Evaluation of Pyrolysis and Steam Gasification Processes of Sugarcane Bagasse in a Fixed Bed Reactor

Jaiver Efren Jaimes Figueroa*, Y. Camacho Ardila, B. Hoss Lunelli, R. Maciel Filho, M. R. Wolf Maciel

Department of Process and Product Development. School of Chemical Engineering. Av. Albert Einstein, 500. Cidade Universitária "Zeferino Vaz", CEP 13083-862. State University of Campinas - UNICAMP. Campinas-SP, Brazil. jaiverej@hotmail.com

Sugarcane bagasse is the main byproduct of sugarcane mill, ready available at the production site so that it may be a suitable raw material for the production of biofuels, chemicals and electricity. Among the methods that have been widely studied, there are thermochemical processes such as gasification, pyrolysis and direct combustion. The direct combustion is used to produce electricity while the pyrolysis and gasification are used to obtain high value-added products such as bio-oil and synthesis gas (Syngas). In this study we performed a comparison between the experimental results by pyrolysis and gasification reactions. The pyrolysis and gasification of sugarcane bagasse was carried out, using a laboratory-scale fixed bed reactor in order to produce bio-oil (pyrolysis) and Syngas (gasification). The gasification and pyrolysis were studied and evaluated the char, tar and gas production as well as the composition of the gas produced. For the pyrolysis temperature was varied from 500 °C to 900 °C and a quite broad reaction time range was considered. In gasification were evaluated the reaction temperature equal to 900 °C, reaction time and steam/bagasse ratio equal 2.0. The behavior for both process was presented.

1. Introduction

The thermochemical processes such as pyrolysis and gasification produce, besides hydrogen, a gas mixture containing carbon monoxide (CO), carbon dioxide (CO₂) and light hydrocarbons. This gas is used in many industrial applications such as production of methanol, hydrogen, ammonia, sulphuric acid, formaldehyde or like saturated steam gas turbine. The pyrolysis process at low temperatures (400 - 600 °C) is formed of liquid and gaseous products are formed from high temperature (900 °C). Gasification and pyrolysis are similar processes however the gasification takes place in the presence of oxygen in the form of air or steam whereas the pyrolysis occurs in the absence of oxygen (Zhou et al., 2008).

Gases and liquids produced in the pyrolysis and gasification processes can be used as energy, as heat and electricity or chemicals production. For example, gases with high contents of CO and H₂ can be a source of synthesis gas (for methanol, DME or Fischer-Tropsch synthesis) or H₂ (fuel cells) (Baumlin et al., 2006).

Products with high added value such as hydrogen or synthesis gas can be produced from pyrolysis of bagasse using a fixed bed reactor. The synthesis gas comprises a mixture of hydrogen and carbon monoxide (H₂+CO). The pyrolysis of sugarcane bagasse can be accomplished in two ways, with or without carrier gas (nitrogen). The literature emphasizes that it is very difficult to perform this process without the use of carrier gas (N₂), this occurs because the formation of soot. The presence of the carrier gas provide a uniform distribution of the reagent in the reactor bed (Skoulou and Zabaniotou, 2013).

The gasification process can be defined as a process of partial combustion of sugarcane bagasse because it uses an amount of air less than that required stoichiometrically. The gaseous product is obtained consisting of hydrogen (H₂), carbon monoxide (CO) and carbon dioxide (CO₂), comprising the synthesis gas (Lan et al., 2013).
Unlike pyrolysis, gasification occurs in the presence of oxygen in the form of air, pure oxygen or steam it is not necessary therefore to use a carrier gas. The gasification corresponds to a thermal conversion process of the biomass into reactive atmosphere (air, O$_2$, steam). The goal is to produce a maximum fraction of gaseous products (mainly CO and H$_2$) (Baumlin et al., 2006).

Thus, this paper presents the use of a fixed bed reactor, (property of Laboratory of Optimization, Design and Advanced Control - LOPCA) for production of synthesis gas from pyrolysis and gasification of sugarcane bagasse. The influence of the temperature, reaction time and steam on: the final distribution of gas, tar and char as well as gas composition obtained were evaluated.

2. Materials and methods

2.1 Raw material

Sugarcane bagasse previously milled (from Costa & Pinto mill located in the state of São Paulo - Brazil) with a particle size of about 0.36 mm was used as the raw material in this work. The ultimate and proximate analysis of raw material is presented in Table 1.

### Table 1: Heat value, proximate and ultimate analysis of sugarcane bagasse

<table>
<thead>
<tr>
<th>Proximate analysis (wt %)</th>
<th>Ultimate analysis (dry and free of ashes wt %)</th>
<th>Heating value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Low</strong></td>
<td><strong>High</strong></td>
</tr>
<tr>
<td>Moisture content</td>
<td>2.00</td>
<td>44.6</td>
</tr>
<tr>
<td>Ash content</td>
<td>6.52</td>
<td>5.9</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>88.12</td>
<td>42.1</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>3.36</td>
<td>0.2</td>
</tr>
<tr>
<td><em>By difference</em></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2 Pyrolysis and gasification system and reaction conditions

Figure 1 shows a schematic drawing of plant for producing synthesis gas that has been acquired and is present in lab. The plant for producing Syngas is proposed in laboratory scale, which allows optimization of process conditions with reduced costs. This plant is available in the LOPCA and the reaction conditions are reported in Table 2.

![Figure 1: Syngas production flowsheet (system developed by LOPCA research group). Aluminum oxide and silica used in the pyrolysis and gasification, respectively.](image-url)
Table 2: Reactions conditions

<table>
<thead>
<tr>
<th></th>
<th>Pyrolysis</th>
<th>Gasification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>Bagasse (50 wt%)</td>
<td>Bagasse (50 wt%)</td>
</tr>
<tr>
<td>Packed material</td>
<td>Aluminum oxide (50 wt%)</td>
<td>Silica (50 wt%)</td>
</tr>
<tr>
<td>Carrier gas (mL/min)</td>
<td>Argon (77.5)</td>
<td>Argon (34)</td>
</tr>
<tr>
<td>Reactor purge time using carrier gas</td>
<td>20 min</td>
<td>20 min</td>
</tr>
<tr>
<td>Condenser temperature (°C)</td>
<td>0.0 -5.0 °C (Ice)</td>
<td>0.0 - 5.0 °C (Ice)</td>
</tr>
<tr>
<td>Water (mL/min)</td>
<td>0</td>
<td>0.017</td>
</tr>
<tr>
<td>Reaction time (min)</td>
<td>135</td>
<td>180</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>500 - 900</td>
<td>900</td>
</tr>
<tr>
<td>Gaseous samples collected</td>
<td>3</td>
<td>9</td>
</tr>
</tbody>
</table>

2.3 Analytical methods for gases quantification
Gaseous products analyses were performed on a gas chromatograph (GC) Agilent Technologies, model 7890A, configured to analyze gases (inorganic and organic light). The chromatograph had two columns: column 1: HP Plot U, 30 m length and diameter, 53 mm and column 2: HP - Molecular sieve, 30 m in length and diameter, 53 mm. The GC is equipped with a thermal conductivity detector (TCD) monofilament and flame ionization detector (FID), with a detection limit of 0.10 %mol/mol for analyses. The columns, detector and sample circuit are connected to a 6-way valve with pneumatic actuator. The mobile phase used was Argon 5.0. Programming oven temperature: 4 min at 50 °C, 8 °C / min to 140 °C, 0.75 min at 140 °C with total analysis time of 16 min until complete elution of propane; spin valve set at 4.20 min. Elution order: H₂, air, CO, CH₄, turning valve, CO₂, ethylene, ethane, propane.

2.4 Pyrolysis of sugarcane bagasse
The pyrolysis process of bagasse is highly temperature dependent. When the pyrolysis is carried out at low temperatures (between 400 and 600 °C), most of the product is liquid, while at temperatures above 750 °C gaseous products are formed. Thus, the determination and control of the process temperature are very important because the desired products are temperature dependent.

The bagasse and aluminium oxide previously dried and weighed, were placed into the reactor. Was used glass wool at the bottom and at the top of the reactor in order to support the fixed bed (bagasse-alumina) and improve the distribution of the carrier gas, respectively.

The reactor was sealed and placed inside the electric oven (100 mm x 100 mm x 163 mm). The valve allows the passage of the carrier gas was opened, allowing the purging of the system for about 15 min. After the input and output valves closed reactor until the furnace temperature reached the reaction. After reaching the reaction temperature was allowed to pass the carrier gas.

The flow rate of carrier gas was adjusted using a needle valve and monitored by a flow meter. The reactor has a stainless steel 130 mm long with an internal diameter of 10.75 mm. The fixed bed occupies 54 % of the reactor, having a length of 70 mm. The reactor temperature is measured at the outer wall of the reactor by means of a thermocouple J.

The reactor product is condensed using an ice-bath with sodium chloride, then forms a liquid stream that is stored in the collector liquid and a gas stream which is collected using collectors type gas bag (SKC Inc., USA) specific for storage of light gases. The liquid product was withdrawn from the condenser and weighed. The gaseous product collected from time to time in the bags was analyzed according to the methodology described below.

At the end of procedure, the reactor was cooled after the removal of a sample of material that was inside. For subsequent calcination and determining the char percentage (discounting in calculation the value of bagasse ash).

Following the procedure described above, several experiments were performed in which the reaction temperature ranged from 500 °C to 900 °C. Gas was collected three times at intervals of 45 min, thereby giving a reaction time equal to 135 min.

2.5 Gasification of sugarcane bagasse using steam at 900 °C
The operating procedure and sample collection in the gasification reaction was exactly like the pyrolysis process, the only difference was that: when the reaction temperature was reached, was allowed the passage of carrier gas and the water. Water was fed by means of a HPLC pump (Waters model 515 analytical pump) which controlled the flow of water throughout the reaction.

Water was supplied in liquid form, but when it came to the reactor existed instantaneous vaporization, which allows us to say that entering the bed reaction was steam.

Only one reaction was performed using a gasification relationship SB = 2. The relationship SB is defined in Eq. (1) and presented below:
3. Results and discussion

3.1 Pyrolysis: gas, tar and char distribution

The following are presented the results obtained from the pyrolysis process, considering the influence of temperature on the amount of gas, tar and char produced as well as the composition of gases obtained in each reaction.

Figure 2 shows the percentages of gas, tar and char when used different reaction temperatures. Figure 2 shows clearly that the increase of temperature favours the production of gas. This increase causes the amount of char is decreased since the production of tar remained almost constant in all reactions. The most significant increase was obtained in the change of temperature of 700 °C to 800 °C, managing to increase the gas percentage by 8.5 wt%.

With those profiles, it can be concluded that the process as was performed presents no great advantage to produce tar or more known as bio-oil, because the production was almost the same in all experiments performed in 22.11 % average. This may have happened for the temperature range used, which was greater-equal 500 °C, range which was not favourable the production of tar.

From the viewpoint of gas production, which is the main objective, it is concluded that the pyrolysis process, needs to be improved. The amount of char is very high which says there is potential to crack this char and turn it into gas.

![Figure 2: Weight percentage Gas, Tar and Char at different temperatures in the bagasse pyrolysis](image)

3.2 Composition of pyrolysis gases

Subsequent to the distribution analysis of gas, tar and char were quantified the gases produced at different temperatures. Figure 3 presents the molar composition of the gas collected after 135 minutes of reaction. As can be appreciated in Figure 3, the molar composition of the gas depends strongly on the reaction temperature, i.e. depending on the temperature some components are not produced.

![Figure 3: Molar composition of pyrolysis gases](image)
With these results it was concluded that:
1) The CO₂ and CH₄ gases which are produced at any temperature (Ardila et al., 2012). Having maximum values of 70 % (T = 500 °C) and 35 % (T = 700 °C), respectively. Minimum values of 20.66 % (CO₂) and 18.14 % (CH₄) at the temperature of 900 °C.
2) The CO which is a component of interest is produced in only relatively low values T = 600 °C and high values T = 800 °C and T = 900 °C. No produces at intermediated temperatures.
3) The hydrogen is produced at temperatures exceeding 600 °C, and the maximum value (49.10 %) at 800 °C.
4) At temperature of 600 °C were produced organic light gases: butane (1.14 %) and ethane (0.51 %). In other experiments were not detected by the chromatograph any other gas.

3.3 Composition variation of the pyrolysis gases with time and temperature constant
The experiment at 900 °C was selected to study the variation of the gas composition during the reaction time. The composition profiles are reported in Figure 4.

As can be appreciated from Figure 4, the gas composition does not vary with time. Coupling this with the information obtained from Figure 3, it can be concluded that the composition of the pyrolysis gases is independent of time and dependent of reaction temperature.

3.4 Bagasse gasification at 900 °C using steam
The gasification reaction at 900 °C using steam present a very different behaviour than shown in the same pyrolysis temperature. The distribution of gas and char percentages changed significantly. In this temperature the product distribution was char 7 wt%, tar 27 wt% and gas 66 wt% agreeing with the results obtained by Figueroa et al. (2012).

The amounts of tar and gas increased, which consequently led to decrease the char. This type of behavior is highly favorable. Another important point was that the percentage of gas obtained was 66 wt%. The high gas production is the main objective of gasification, but it was also important to know what kind of gas had been produced. So chromatographic analysis was done on gas samples collected from time to time, to be
able to report on the final composition of the gases accumulated at each moment. The molar composition profiles of the gases versus time are shown in Figure 5.

In Figure 5 it was possible to appreciate that the compositions of CO₂ and CH₄ remain almost constants over time. The changes are more visible in the profiles of H₂ and CO in which the H₂ increases while that of CO decreases. This is the typical behaviour of the reaction Water-Shift.

![Figure 5: Composition profiles obtained in the gasification gas (T = 900 °C and SB = 2.0)](image)

4. Conclusions

The pyrolysis and gasification processes have the potential to transform crushed sugarcane bagasse to gases, which are mainly composed of H₂, CO, CO₂ and CH₄.

In the tar production (bio-oil) were obtained values close in the experimental tests carried out at different temperatures, i.e. for each 100 g of bagasse used were produced approximately 20 to 30 g of tar. This behaviour may be due to the studied temperature range (T > 500 °C). According to the literature, at lower temperatures the amount of tar always increases.

The use of an agent gasifier, in this case steam, promotes the increased quantity of gas produced, reaching almost 70 wt% and furthermore decreases the production of char, indeed highly desirable.

The fixed bed reactor is a recommended equipment to study the pyrolysis and gasification reactions at laboratory scale. What allows you to use small amounts of raw material and lower operating times.

5. Acknowledgment

This research was supported by CNPq and BIOEN - FAPESP.

References


