Enzyme Engineering and Biotechnology* 2000;84-86:5–37.
- [11] Y. Sun, J. Cheng. Hydrolysis of lignocellulosic materials for ethanol production: A review. *Bioresource Technology* 2002;83(1):1–11.
- [12] C. Elian, R. Jorge, R Luis. Effects of the pretreatment method on enzymatic hydrolysis and ethanol fermentability of the cellulosic fraction from elephant grass. *Fuel* 2014;118:41–7.
- [13] Kannika Rengsirikul et.al. Biomass Yield, Chemical Composition and Potential Ethanol Yields of 8 Cultivars of Napiergrass (*Pennisetum purpureum* Schumach.) Harvested 3-Monthly in Central Thailand. *Journal of Sustainable Bioenergy Systems* 2013; 3:107–12.
- [14] Yong Cheol Park, Jun Seok Kim. Comparison of various alkaline pretreatment methods of lignocellulosic biomass. *Energy* 2012; 47(1):31–5.