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CO_2 gasification of elephant grass in a fixed bed reactor

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Abstract

In order to supply the growing world demand of energy and relieve the global warming, biomass is considered a potential clean energy source. In this work, the thermochemical conversion of the elephant grass, through CO_2 gasification, for the production of a combustible gas was evaluated. The gasification experiment was conducted at the temperature of 900 °C for 90 min under a carbon dioxide atmosphere. CO presented a maximum production rate of 2.25 mmol/min.$g_{biomass}$ and a maximum concentration of 82 %mol/mol. The fuel gas produced had an average high heating value of 8.5 MJ/Nm³. Considerable hydrogen production rates were observed throughout the experiment. The experiment had an energy yield of 28.4 kJ/$g_{biomass}$. Tar produced was mainly composed of primary products and phenolic derivatives compounds. The results showed that CO_2 gasification of elephant grass has the potential to produce a combustible gas allowing the reduction of CO_2 emissions to the atmosphere.

Keywords

CO_2 gasification. Elephant grass. Renewable energy.

I. INTRODUCTION

The explosive increase in energy consumption is one of the critical challenges faced by world today. A significant percentage of the currently consumed energy derives from fossil fuels, such as petroleum, coal and natural gas [1]. According to Kirkels and Verbong [2], the search for a reliable, affordable, and clean energy supply will prove to be crucial in the 21st century. In this respect, biomass has been widely recognized as alternative and potential energy source to supply the actual and future energy consumption demands [3]. Countries with high biomass production capacity (e.g. Brazil) will be able to significantly decrease their dependence on foreign fossil fuels. Biomass is a CO_2 neutral and environmentally friendly energy source, as it is formed by the plant photosynthesis process, which absorbs CO_2 from the atmosphere [1].

Although the first generation biofuels can offer some CO_2 benefits, there are concerns about the impact it may have on biodiversity and competition with food crops [4]. Second generation biofuels can be obtained via biochemical or thermochemical routes, by using either non-food crops, purpose-grown perennial grasses, trees or residues [5]. Combustion, pyrolysis and gasification are three main thermochemical conversion methods. According to Asadullah [6], gasification is one of the most promising technologies to exploit energy from renewable biomass. Gasification converts biomass through partial oxidation into a gaseous mixture of syngas consisting of hydrogen (H_2), carbon monoxide (CO), methane (CH_4) and carbon dioxide (CO_2) [7]. As carbon emissions become increasingly regulated, gasification based technologies are benefited from its characteristics, offering increased efficiency and allowing carbon capture and storage [2]. In this sense, the modern use of biomass (as opposed to the traditional combustion) is considering very promising [2; 8]. Furthermore, the use of CO_2 as gasifying agent in gasification processes provides a reliable and long-term alternative to mitigate the accumulation of CO_2 in the atmosphere and allows for production of clean fuels [9].

Elephant grass (*Pennisetum purpureum,* Schum.) is a perennial grass of the *Poaceae* family, which is a promising source of renewable energy due to its fast growth (can be harvested up to four times a year), disease resistance, easy adaptability and can grow on different types of soils [10]. Even though most of works in biomass gasification has been performed on wood, according to Mohan, Pittman and Steele [11], nearly 100 types of biomass have been already tested, ranging from agricultural wastes to energy crops. Despite the numerous papers published, biomass gasification with CO_2 as gasifying agent is seldom addressed [1]. Therefore, the objective of the present study was to evaluate the gasification of elephant grass with CO_2 and to perform the characterization of the fuel gas produced.

II. MATERIAL E METHODS

The elephant grass used in the gasification experiments was planted in a rural unit of the University of Caxias do Sul. The biomass was milled in a knife mill and sieved to select the granulometry in between 425 and 841 μm (40 to 20 Tyler mesh), suitable for the gasification experiment. Prior to the experiment, the sample was dried in an oven at 105 °C for 10 h.

In this work, the elephant grass gasification was conducted with 20 g of sample in a laboratory scale tubular reactor which operates in batch system. The reactor is heated by two electrical resistances and the temperature is measured by two type K thermocouples positioned inside the reactor. Fig. 1 presents the gasification system used in the experiment. A complete description of the reactor was given by Perondi et al. [12]. Initially, the furnace was heated until the final

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temperature of 900 °C. After reaching the desired temperature, the CO_2 flow rate was set at 0.5 NL/min, the tubular reactor. was inserted into the hot furnace and the gasification experiment was started

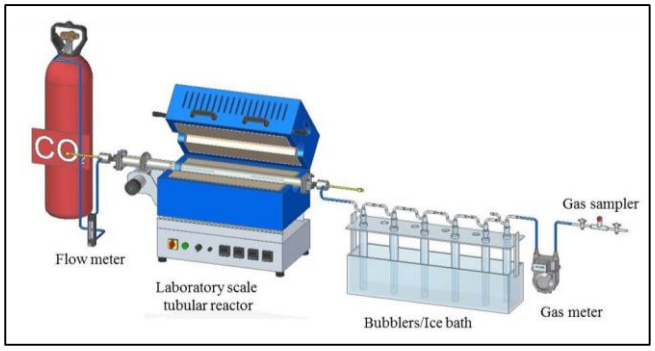

Fig. 1: Gasification system used in the experiment.

The removal of the condensable vapors was conducted with six bubblers. In each one, 100 mL of isopropyl alcohol was added, with the exception of the first and last bubbler which remained empty. All the bubblers were placed in an ice-bath in order to keep them under low temperature. The chemical characterization of obtained tar was carried out in a Bruker Scion 456 TQ GC-MS system equipped with a HP-5MS (30 m x 250 µm) capillary column. An initial temperature of 37 °C and a final temperature of 320 °C was used. From 37 to 200 ºC the heating rate was 12 ºC/min, 200 to 320 ºC the heating rate was 5 ºC/min and the total time was 37.58 min. The injector temperature was 280 ºC and He was used as a carrier gas at a flow rate of 1.0 mL/min. The compounds obtained in the chromatograms were identified by matching with those of the National Institute of Standards and Technology (NIST) mass spectral library, together with literature data to obtain the highest likelihood of compound identification.

The non-condensable gases were collected at intervals (3, 6, 9, 12, 15, 20, 25, 30, 45, 60, 75 and 90 min) and were analyzed by using a gas chromatograph Dani Master GC. The gases analyzed were H_2, CO, CO_2 and light hydrocarbons ($<C_5$). H_2/CO/CH_4/CO_2 analysis was performed using a thermal conductivity detector. A capillary column Carboxen™ model 1006 (30 m x 530 µm) (SUPELCO) was used. Hydrocarbons (CxHy) with higher molar mass were identified from a flame ionization detector (FID) and a PLOT-Al_2O_3/KCl (50 m x 530 µm) capillary column of Agilent® Technologies.

The non-condensable gases volume was measured with a diaphragm type gas meter with capacity to measure flow rates in the range of 0.27 to 27 L/min. At the end of the gasification experiment, the reactor was cooled to room temperature and the remaining solid was collected.

III. Results and Discussion

The mass balance for CO_2 gasification of elephant grass at 900 °C is presented in Fig. 2. The overall mass balance achieved was 99 %. According to De Conto et al. [13], the elephant grass presents an ash content of 8.3 wt.%. Thus, based on the solid yield (10.5 wt.%) it can be concluded the process was conducted until almost complete conversion of the biomass.

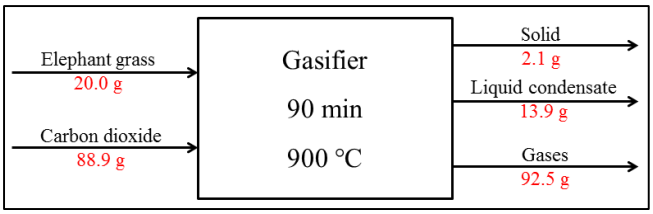

Fig. 2: Mass balance for CO_2 gasification of elephant grass.

The concentration of non-condensable gases produced in the gasification experiment is shown in Fig. 3. As can be seen from the figure, some time is needed for the system to achieve the stabilization. This behavior is mainly due to the initial heating of biomass until the working temperature of 900 °C. The CO concentration in the gas increased continuously until 9 min and then it remained in a value of approximately 80 %mol/mol during the time interval of 9 - 30 min. Similarly, CO_2 presented a stable concentration of 10 %mol/mol in the same range. The composition gas profile described supports the occurrence of Boudouard reaction (Equation 1), responsible for the high concentration of CO in the non-condensable gases. Moreover, according to Pohořelý et al. [14], the Boudouard reaction presents a very slow kinetic, and this characteristic was responsible for the slow consumption of carbon in the solid resulting in the constant CO and CO_2 concentration profile observed in the time interval of 9 - 30 min in Fig. 3.

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2\,CO_{2(g)} \qquad (1)$$

Fig. 4 shows the average gas production rate (H_2/CO/hydrocarbons) at different intervals of time throughout the experiment. Therefore, the CO_2 average production rate was not reported in the graphic. After the initial transitional stage, the higher gas production rates were obtained.

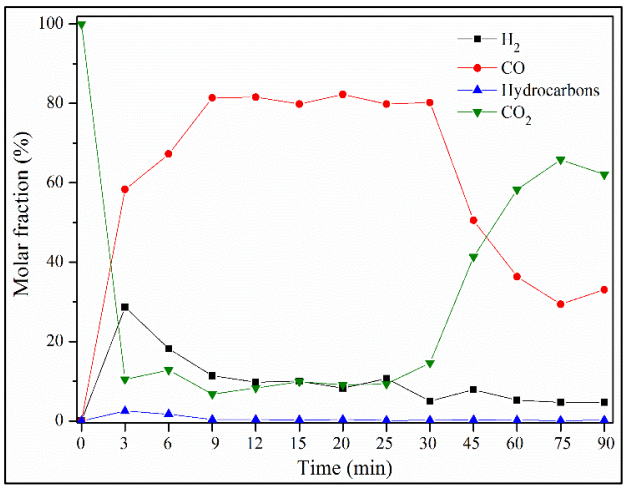

Fig. 3: Molar fraction of non-condensable gases in the gasification experiment.

The CO achieved the maximum production rate of 2.25 mmol/min.$g_{biomass}$ and then decreased continuously over time. The maximum production rate observed in the initial stage is due to the cooperation of the initial devolatilization of organic mater and the high concentration of carbon in the remaining

solid material. The continuously reduction of carbon content in the solid material throughout the experiment caused the expected reduction of CO production rate.

Although H_2 concentration kept reasonably constant during the experiment (Fig. 3), the continuous reduction in the volume of gas produced caused the decrease in H_2 production rate observed in Fig. 4. Taking into account the energy contained in the fuel gas, the gasification presented an energetic yield of 28.4 kJ/$g_{biomass}$.

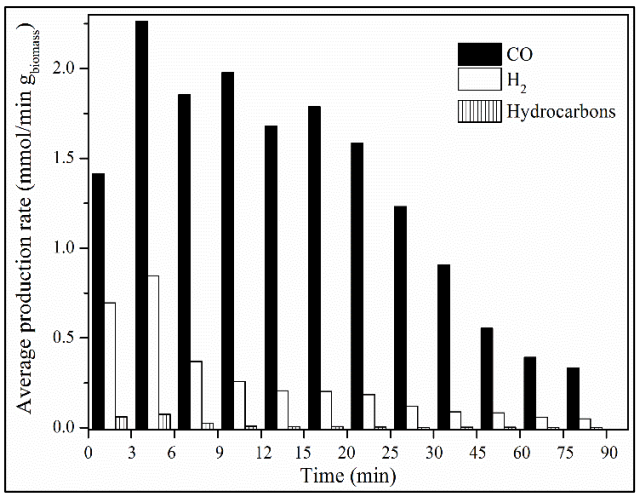

Fig. 4: Average production rate of non-condensable gases in the gasification experiment.

Since the higher gas production rates were obtained in the initial stage of the experiment, this stage is responsible for most of the energy produced. Fig. 5 shows the accumulated energy produced as well as the contribution of the gas produced along the experiment in the total energy production. It can be seen from the figure that about 50 % of the energy was produced in the first 20 min. Furthermore, as the CO is the main combustible component contained in the non-condensable gas, the energy production rate profile presented in Fig. 5 is very similar to the CO average production rate shown in Fig. 4.

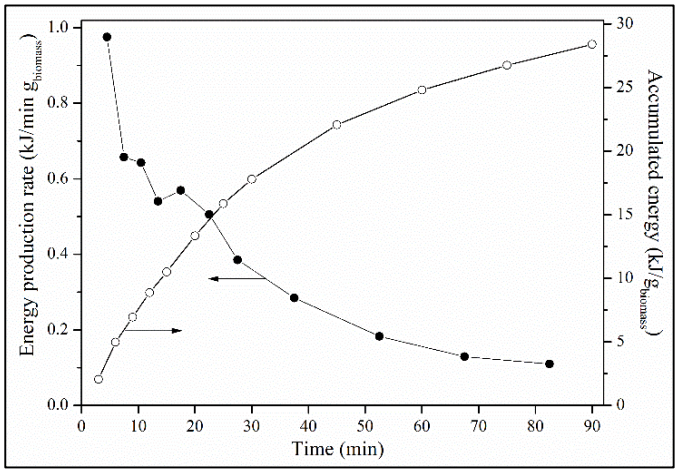

Fig. 5: Energy production versus time in the gasification experiment

Tab. 1 shows all the compounds that had been identified, by the GC-MS analysis, in the tar. According to the analysis, tar from CO_2 gasification of elephant grass is composed by primary tar (35.1 wt.%), phenolic compounds (28.3 wt.%) and light polyaromatic hydrocarbons (PAH) (13.6 wt.%). Heavy PAH, with more than 4 rings, were not observed in the chromatogram.

Tab. 1: Composition of tar by GC-MS analysis (% area)

Compound	Retention time (min)	% area
Methylpentanols	3.588	3.6
Phenol[1]	13.331	8.0
Methylphenols[1]	15.579; 16.177	11.1
Dimethylphenols[1]	17.860; 18.825	3.5
Ethylphenols[1]	18.281	5.7
Naphtalene[2]	18.411	7.9
Methylnaphtalenes[2]	20.651; 20.961	2.4
Acenaphthylene[2]	23.338	1.6
Anthracene[2]	28.218	1.7
Palmitic acid	30.641	14.5
Pentadecanoic acid	32.997	17.0

[1]Phenol derivatives

[2]Light polyaromatic hydrocarbons (PAH)

The high amounts of primary tar observed should be related to the first step of the reaction, when the material is heated at a high heating rate to the final gasification temperature. This process leads to the formation of compounds such as alcohols and organic acids [15]. Palmitic and other organic acids were also observed in the pyrolysis of elephant grass by Strezov, Evans and Hayman [16]. Michel et al. [17] found a similar concentration of phenols (22.7 wt.%) in the steam gasification of *Miscanthus x giganteus* at 880 °C using olivine as catalyst. On the other hand, a higher concentration of tertiary tars, such as toluene (22.2 wt.%), naphthalene (14.0 wt.%) and phenanthrene (3.8 wt.%) was observed by the authors. The absence of tertiary tar in elephant grass experiments may be associated with the absence of catalysts. Thus, the primary and secondary compounds where not converted by the secondary and tertiary reactions, which have as products a smaller amount of tar and a lot of combustible gas. The high amount of primary and secondary tar (phenolic compounds) in the present study encourages the use of catalysts in the process. Thus, these products can be converted to tertiary tars and more fuel gas, increasing the efficiency of the process and decreasing the yield of tar [17].

IV. CONCLUSIONS

The fuel gas produced in the CO_2 gasification of elephant grass presented a high CO concentration and it had an average high heating value of 8.5 MJ/Nm³. The results showed a high rate of carbon monoxide production, achieving the maximum value of 2.25 mmol/min.$g_{biomass}$. Considerable hydrogen production rates were observed throughout the experiment. The gasification of elephant grass presented an energetic yield of 28.4 kJ/g. Finally, the results presented shows that the CO_2 gasification of elephant grass represent a promising alternative

to mitigate the accumulation of CO_2 in the atmosphere and for the production of a fuel gas.

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