



Physical and chemical characterization of hydrolyzed Napier grass waste for biomass pellets

Duangkanok Tanangteerapong*

Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen 40002, Thailand

Received December 2016

Accepted March 2017

Abstract

Utilizing agricultural waste for energy and to conserve the environment has been an active research area recently. In this study, Napier grass waste resulting from its hydrolysis with acids was pelletized and its use was studied as a biomass fuel. An investigation of its physical characteristics, including pellet dimensions and weight, was performed at a laboratory scale. Flat-faced pellets were obtained with enhanced stability necessary for transportation. Chemical characterization of the hydrolyzed waste included determination of its nitrogen, chloride and sulfur content. These values were marginal. After pelletization, experimental determination of its heating values, moisture content and density was examined. It was found that these values exceeded the European standard for biomass pellets. The average of heating value of pelletized biomass was greater than 3500 cal/g. Therefore, a binding material was not necessary. Overall, the investigation revealed that the pellets produced from hydrolyzed Napier grass waste could potentially be exploited as an alternative energy source after some residual chemicals were removed.

Keywords: Napier grass, Biomass, Pellet, Waste, Hydrolysis

1. Introduction

Napier grass (or elephant grass) has been widely used as an animal feed and alternative source of energy [1-2]. Hydrolysis is one of the methods used to break down the chemical bonds of agricultural feedstocks such as Napier grass), thus producing various types of monosaccharides [3]. Recently, it was reported that the main products after acid hydrolysis of sugar cane bagasse and rice straw were xylose and pentose, which can be used as a nutrient source for microbes during fermentation [4-5]. A similar study on hydrolyzing Napier grass with acid and alkaline was also conducted [6]. A relatively high yield of solid residue after hydrolysis was obtained, approximately 60% by weight. However, these solid wastes required specialized disposal due to environmental concerns. One way in which these solid wastes can be further exploited is to produce biomass pellets that offer economical and environmental advantages such as ease of transportation, high heating values and use of waste material. In addition to numerous advantages, use of biomass materials is environmentally friendly and could mitigate environmental problems caused by fossil fuel use.

The physical characteristics and chemical composition of biomass fuels are the main factors contributing to the quality of biomass pellets [7]. If the raw biomass contains high concentrations of elements such as sulfur and nitrogen or heavy metals, it would result in pollution during combustion thus, raising the risk of greenhouse gas emissions. It has been reported that chloride, nitrogen and

sulfur can be released by combustion leading to negative environmental impacts [7]. When material containing nitrogen and sulfur is burned, these elements react with oxygen and form NO_x and SO_x gases, respectively. These gases are problematic. They cause air pollution and have an impact on the ozone layer [8]. It is therefore very important to consider the composition of biomass prior to pellet production.

In the present study, a Napier grass solid waste was hydrolyzed with two types of acid and utilized in a dry biomass pellet without inclusion of a binder. The objective of this study was to produce a biomass pellet product from Napier grass waste. The physical characteristic and chemical composition these pellets were determined for sulfur, chloride and nitrogen. The results were compared with a biomass fuel standard. The heating value, moisture content and density of the resulting product were determined.

2. Materials and methods

2.1 Hydrolysis of Napier grass

Fresh Napier grass received from Sriwiroj Company was dried at 100°C for 48 hours prior to hammer milling and passing a 100 mesh sieve. After that, 10 g of dried Napier grass were soaked in 2% v/v of either hydrochloric or sulfuric acid and hydrolyzed at 122°C and 15 psi for 90 minutes. This condition produced the highest concentration of sugar in the study of Tanangteerapong *et al.*, 2016 [6].

*Corresponding author. Tel.: +66 4336 2240 Ext. 45708

Email address: duangkanok@kku.ac.th

doi: 10.14456/easr.2017.19

Table 1 Analysis of pelletized biomass

Parameter	Analysis Method (Standard test)
Heating value (cal/g)	Bomb calorimeter (ASTM D1989)
Moisture content (%)	Dried at 105°C for 24 hours (ASTM D3173)
Specific density (kg/m ³)	Mass divided by volume of pellet (ASTM D4784)

2.2 Preparation and physical characterization of the pellet

Napier grass waste after hydrolysis was soaked and washed twice with distilled water to remove sulfuric and hydrochloric acid residues prior to drying at 70°C for 12 hours. The biomass pellet was prepared using a single pelletizer by filling the waste into a pellet die and applying pressure (Figure 1). The dimensions of individual pellets were measured using a vernier caliper.

**Figure 1** Pelletizing machine used to produce biomass pellets from dry hydrolyzed Napier grass waste

2.3 Determination of the heating value, moisture content and specific density

Physical characteristics of pelletized biomass were analyzed according to the standard methods given in Table 1. Heating values were determined using a bomb calorimeter (ASSOM, ART2060/2070). Benzoic acid was used as a standard with a heat of combustion of 6314.6 cal/g. Moisture content and specific density were determined according to ASTM D3173 and ASTM D4784, respectively [9].

2.4 Determination of sulfur, chloride and nitrogen

A mass of 200 g of dried waste sample from the hydrolysis of Napier grass with either 2% v/v of hydrochloric or sulfuric acid was measured and tested for sulfur, chloride and nitrogen according to the Manual on Fertilizer Analysis, APSRDO.DOA; 4/2551 at the Central Laboratory (Thailand) Co, Ltd. These results elements were compared with the biomass pellet standard (EN 14961-1) and fresh Napier [16].

3. Results and discussion

3.1 Pellet characteristic and dimension

Napier grass was milled before hydrolysis with a hammer mill and sieved through a No. 100 mesh sieve corresponding to a particle size of 140 µm. After hydrolysis, the particle size was smaller than 140 µm due to the breakdown of cellulosic materials. The dried residue was compacted into the pellets using a press (Figure 1) with no additional binders. The average dimensions of three randomly selected pellets are shown in Table 2. It was found that the average diameter of the uniformly flat-faced plain shape pellets was around 11 mm and the height was 4-5 mm (Figure 2). Due to the very small particle sizes, it is possible that some particles could break free of the pellet after compaction. However, increasing the compaction pressure during pelletizing could potentially overcome this problem by more densely packing the material.

Table 2 Average dimensions of pellets treated with two acids

Acid used	Diameter (mm)	Height (mm)	Weight (g)
H ₂ SO ₄	11.27 ± 0.03	4.84 ± 0.61	0.44 ± 0.02
HCl	11.47 ± 0.10	4.47 ± 0.66	0.36 ± 0.05

**Figure 2** Pellets containing dry hydrolyzed Napier grass waste

3.2 Properties of biomass pellet

After pelletization, three individual pellets similar to those in Figure 2, were used for measurement of their heating value, moisture content and density. The standard and average values are shown in Table 3. It is notable that the heating value, moisture content and specific density of the pellets after hydrolysis with two different acids appeared to meet the European pellet standard (EN 14961-1) [10]. The water content tends to have a negative effect on the energy required to dry the fuel resulting in a lower heating value. If the heating value of biomass pellets was less than 3500 cal/g, a binder, e.g., starch or molasses, might have been necessary [11]. The advantage of a binder is that it not only increases the heating value, but also increasing the compressive strength of the pellets.

Table 3 Heating value, moisture and specific density of pelletized biomass hydrolyzed with sulfuric or hydrochloric acid. The values shown are the average measurements of three measurements.

Measurement	Pellets made from waste hydrolyzed with H ₂ SO ₄	Pellets made from waste hydrolyzed with HCl	Standard (EN 14961-1)
Heating value (cal/g)	3500 ± 436	4000 ± 208	≥ 3500
Moisture (%)	4.6 ± 0.2	10.2 ± 0.4	≤ 10%
Specific density (kg/m ³)	928 ± 114	791 ± 87	> 600

Table 4 Chemical characteristics of hydrolyzed solid waste compared with the biomass pellet standard (EN 14961-1)

Element (%)	Pellets made from waste hydrolyzed with H ₂ SO ₄	Pellets made from waste hydrolyzed with HCl	Standard (EN 14961-1)	Fresh Napier grass [16]
Nitrogen	0.56	0.55	< 0.3	1.01
Chloride	0.02	1.33	≤ 0.02	-
Sulfur	1.01	0.14	< 0.08	0.27

3.3 Chemical characterization of pelletized fuel

Analyses of residual elements such as chloride, nitrogen and sulfur were examined on the hydrolyzed solid waste according to the Manual on Fertilizer Analysis, *APSRDO.DOA; 4/2551*. This was done to determine the residual amount of these elements and compare the results with the requirements of the biomass pellet standard (EN 14961-1) [10]. Several previous studies noted potential harmful effects resulting from the production of nitrogen oxides during combustion. The results shown in Table 4 show that hydrolyzed Napier grass contained residual amounts of nitrogen, chloride and sulfur. The pellets exhibited a higher nitrogen content than the standard. Therefore, NO_x emissions might result from combustion [12-13]. The chloride constituent can produce chlorinated aromatic compounds upon incineration [14]. Similarly, the content of sulfur in the pellets was slightly higher than that of standard. This was likely due to residual acids from the hydrolysis of the solid waste.

To confirm whether the residual elements in Napier solid waste resulted from the acids used during hydrolysis, the contents of nitrogen and sulfur in fresh Napier are compared in Table 4. Nitrogenous compounds are generally in high concentration in plants. They were broken down due to the high temperature of hydrolysis therefore, their nitrogen content was reduced. Adding excess air to the combustion chamber can greatly reduce NO_x production and ensure a complete combustion process [15]. Sulfur is necessary in the production of chlorophyll, but contained in lesser amounts than nitrogen. Higher contents of sulfur in the waste after hydrolysis with sulfuric acid were observed. This is likely due to the effect of residual sulfuric acid. Similarly, chloride in solid waste was increased when hydrochloric acid used for hydrolysis. This finding suggests that further washing of Napier grass waste may solve this problem.

Although these pellets had slightly high amounts of some elements, overall they had significant heating values with acceptable moisture contents and densities.

4. Conclusions

Biomass pellets made from Napier grass solid waste hydrolyzed with two different acids were produced and their properties investigated. The following conclusions can be drawn from the present study. Heating values, moisture contents and densities were acceptable and met the biomass pellet standard. Nevertheless, all pellets contained marginally excessive amounts of nitrogen, chloride and

sulfur, which might cause adverse environmental effects after combustion. It is advisable that these harmful residues be removed before pelletization. For nitrogen removal, a biological process of denitrification is suggested where nitrogen can be converted to unreactive dinitrogen gas. For chloride and sulfur, they can be removed by re-washing the waste a few more times. Overall, these results suggest that acid hydrolyzed Napier grass waste could potentially give rise to a new alternative energy industry.

5. Acknowledgements

The authors would like to thank Sriwiroj Company, Khon Kaen for providing Napier grass and also would like to acknowledge the Agricultural Machinery and Postharvest Technology Center, Khon Kaen University for their kind technical assistance.

6. References

- [1] Lewandowski I, Scurlock JMO, Lindvall E, Christou M. The development and current status of perennial rhizomatous grasses as energy crops in the US and Europe. *Biomass Bioenerg.* 2003;25(4):335-61.
- [2] Magcale-Macandog DB, Predo CD, Menz KM, Predo AD. Napier grass strips and livestock: a bioeconomic analysis. *Agroforest Syst.* 1998;40(1):41-58.
- [3] Takata E, Tsutsumi K, Tsutsumi Y, Tabata K. Production of monosaccharides from Napier grass by hydrothermal process with phosphoric acid. *Bioresour Technol.* 2013;143:53-8.
- [4] Aguilar R, Ramírez JA, Garrote G, Vázquez M. Kinetic study of the acid hydrolysis of sugar cane bagasse. *J Food Eng.* 2002;55(4): 309-18.
- [5] Sarkar N, Aikat K. Kinetic study of acid hydrolysis of rice straw. *ISRN Biotechnol.* 2013;2013:1-5.
- [6] Tanangteerapong D, Tunjaroensin T, Trakun-ung P, Kamwilaisak K. Production of reducing sugars from hydrolysis of Napier grass by acid and alkaline. *CMU J Nat Sci* 2016;16(1):31-6.
- [7] Obernberger I, Thek G. Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour. *Biomass Bioenerg.* 2004;27(6):653-69.
- [8] Hameed S, Dignon J. Changes in the geographical distributions of global emissions of NO_x and SO_x from fossil-fuel combustion between 1966 and 1980. *Atmos Environ.* 1967;22(3):441-9.

- [9] ASTM International. ASTM D3172-73 (Reapproved 1984). Standards method of proximate analysis of coal and coke gaseous fuels; coal and coke; annual book of ASTM standards. West Conshohocken: ASTM International; 1989.
- [10] European Committee for Standardization. EN14961-1: 2010. Solid biofuels - fuel specification and classes, part 1 - general requirements. Brussels: European Committee for Standardization; 2010.
- [11] Demirbaş A, Şahin A. Evaluation of biomass residue: 1. Briquetting waste paper and wheat straw mixtures. Fuel Process Tech. 1998;55(2):175-83.
- [12] Jenkins BM, Baxter LL, Miles Jr TR, Miles TR. Combustion properties of biomass. Fuel Process Tech. 1998;54(1-3):17-46.
- [13] Spliethoff H, Hein KRG. (1998). Effect of co-combustion of biomass on emissions in pulverized fuel furnaces. Fuel Process Tech. 1998;54(1-3):189-205.
- [14] Shaub WM. (1982). Procedure for estimating the heats of formation of aromatic compounds: chlorinated benzenes, phenols and dioxins. Thermochim Acta. 1982;55(1):59-73.
- [15] Fernando S, Hall C, Jha S. NO_x reduction from biodiesel fuels. Energ Fuel. 2006;20(1):376-82.
- [16] Mohammed IY, Abakr YA, Kazi FK, Yusup S, Alshareef I, Chin SA. Comprehensive characterization of Napier grass as a feedstock for thermochemical conversion. Energies. 2015;8(5):3403-17.