Lignin: a valuable feedstock for biomass pellet

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Abstract

Pelletization and briquetting have been extensively used for mass and energy densification of biomass. As the demand for pellets increases, the biorefinery waste lignin can be used with the conventional raw materials for pellet preparation. Sugarcane bagasse (20-40 mesh) is treated with NaOH (8% & 16%) for bioethanol production and obtained lignin is used to prepare pellet along with sugarcane bagasse (SB). SB, Lignin1 (8% NaOH treated SB), Lignin2 (16% NaOH treated SB) and various composition of SB and Lignin were used to produce pellets with different applied pressures (5kN, 10kN, 15kN and 20kN). Pellet density and heating value were gradually increase with the applied pelletization pressure. Among the samples Lignin1 showed highest heating value at 20kN (3581.54 kcal/kg). Results revealed that 5kN is enough to produce pellet from different composition of SB and Lignin1 and the pellet composition of SB (40%) and Lignin1 (60%) showed the highest heating value (3456.21 kcal/kg).

Keywords: Sugarcane bagasse; Alkali treatment; Lignin; Pellet; Heating value; Pressure

Introduction

In recent years biomass gaining interest not only to produce heat and power but also to reduce carbon dioxide emissions into the atmosphere. In Bangladesh lignocellulosic plants and agricultural waste biomass is available in substantial quantities, and can be utilized as sustainable energy sources (Jahan et al., 2016; Stelte et al., 2011). Energy consumption and environment concern are the key issues in recent time. A considerable amount of lignin is generated in a biorefinery, which is potential for biomaterials and biofuel (Jahan et al., 2016a; Sarkar et al., 2018). In this perspective, lignin can be a potential renewable feedstock to prepare pellet. Pellets are usually made from primary biomass materials wood residues, such as sawdust, wood shavings and wood chips, but now a days agro-residues, such as straw, sugarcane bagasse, wheat straw etc and waste products of the food industry are also used for pellet preparation (Jiang et al., 2016; Liu et al., 2016).

Pelleting and bricking is a simple process, can use various types of waste materials. Biomass pellet has some major benefits that’s are: a higher energy density, lower transportation and storage costs, prepare desired sizes and composition, which could be used as domestic and industrial purposes (Stelte et al., 2011). In lignocellulosic plant tissue, lignin can be found as deposited cell walls adjacent with cellulose and hemicellulose. It may include 15-25% of total feedstock dry matter. The lignin content in non-wood generally lower than wood and easier to separate from the plant tissue. Lignin available from biomass is an aromatic and rigid polymer and its heating value is about from 22.2 MJ/kg to 28.5 MJ/kg (Demirbas, 2017). Lignin is a complex polymer compound contained in woody plant tissue. In sugar extraction and bioethanol production from lignocellulosic materials, it is necessary to remove lignin due to its recalcitrant nature (Wunna et al., 2017). Lignin has versatile application but it requires purification which is a costly and difficult process.

The present work aimed to study the effect of direct use of crude lignin obtained from different percentage of alkali pretreatment of sugarcane bagasse for pellet making alone and in combination with sugarcane bagasse.

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Materials and methods

Materials

Sugarcane bagasse (SB) was collected from street sugarcane juice sellers and pretreated and stored as described by Sujan et al. (2018). The dried bagasse was converted into small pieces by using a crusher (locally made crusher) and 40-60 mesh size SB, Lignin1 (Lignin from SB treated with 8% NaOH), Lignin2 (Lignin from SB treated with 16% NaOH) was used in this experiment (Figure 1).

Fig. 1. (a) 40-60 mesh size SB (b) Lignin1 (8% NaOH treated SB) (c) Lignin2 (16% NaOH treated SB)

Proximate analysis

Moisture and Ash content

Moisture content of raw materials was determined by using method ASTM D 4442-07. About two grams of pretreated sample (20-40 mesh) was taken in a glass crucible and oven-dried at 105±2°C. Weight measurement was carried out in a 3 hours interval and moisture content was expressed in percent wet basis. To determine ash content, oven-dried samples were heated in a muffle furnace at 575±25°C as stated in ASTM E 1755-01.

Volatile matter

Analysis of volatile matter was accomplished according to ASTM D 271-48. Raw samples of about 4 grams were heated in a furnace for 7 min at 950±20°C. Volatile matter is then determined by measuring the weight loss, excluding weight of moisture driven off at 105°C.

Fixed carbon

The fixed carbon in percentage was calculated by difference between 100 and the sum of the volatile matter, moisture and ash content.

Ultimate analysis

Ultimate analysis of samples was done by organic elemental analyzer (Reactor temp. 900°C, He: 250 kPa, O2: 250 kPa, TCD, Flash 2000, Thermo Scientific, USA). This instrument analyzes in accordance with the procedures stated in ASTM Standard D5291-02.

Alkali treatment

SB was treated with two different concentration of NaOH. Lower %alkali was used to produce bioethanol from SB and higher % of alkali was used to separate all possible lignin content of SB. The first experiment was carried out with 8% NaOH concentration, 1 hour at 80°C whereas the second experiment was performed with 16% NaOH concentration, 1.5 hour at 150°C. Filtrates obtained from both the experiments were dried in an oven at 105°C temperature for 72 hours and stored them in air tight containers. The lignin along with extractives, hemicellulose and NaOH obtained from SB by 8% and 16% NaOH treatment were denoted as Lignin1 and Lignin2, respectively.

Pellet preparation

The pellets were prepared using sugarcane bagasse 20-40 mesh size (SB), Lignin1 (8% NaOH treated SB), Lignin2 (16% NaOH treated SB) and different composition of SB and lignin such as SB_Lignin1 40 (SB 80% & Lignin1 20%), SB60_Lignin1 40 (SB 60% & Lignin1 40%), SB50_Lignin1 50 (SB 50% & Lignin1 50%) and SB40_Lignin1 60 (SB 40% & Lignin1 60%) (Figure 2). Universal testing machine (UTM) (FS-300kN, Testometric, England) was used for preparing pellets at 25°C which has carbon steel cylindrical die (10mm diameter). Each time sample was placed into the cylinder in between two carbon steel pellets. Pressure was applied on the sample by another carbon steel pellet, a metal piston and crosshead of the UTM machine. The compression force was measured using a 300kN load cell, connected to a computer and data analysis software. Before each use of the die for preparing pellet was rinsed with acetone and wiped clean. Most of the time, sample was loaded in amounts less than 0.30g into the die and then compressed at a rate of 2 mm/min until the desired pelletizing pressure was reached and after 30s the piston was removed. The pellets were removed from the die by removal of the backstopand pushed out by applying pressure on the pellet by the same arrangement. The pelletizing pressures used in this study were 5kN, 10kN, 15kN and 20kN.

Fig. 2. Right to left (a) Bagasse pellet 4Nos. (20kN, 15kN, 10kN and 5kN) (b) Lignin1 pellets 4Nos. (20kN, 15kN, 10kN and 5kN) (c) Lignin2 pellet 4Nos. (20kN, 15kN, 10kN and 5kN) (d) SB & Lignin1 pellet at 5kN4Nos. (SB60_Lignin1 40, SB50_Lignin1 50, SB40_Lignin1 60, SB80_Lignin1 20)
Pellet density

The dimensions of pellets pelletized at different pressures were determined using Vernier or slide calipers. Their weights were estimated by using analytical balance capable of weighing accurately within ± 1.0mg up to four decimal places. Then pellet density at different pressures was calculated by taking the ratio of weight to volume of pellets.

Heating value

Gross heat of combustion of raw bagasse and pellets of lignin1, lignin2 and different composition of SB and lignin' were made at various pressures were determined according to ASTM Standard D 5865 by using oxygen bomb calorimeter (Julius Peters, Berlin- NW 21). Upon burning of the samples, the liberated heat causes the temperature to rise. The amount of heat liberated by the sample was determined by multiplying the measured temperature rise with the energy equivalent of the calorimeter. To obtain the heating value on a unit weight basis, the liberated heat was divided by the weight of the sample.

Heating value (kcal/kg) = \[W \times (T_f - T_i)/X\]

where, \(W\) is denoted as the energy equivalent of the calorimeter, \(T_f - T_i\) is the temperature increase in a calorimeter, and \(X\) is mass of the sample. Energy equivalent (\(W\)) of calorimeter was found to be 10027.42 kJ/°C by using standard benzoic acid.

Results and discussion

Proximate analysis

In proximate analysis, moisture content, ash content, volatile matter and fixed carbon of 20-40 mesh size SB, lignin1, lignin2 were determined and is presented in Table I. Primarily analysis usually evaluate the fuel characteristics of raw materials. The significance of higher ash content and moisture content in raw materials reduce the heating value (Sun et al., 2009). The ash content in SB was 1.75%, while the same in lignin was 35.65%. This large difference can be attributed by the presence of NaOH.

Table I. Proximate analysis of biomass samples

| Name of sample | Moisture content (%) | Ash content (%) | Volatile matter (%) | Fixed carbon (%) |
|---------------|---------------------|----------------|-------------------|-----------------|
| SB            | 9.44                | 1.75           | 4.99              | 83.82           |
| Lignin1       | 8.25                | 1.39           | 22.41             | 67.95           |
| Lignin2       | 7.20                | 35.65          | 33.57             | 23.58           |

Ultimate analysis

Carbon, hydrogen and oxygen are the main components in biomass. The ultimate analysis refers the elemental composition of raw materials such as carbon, hydrogen, oxygen, nitrogen and sulfur. Ultimate analysis of 20-40 mesh size SB is shown in Table II. This analysis helps to determine the quantity of air required for complete combustion, the volume and composition of combustion gases and heat of combustion of biomass which depends primarily on its carbon and hydrogen content (Poddar et al., 2014).

Table II. Ultimate analysis of 20-40 mesh size SB, Lignin1 and Lignin2

| Name of sample | Carbon (%) | Oxygen (%) | Hydrogen (%) | Nitrogen (%) | Sulfur (%) |
|---------------|-----------|------------|--------------|--------------|------------|
| SB            | 44.89     | 49.6       | 5.51         | 0.00         | 0.00       |
| Lignin1       | 45.01     | -          | 0.80         | 4.335        | 4.379      |
| Lignin2       | 23.61     | -          | 2.80         | 0.07         | 10.379     |

Heating value of biomass samples

Heating value usually express the energy content of any types of fuel. This property depends on the biomass constituents, moisture content of materials and sometimes ash content. The heating values of raw materials are presented in Table III. Among the biomass components (extractive free) lignin plays the prominent role in higher heating values other than cellulose and hemicellulose (Demirbas, 2001). Seven samples such as SB, Lignin1, Lignin2, SB_Lignin1_20% (SB 80% and Lignin1 20%), SB_Lignin1_80 (SB 60% & Lignin1 40%), SB_Lignin1_50 (SB 50% and Lignin1 50%) and SB_Lignin1_0 (SB 40% and Lignin1 60%) have been studied in this work. Among the seven samples lignin1 had the highest heating value (3581.54 kcal/kg) as the percentage of carbon content is higher i.e. 45.01% (Table II) in compare with SB and lignin2. It was assumed that Lignin2 would have contained the highest heating value due to more lignin was separated from SB with the treatment of 16% NaOH but practically Lignin2 has lowest heating value (2282.02 kcal/kg) due to lignin associated with some other substances. Although in all cases heating value was slightly increased with the increase of pelletizing pressure (Table III and Table VII) though 5kN was enough to produce pellet from all raw materials. This study also reveals that at 5kN applied pressure heating value gradually increase with increasing of Lignin1 percentage (20 to 60%) in SB as presented in Table VII.
Table III. The higher heating values of SB, Lignin\textsuperscript{1} and Lignin\textsuperscript{2} at different pelletizing pressure

| Name of sample | Higher heating values (kcal/kg) at pelletizing pressure |
|---------------|------------------------------------------------------|
|               | 5 kN | 10 kN | 15 kN | 20 kN |
| SB           |      |       |       |       |
|              | 2827.23 | 2943.73 | 3035.58 | 3173.33 |
| (4.0803)\textsuperscript{a} | (6.4676) | (3.5995) | (21.1707) |
| Lignin\textsuperscript{1} |      |       |       |       |
|              | 3266.78 | 3350.62 | 3480.11 | 3581.54 |
| (17.1817) | (26.7522) | (15.8300) | (13.3468) |
| Lignin\textsuperscript{2} |      |       |       |       |
|              | 2096.94 | 2149.29 | 2208.35 | 2282.02 |
| (3.0626) | (16.9559) | (14.6248) | (20.8380) |

Table IV. Weight of pellets at various pressures

| Name of sample | Pellet weight (g) at pelletizing pressure |
|---------------|-----------------------------------------|
|               | 5 kN | 10 kN | 15 kN | 20 kN |
| SB           |      |       |       |       |
|              | 0.2801 | 0.2772 | 0.2530 | 0.2923 |
| Lignin\textsuperscript{1} |      |       |       |       |
|              | 0.2522 | 0.2794 | 0.2668 | 0.2614 |
| Lignin\textsuperscript{2} |      |       |       |       |
|              | 0.2747 | 0.2756 | 0.2682 | 0.2801 |

Table V. Pellet sizes at various pressures

| Name of sample | Pellet sizes (mm) at pelletizing pressure |
|---------------|-----------------------------------------|
|               | 5 kN | 10 kN | 15 kN | 20 kN |
|               | Hight | Diameter | Hight | Diameter | Hight | Diameter | Hight | Diameter |
| SB           |      |       |       |       |       |       |       |       |
|              | 4.4967 | 10.2700 | 3.9533 | 10.2700 | 3.3600 | 10.2800 | 3.6733 | 10.2700 |
| Lignin\textsuperscript{1} |      |       |       |       |       |       |       |       |
|              | 2.6100 | 10.1900 | 2.7300 | 10.2000 | 2.5300 | 10.1900 | 2.4200 | 10.1800 |
| Lignin\textsuperscript{2} |      |       |       |       |       |       |       |       |
|              | 2.3100 | 10.1467 | 2.2800 | 10.1533 | 2.1600 | 10.1533 | 2.2200 | 10.1533 |

Table VI. Pellet density (kg/m\textsuperscript{3}) at different pelletizing pressures

| Name of sample | Pellet density (kg/m\textsuperscript{3}) at pelletizing pressure |
|---------------|---------------------------------------------------------------|
|               | 5 kN | 10 kN | 15 kN | 20 kN |
| SB           |      |       |       |       |
|              | 752.03 (11.1589)\textsuperscript{a} | 848.38 (33.2606) | 908.37 (13.3327) | 961.00 (6.6785) |
| Lignin\textsuperscript{1} |      |       |       |       |
|              | 1187.52 (6.2740) | 1255.38 (23.4819) | 1293.24 (5.5734) | 1328.66 (2.5028) |
| Lignin\textsuperscript{2} |      |       |       |       |
|              | 1469.23 (3.7096) | 1491.28 (2.3534) | 1536.61 (3.7733) | 1558.54 (8.7574) |

\textsuperscript{a} Number enclosed in parenthesis are relative standard deviations for n = 3
**Influence of pelletizing pressure on pellet density**

The pellet mass and sizes are represented in Tables IV and V, respectively. The diameter of pellets for seven samples such as SB, Lignin1, Lignin2, SB-Lignin1, SB-Lignin1, SB-Lignin1, SB-Lignin1, and SB-Lignin1 were almost same with increasing pressure (Table V and Table VII). Different biomass samples used for this experiment show gradual increase in pellet density with increasing pelletizing pressure from 5 to 20 kN (Table VI). Moisture content, vacuum space and particle size were decreased with the increasing pressure of pelletization which contributes to the reduction of the radial and longitudinal expansion of pellets. Although about 0.26 g of SB and Lignin1 mixture were taken to prepare the pellets used in density measurement, the final weights range between 0.2581 g and 0.2596 g (Table VII). This occurred mainly because of the interaction between moisture content, and temperature due to applied pressure (Carone et al., 2011). In case of unheated biomass, heat is generated during pelletization owing to friction between biomass particles and the press channel of die hole. Friction and temperature were increased within die because of increased pressure cause the water within the biomass to expel and the pellet mass decrease (Poddar et al., 2014).

**Conclusion**

In this study bagasse and lignin (some extractives and hemicellulose) removed from bagasse were used as valuable feedstock for biomass pelleting. Pellet density and heating value were seen to increase with the increase of pelletizing pressure 5kN to 20kN. Among SB, Lignin1 and Lignin2, Lignin1 showed highest heating value at pressure ranges from 5kN to 20kN as the percentage of carbon content is higher i.e. 45.01% than others. Although for Lignin'20kN gave slightly higher heating value but 5kN is enough to prepare pellet from it. Finally, among different compositions of SB and Lignin1 pellet samples at pressure 5kN, SB-Lignin1 sample gave the highest heating value (3456.21 kcal/kg) and more compactness compared with other compositions of SB and Lignin1/pellet samples. This result open a new pathway where crude lignin obtained from biorefinery waste could be used as alternative fuel.

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**Table VII. Pellet parameters different composition of SB and Lignin1 at 5kN pelletizing pressures**

| Name of sample | Pellet parameters different composition of SB and Lignin1 at 5kN pelletizing pressures. | \begin{tabular}{lcccc}
| Sample wt. (g) | Pellet wt. (g) | Height (mm) | Diameter (mm) | Pellet Density (kg/m³) | Heating value (kcal/kg) |
|----------------|---------------|-------------|---------------|------------------------|------------------------|
| SB80-Lignin1 | 0.2600 | 0.2581 | 4.2000 | 10.3400 | 733.66 (2.8340)\(^a\) | 3125.81 (8.2350)\(^a\) |
| SB60-Lignin1 | 0.2602 | 0.2586 | 3.8100 | 10.3350 | 809.50 (4.1125) | 3301.98 (6.4531) |
| SB50-Lignin1 | 0.2601 | 0.2593 | 3.5100 | 10.3350 | 882.32 (5.0915) | 3334.00 (10.2341) |
| SB40-Lignin1 | 0.2602 | 0.2596 | 3.3200 | 10.3350 | 925.72 (9.7293) | 3456.21 (11.8932) |
| | | | | | | |

\(^{a}\) Standard D5291-02.
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