Two-stage pyrolytic conversion of raw and pretreated bagasse into synthesis gas

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Abstract. Sugarcane bagasse is an abundant waste formed after extraction of sugarcane juice in the sugar-manufacturing process. This large-tonnage waste creates an ecological problem in countries—sugar producers. The study considers bagasse gasification, which is a two-stage pyrolytic conversion into synthesis gas. Raw bagasse and bagasse biocoal obtained by torrefaction and hydrothermal carbonization were used as initial materials. Experimental data are discussed including composition and quantity of gaseous products formed in the process. The results indicated that the process allows obtaining 1.26 m$^3$ of synthesis gas from 1 kg of raw material. Its higher calorific value is 11 MJ/m$^3$.

1. Introduction
Sugarcane bagasse is one of the largest cellulosic agro-industrial by-products [1]. It is a fibrous residue obtained after the extraction of the sucrose-rich juice from the sugarcane stalks. It contains about 50% cellulose, 25% hemicellulose and 25% lignin. Bagasse has such advantages as abundant availability, high yields, and annual regeneration capacity. Sugarcane annual global production of approximately 1.6 billion tons generates several hundred million tons of bagasse after the extraction of the sugar-bearing juice [2]. Brazil is the largest sugarcane producer in the world. Sugarcane production in this country reaches around 690 million tons resulting in around 186 million tons of sugarcane bagasse. China is the world’s third largest sugar producer, after Brazil and India [3, 4]. Thailand is also among largest producers of sugarcane with an annual production of approximately 140 million tons [5]. In South Africa about 3.3 million tons of raw bagasse is generated per annum. On average, about 30 tons of wet sugarcane bagasse (about 50% moisture) is produced per 100 tons of cane crushed per annum. Thus, for every 3 kg of cane crushed, 1 kg of bagasse is produced [6].

Bagasse is usually combusted in furnaces to generate heat and power in sugarcane mills for its own consumption. However, this method of recycling bagasse has a number of difficulties. High moisture of bagasse suppresses its combustion efficiency. Since the countries that produce sugarcane have commonly hot and humid climate, bagasse can be stored for no more than 10 weeks. Bagasse is prone to chemical biodegradation due to its hydrophilic nature [7], bagasse has low calorific value and bulk density.

There are various methods improving properties of the feedstock and solving the problem of inefficient combustion. Biomass pretreatment processes, such as torrefaction and hydrothermal
Carbonization, are promising methods to produce hydrophobic and energy-dense solid fuels. Torrefaction proceeds in the temperature range of 250–300 °C in an oxygen-free environment during about 1 h. Hydrothermal carbonization proceeds at about 200 °C in water and without air access. In this case, a pressure is corresponding to the pressure of saturated vapors at a given temperature [8].

In addition to direct bagasse combustion to produce heat and power, it can be converted to other useful forms of energy products. For the cellulosic biomass, such as bagasse, an expedient method of utilization is the processing of raw material into synthesis gas with a high calorific value.

Gasification is a partial oxidation process. The main product of gasification is a generator gas, containing mainly nitrogen, carbon monoxide, carbon dioxide, and hydrogen, and such impurities as methane and water vapor [9]. The gas can be transported and used as fuel in gas turbines or in internal combustion engines. Pyrolysis is the heating of feedstock in the absence of oxygen, accompanied with the destruction of high molecular compounds. Products obtained during the pyrolysis are liquid, solid, and gaseous. The solid residue (biochar) is usually 20 to 40% by weight of the dry feedstock [10]. Process conditions should be optimized to maximize the yields of gas, liquid, and char at different stages. The increase in the degree of conversion of the raw material to the gas can be achieved owing to the high-temperature thermal processing of the liquid fraction.

Technology of two-stage thermal conversion of biomass is developed at the Joint Institute for High Temperatures RAS [11]. The process takes place in two stages. The first stage is the feedstock high-temperature pyrolysis. In the second stage, the vapor mixture from the first stage is chemically converted over the porous carbon material at 1000 °C. Synthesis gas is formed as a result of the vapor interaction with carbon. It consists mainly carbon monoxide and hydrogen with admixtures of carbon dioxide, methane, and nitrogen. The advantage of this technology is a high conversion of raw material and the absence of a liquid fraction in products.

This study was aimed to demonstrate the applicability of this technology to the processing of sugarcane wastes. The purpose of this work is to find out how the pretreatment of the raw material will affect the gas yield, volume fractions and calorific value of the synthesis gas.

2. Materials and techniques

2.1. Raw material
Bagasse used consists of different sizes fibers. The moisture of the material was 40%. The samples were ground and dried at 105 °C to decrease moisture down to 2% by weight. The samples were stored in a desiccator.

2.2. Torrefaction
Torrefaction was carried out in a tubular reactor placed into an electric tubular furnace. A sample of bagasse was placed into the reactor and purged with argon to remove oxygen. The target torrefaction temperature was selected as 270 °C. The reactor was heated to the target temperature under heating rate at 7 °C/min and then holds there for 1 h. After torrefaction was completed, solid products were collected and placed to desiccator for further processing.

2.3. Hydrothermal carbonization
Hydrothermal carbonization process of bagasse has been carried out in an autoclave reactor, placed in an electric tube furnace. Bagasse was mixed with water in a ratio of 1 : 6. The mixture was placed into a cylindrical reactor and was kept there 6 h at the temperature of 200 °C and pressure of 16.2 bar. When hydrothermal carbonization was completed, the reactor was removed from the furnace and forcibly cooled with water to room temperature. The resulting
Table 1. The characteristics of raw materials.

| Material          | Element composition (wt %) | Ash (wt %) | Q (MJ/kg) | Lower | Higher |
|-------------------|-----------------------------|------------|-----------|-------|--------|
|                   | N  | C  | H  | S  | O  |       |          |         |
| Raw               | 0.30 | 38.68 | 4.80 | 0.05 | 54.12 | 2.05 | 12.17 | 13.26 |
| Torrefied         | 0.44 | 51.90 | 5.16 | 0.10 | 35.83 | 6.57 | 19.02 | 20.19 |
| Hydrocarbonized   | 0.19 | 52.38 | 5.79 | 0.02 | 39.28 | 2.34 | 19.44 | 20.75 |

Figure 1. The samples of raw (a), torrefied (b) and hydrocarbonized (c) bagasse.

The suspension was divided into liquid and solid residue on filter paper. The solid particles were dried at 105 °C for 24 h and placed to desiccator for further processing.

2.4. Characteristics of the initial materials

Raw materials and processed materials were analyzed using elemental analysis. Table 1 depicts the characteristics of studied materials in terms of the dry state: element composition, ash content and calorific value $Q$. The weight percentages of N, C, H and S in the initial materials were measured via a Vario Macro Cube analyzer. For the determination of ash content, a muffle furnace was used. The oxygen content was determined by difference. Calorific value was calculated.

As indicated in table 1 improving the properties of bagasse as a fuel is achieved through heat treatment. The carbon content in raw bagasse is 38.68 wt % and it can be increased up to 51.90 wt % due to the torrefaction and to 52.38 wt % due to the hydrothermal carbonization. Calorific value increased by an average of 55%. Figure 1 shows the samples of initial materials.

2.5. Porous carbon material

Charcoal was obtained by pyrolysis of wood at the temperature of 1050 °C. Similarly, bagasse charcoal was obtained. Figure 2 shows the samples of carbon materials. The bulk density of charcoal and bagasse charcoal is 250 and 96 kg/m$^3$, respectively.

2.6. Experimental set-up and the process

Figure 3 shows the lab-scale setup contained of a two-chamber fixed-bed reactor, two-section electric furnace, a glass heat exchanger and a system for collecting and analyzing gaseous
The samples of charcoal (a) and bagasse charcoal (b).

Scheme of the experimental setup.

products formed as a result of a two-stage pyrolytic conversion. The reactor in the form of a stainless steel pipe with an inner diameter 37 mm and height of 1000 mm was placed in a two-section furnace equipped with two independent heaters. In the lower and upper parts of the tube, cylindrical bowls were installed fitted tightly to the walls of the reactor. The initial material was located in the lower bowl. The porous carbon material was placed in the top bowl of the reactor. The mass ratio of carbon and initial material was 1:1.5. The assembled set-up was purged with argon to provide the absence of oxygen. At the beginning of the experiment the upper part of the reactor was heated up to temperature of 1000 °C and then was held further...
at the constant level. After that the lower part of the reactor was heated up to temperature of 1000 °C. The heating rate was 7 °C/min. The temperature inside the upper and lower parts was controlled by means of thermocouples.

The gaseous and vaporous products formed during the pyrolysis process passed through charcoal at the temperature of 1000 °C. As a result of homogeneous and heterogeneous chemical reactions in the high-temperature zone, the pyrolysis products decomposed, forming mainly hydrogen and carbon monoxide. The resulting gas mixture passed through a glass heat exchanger and was cooled to room temperature. The volume of non-condensable gases was measured by drum-type gas meter. The composition of the collected gas was determined using the gas flow analyzer Vario Plus Industrial.

3. Results and discussion
Experiments were conducted with six different combinations of samples in the lower and upper bowls. Raw bagasse (RB), torrefied bagasse (TB), and hydro carbonized bagasse (HCB) were used as the initial materials and were placed in lower bowl. Coal obtained from wood (charcoal or CC) and coal obtained from raw bagasse (bagasse charcoal or BCC) was used as the porous carbon material in the upper part of the reactor.

The calorific value of the gas mixture obtained by a two-stage pyrolytic conversion of initial materials was calculated on the basis of experimental data. Table 2 shows the characteristics of the obtained gas mixture, such as volume fractions of components, gas yield per 1 kg of feedstock and calorific value calculated for a temperature of 20 °C.

Table 2 shows that the composition of the obtained gas mixture is almost the same for all experiments. It is observed that the resulting gas is composed of hydrogen and carbon monoxide in the amount of 95–97%. Hence, it could be deducted that synthesis gas is obtained as a result of heat treatment of bagasse using this method. The gas yield ranges from 0.96–1.26 m³ per 1 kg of raw material. Higher calorific value of the gas mixture reaches 11.84 MJ/kg.

Table 2 also shows the influence of the choice of raw and carbon materials on H₂-to-CO volume ratio $R_{H_2/CO}$. For synthesis gas derived from raw bagasse this ratio is in the range of 0.81–0.83; from torrefied bagasse is nearly 0.9; from hydro carbonized bagasse is about 0.64–0.69. Interestingly, the choice of carbon material ambiguously affects the H₂-to-CO volume ratio. For example, for torrefied and hydro carbonized bagasse, charcoal gives a greater ratio than bagasse charcoal, and vice versa for the raw bagasse.

Table 3 shows the characteristics of the obtained pyrocarbon. The yield is calculated as the ratio of the mass of dry residue in the lower bowl of the reactor to the dry mass of the raw material. The carbon efficiency is calculated as the ratio of the mass of carbon in the residue to the mass of carbon in the starting material in terms of the dry state.

| Material | Carbon | Fractions (vol %) | Gas yield (m³/kg) | Q (MJ/m³) | $R_{H_2/CO}$ |
|----------|--------|-----------------|-----------------|----------|---------------|
|          |        | CO              | CO              | H₂       | CH₄           | N₂          | Lower | Higher |
| RB CC    | 1.80   | 52.82           | 42.67           | 1.81     | 0.90          | 1.18        | 10.90 | 11.71 | 0.81 |
| RB BCC   | 1.80   | 53.05           | 43.94           | 0.34     | 0.87          | 1.26        | 10.78 | 11.59 | 0.83 |
| TB CC    | 1.23   | 51.04           | 46.32           | 0.88     | 0.53          | 1.10        | 10.96 | 11.84 | 0.91 |
| TB BCC   | 0.60   | 51.59           | 45.90           | 0.59     | 1.32          | 1.03        | 10.89 | 11.75 | 0.89 |
| HCB CC   | 1.81   | 56.65           | 39.22           | 0.92     | 1.40          | 0.93        | 10.92 | 11.67 | 0.69 |
| HCB BCC  | 2.76   | 57.94           | 37.15           | 0.83     | 1.32          | 1.14        | 10.84 | 11.54 | 0.64 |
Table 3. The characteristics of the pyrocarbon.

| Material | Yield Carbon (%) | Carbon efficiency (%) |
|----------|------------------|-----------------------|
| RB CC    | 23.63            | 55.08                 |
| RB BCC   | 35.00            | 73.21                 |
| TB CC    | 39.72            | 66.64                 |
| TB BCC   | 48.01            | 79.13                 |
| HCB CC   | 38.88            | 57.85                 |
| HCB BCC  | 43.79            | 74.67                 |

Figure 4. Two-stage thermal conversion of bagasse.

Figure 4 illustrates the gas yield as a function of the temperature of the material in the bottom bowl in the reactor. It is observed that the thermal degradation of the raw bagasse mainly occurs at temperatures between 200 and 500 °C. However, thermal degradation of torrefied and hydro carbonized bagasse begins at temperatures above 300 °C. This is explained by the fact that torrefied and hydro carbonized materials have already been thermally processed at temperatures of 270 and 200 °C, respectively. Therefore, devolatilization has already occurred at these temperatures. For the same reason, the gas yield corresponding to heat treatment of torrefied and hydro carbonized bagasse is lower by 7 and 21% compared to raw bagasse, respectively (charcoal is carbon material); by 19 and 11% compared to raw bagasse, respectively (bagasse charcoal is carbon material).
4. Conclusions

Two-stage thermal conversion of raw and pre-processed bagasse was performed. This technology allows obtaining synthesis gas from sugarcane waste. Changes in the raw materials and the carbon materials did not significantly affect the calorific value and composition of the synthesis gas obtained by the two-stage pyrolytic conversion of bagasse. However, the pretreatment of the raw material slightly reduced the synthesis gas yield and also led to additional energy spent and complicated the technology. Despite these drawbacks, the pretreatment may be a necessary measure in hot and humid climate where sugar cane grows.

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