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EXPERIMENTAL STUDY OF EX-SITU CATALYTIC PYROLYSIS OF SUGARCANE BAGASSE USING CALCIUM OXIDE AS CATALYST

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Abstract. *Thermal pyrolysis of biomass produces a bio-oil of low quality, thereby it was proposed the use of a catalyst in order to improve the quality and yield of products. Several studies have highlighted the use of catalysts to improve bio-oil quality. There are many types of catalyst, alkaline catalysts such as metallic oxide have demonstrated a deoxygenating capacity. In literature, there are many studies about catalytic pyrolysis in-situ because of their simplicity and low cost, however, there are few studies about ex-situ catalytic pyrolysis. In this type of pyrolysis, the catalyst is separated from biomass. In Brazil, sugarcane is an important energy crop used for ethanol production, thereby, large quantities of sugarcane bagasse are generated. Nowadays there are many alternatives for using this resource, one of them is pyrolysis. In literature, the are scarce studies about ex-situ catalytic pyrolysis of sugarcane bagasse, moreover, the possibility of obtaining bio-oil has not yet been studied. Thus, the objective of this work is to study the ex-situ catalytic pyrolysis of sugarcane bagasse for bio-oil production. The results show that bio-oil has more higher heating value. The temperature of the catalytic reactor has influenced on properties of bio-oil. Calcium oxide has the potential to be used as a catalyst in ex-situ catalytic pyrolysis.*

Keywords: *Ex-situ catalytic pyrolysis, biomass, sugarcane bagasse, biochar, bio-oil*

1. INTRODUCTION

Currently in the world to satisfy the great energy demand aiming at the reduction of GHG emissions, mainly CO2, several alternatives have been proposed, among them the use of biomass. Biomass is the fourth energy source in the world and has been touted as a potential source of renewable energy, as it can simultaneously solve energy demand problems and reduce GHG emissions (Saidur et al., 2011; Tinwala et al., 2011; Tinwala et al. al., 2015; Kim et al., 2017). The use of biomass can be carried out through biochemical and thermochemical conversion processes. However, thermochemical conversion has received more attention due to its speed and greater efficiency when compared to biochemical conversion (Tripathi et al., 2016).

Among all thermochemical processes, pyrolysis has the potential to produce energy-dense biofuels from non-food resource sources (agricultural, urban, industrial and animal waste) (Demiral and Sensöz 2006). According to Kabir and Hameed (2017), pyrolysis using lignocellulosic biomass not only produces renewable fuels, but also petrochemicals; consequently this can minimize dependence on fossil fuels. Biomass pyrolysis is the process of thermal decomposition in an inert medium which results in three products: a solid (biochar), a liquid (bio-oil) and a gas (pyrolytic gas)

(Demiral and Sensöz 2006; Tripathi et al. al., 2016). The most studied types of pyrolysis are fast pyrolysis and slow pyrolysis. Slow pyrolysis of biomass is primarily intended for biochar production (Russell et al., 2017). Biochar can have diverse applications, such as in agriculture, water treatment and in catalytic chemical processes (Tan et al., 2015; Lee et al., 2017). In the slow pyrolysis process, biochar is the dominant product fraction, however, a significant fraction of bio-oil and a smaller fraction of pyrolytic gas are also produced. In slow pyrolysis, the bio-oil produced has a considerable content of oxygenated components, therefore, it receives less attention (due to its low calorific value) and is discarded as waste (Kabir and Hameed, 2017). However, several studies indicate that the bio-oil and pyrolytic gas fractions produced in slow pyrolysis can be used as a source of heat in the process itself, reducing the processing cost (Park et al., 2014; Dunningan et al., 2018).

On the other hand, based on the experience obtained in the production of bio-oil through fast catalytic pyrolysis, there is a great interest in the use of catalysts in the slow pyrolysis of biomass as it can increase the yield of biochar, and the quality of the bio-oil. produced (Russell et al., 2017). In this way, both products (i.e., biochar and bio-oil) could be used as an energy source or as a chemical base for the synthesis of other products, improving the yield of this process. There are two types of catalytic pyrolysis, in-situ where the biomass is previously mixed with the catalyst and ex-situ, where the pyrolysis vapors come into contact with the catalyst (Daí et al. 2020; Hu et al. 2020).

There are few studies on the effect of using catalysts in the process of slow pyrolysis of biomass. There are several types of catalysts, however, alkaline catalysts (calcium oxide - CaO and magnesium oxide - MgO) in biomass pyrolysis have been rarely studied (Case et al., 2015; Chen et al., 2017; Kabir and Hammed 2017).). Some studies investigated the effect of CaO, and verified a deoxygenating activity, which could improve the characteristics of bio-oil, in addition, it does not undergo deactivation as in the case of zeolites (Case et al., 2015; Chen et al., 2017).).

Brazil has an energy matrix with a considerable share of renewable sources, where sugarcane has a representation of 18% (base year 2019) (EPE 2020). The share of sugarcane should increase due to the improvement in its productivity, thus, there will be a greater availability of bagasse. Due to the availability of sugarcane bagasse in the state of São Paulo, a study on its use through slow catalytic pyrolysis for the production of biofuels is relevant. The literature presents some works on ex-situ catalytic pyrolysis of sugarcane bagasse (Ghorbannezhad et al. 2018; Iftikhar et al. 2019), however, there are few works that use alkaline catalyst.

2. MATERIALS AND METHODS

2.1 Sugarcane bagasse and catalyst

Figure 1 shows the sugarcane bagasse (BCA) used for the study (Fig 1a) supplied by the Iracema distillery in the city of Itaí – SP. The input used as catalyst is calcium oxide (CaO), which was pelleted in order to produce cylinders of 10 mm in diameter and 7 mm in height (Fig 1b). As no binding substance was used in the manufacture of the pellets, some of them were fragmented. In the tests, both pellets that maintained their shape and those that fragmented were considered.

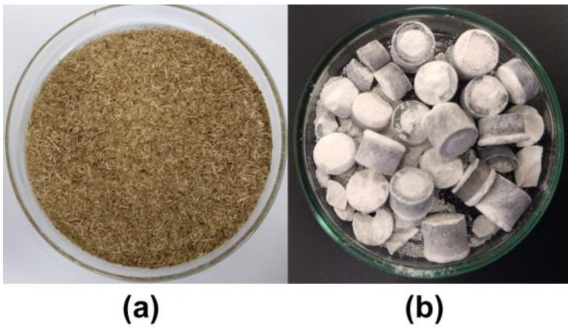


Figure 1. Materials (a) Sugarcane bagasse milled and then screened at 250 μm; (b) Calcium oxide pellet

2.2 Experimental setup

Figure 2 presents a schematic of the experimental bench for the study of ex-situ catalytic pyrolysis of sugarcane bagasse. The bench consists of a muffle furnace with temperature control and heating ramp. The reactor has two inlets, one for the injection of carrier gas and the other for the output of volatile material. A stream of nitrogen gas will be used to inert the medium and promote the output of volatiles, the flow will be controlled by a controller by a rotameter. The volatile material leaving the first reactor passes to the catalytic reactor where a bed of CaO pellets is mounted. A stainless-steel tube with a length of 30 cm and an internal diameter of 4 cm will be used as a catalytic reactor and will be heated by a ceramic collar type resistor with temperature control. A condensation system formed by a set of Liebig connected in series will allow the condensation of volatile material. The condensers are connected to 2 balloons, which have the function of collecting the bio-oil. The water used by the condensing system comes from a chiller, which keeps the water cooled to 5°C.

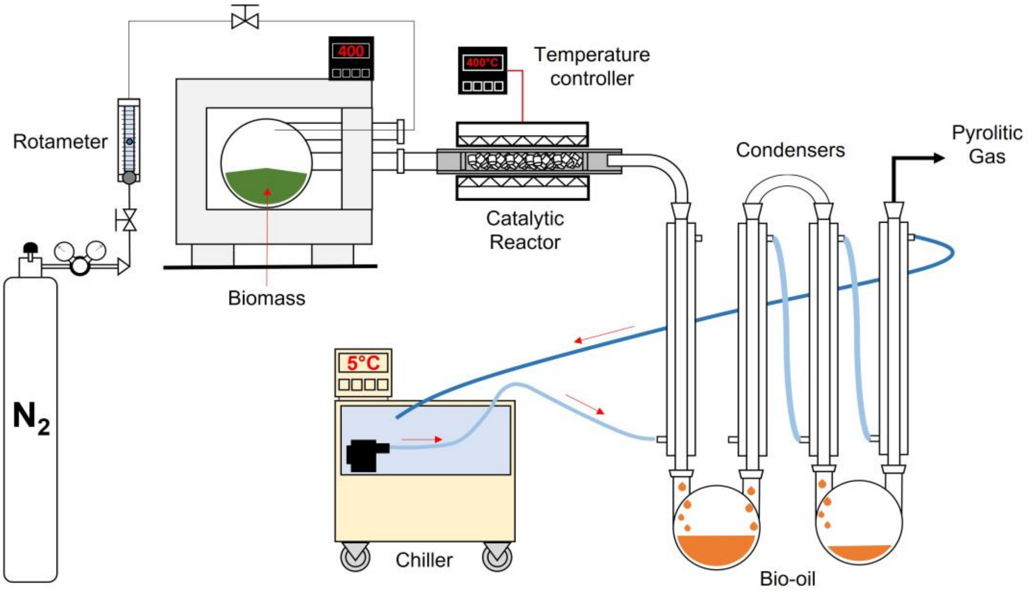


Figure 2. Experimental set-up for EX-SITU catalytic pyrolysis

2.3 Experimental design

For the development of the experiments, variables such as granulometry (250-500µm), mass of the biomass sample (20g) and carrier gas flow (100ml/min) will be kept constant. The catalyst will be loaded into the catalytic reactor in the form of pellets (1cm in diameter and 1.5cm in length). The catalyst pellets will form a bed that will allow the flow of vapors from the pyrolysis reactor. The study considers that the temperatures of the pyrolysis reactor and the catalytic reactor are the same (300, 400 and 500°C). The reaction time will be 30 minutes, counted after reaching the reaction temperature. Assays will be performed in duplicate to ensure the reliability of the results. The bio-oil yield will be determined from a mass balance of the pyrolysis process (Equation 1), where “m” represents the mass. It should be noted that the mass of pyrolytic gas formed will be determined by difference.

$$m_{biomass} = m_{bioc\,har} + m_{bio-oil} + m_{pyrolytic\quad gas} \tag{1}$$

3. RESULTS AND DISCUSSIONS

3.1 Sugarcane bagasse characterization

On Table 1, it is possible to verify a high cellulose content (41.64%), and the other components are within the literature range. What may have caused this variation in levels is the place of cultivation and the harvest of the biomass. When there is a higher concentration of cellulose and hemicellulose, it implies a greater amount of the liquid fraction (bio-oil), and when high concentrations of lignin are obtained, the production of the solid product (biochar) is favorable. Immediate analysis is used to explore the combustion properties and quality of bagasse as biomass. The moisture content found for SCB is 5.5%, which is close to the values found in the literature. The moisture of the biomass can lead to a large generation of acid extract, which causes a decrease in the calorific value of the bio-oil. Thus, the process may become infeasible as it would require more energy and time (SILVA, 2013). The contents of fixed carbon and volatile material are within the studied literature. It is observed that there is a large percentage of volatile material, in which the production of bio-oil and gasses through pyrolysis becomes viable, being derivatives of cellulose and hemicellulose. Fixed carbon influences the production of biochar, where it is derived from lignin. The ash content obtained is also in accordance with the limits of the literature presented. In order to carry out pyrolysis aiming at the production of bio-oil, it is interesting that this content is low, as it can cause energy loss and reduce the conversion rate of the process, in addition to forming incrustations, slag and corroding the interior of the reactor.

Table 1. Chemical composition and Immediate analysis of SCB

Characteristics	In this study	Varma and Mondal (2017)
Composition	%	
Cellulose	41,64	47,60
hemicellulose	29,74	39,00
lignin	22,86	11,20
Extractives	6,49	2,20
Immediate analysis		
Moisture	5,5	5,40
Volatile Material	80,8	80,20
fixed carbon	11,2	11,30
ashes	2,5	3,10

Figure 3 represents the thermogravimetric (TG) and thermogravimetric differential (DTG) curves of in natura SCB. The thermogravimetric curve represents the change in SCB mass percentage with increasing temperature. Through the analysis of figure 3, it can be seen that the percentage of mass reduction increases sharply after reaching 200 °C and stabilizes above 450 °C, showing a degradation of approximately 90% in mass in this temperature range. The DTG curve represents the variation of mass per minute, it can be observed that the SCB in natura showed two peaks of mass reduction, at temperatures of 325 °C and 431 °C. Where at a temperature of 325 °C occurs mainly the thermal decomposition of cellulose, while at 431 °C it corresponds to lignin. The curve also presents a shoulder which corresponds to the decomposition of hemicellulose, which occurs around 280 °C. To verify the effect of temperature and residence time on the components of SCB the DTG curve of SCB in natura will be used as a reference.

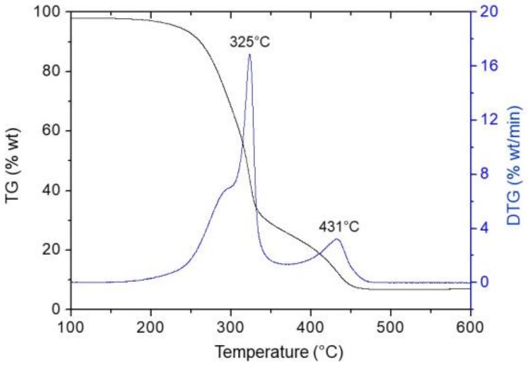


Figure 3. Curvas TG/DTG do SCB in natura.

3.2 Pyrolysis yield

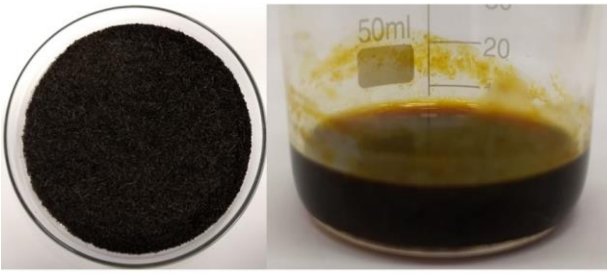
Slow pyrolysis is conventionally used for the production of biochar, at low temperature and short sample residence time. However, an almost proportional amount of bio-oil and pyrolytic gas is also generated. The yield obtained for the solid, liquid and gaseous fractions in this study are presented in Table 2. From the results it is possible to verify that the fractions of the products are significantly different when compared with the values found by Bridgwater (2003), where the biochar, bio-oil and pyrolytic gas present 30, 30 and 40%, respectively.

Table 2. Thermal and catalytic pyrolysis products yield

Condition	Thermal			Catalytic		
Temperature (°C)	Biochar (%)	Bio-oil (%)	Pyrolytic gas (%)	Biochar (%)	Bio-oil (%)	Pyrolytic gas (%)
300	34	52	14	36	40	24
400	22	51	27	25	42	33
500	23	51	16	22	38	40

3.3 Characterization products of pyrolysis

Figure 4 shows the biochar and bio-oil obtained by the thermal pyrolysis of sugarcane bagasse. The biochar obtained at different temperatures has the same qualitative characteristics, being an odorless black material. Likewise, the bio-oil obtained at different temperatures exhibits a brown color containing two phases, one aqueous and the other dense.



(a) (b)

Figure 4. Pyrolysis products (a) Biochar; (b) bio-oil from thermal pyrolysis.

Figure 5 shows the FTIR spectra of bio-oil from thermal and catalytic sugarcane bagasse pyrolysis. A chance of chemical composition of the bio-oil can be observed by the use of catalyst (CaO). An increase in catalyst has no significant chance on the chemical composition of the bio-oil. The peak at 3395 cm-1 is related to the O-H stretching vibration caused by water or alcohol in the bio-oil. The peak at 2928 cm-1, which can be attributed to C-H stretching, by the presence of C-H alkyl. The stretching vibration C = O at 1705 cm-1 indicates the presence of ketones, aldehydes, esters or acids. The peak at 1367 cm-1 indicates the presence of alkanes by the C-H curvature vibrations. The peak at 1514 cm-1 indicates the presence of alkenes by the skeletal vibration C = C. The bands of 1232, 1115 and 1021 cm-1 are related to the stretching vibration of C-O, showing possible existence of acids or alcohols in the bio-oil.

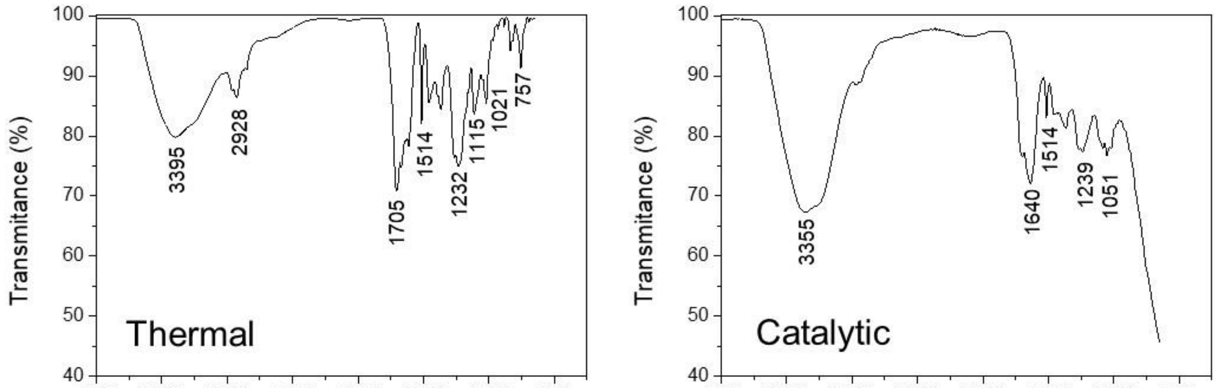


Figura 5. FTIR of bio-oil from termal and catalytic pyrolysis.

Table 3 presents the average HHV of biochar and bio-oil obtained in the thermal pyrolysis obtained at different temperatures. Considering an average HHV of the biochar obtained equivalent to 28 MJ/kg, an increase of almost 56% is observed when compared to the in natura SCB (15.80 MJ/kg). The analyzes concerning the HHV of the bio-oil were carried out in triplicates considering the different process temperatures (300, 400 and 500 °C). Preliminary tests demonstrated a lack of ignition of the bio-oil. One can speculate that it is due to the high-water content. On Table 3, it is observed that the HHV of bio-oil does not change as a function of temperature. Furthermore, since the bio-oil yield exhibits similar values at all temperatures, obtaining bio-oil at 300°C is the most favorable considering the energy consumption in the process.

Table 3. HHV of biochar and bio-oil samples

Temperature (°C)	Biochar Thermal (MJ/kg)	Bio-oil Thermal (MJ/kg)	Bio-oil Catalytic (MJ/kg)
300	28.23	10.45	15.85
400	27.00	10.64	17.78
500	29.16	10.68	18.62

Figure 6 shows the catalyst after ex-situ catalytic pyrolysis. The formation of a dark layer on the pellet is observed. This dark layer is the formation of a soot resulting from the deposition of carbon-rich substances. The formation of a soot layer on the catalyst pellets was more intense in the pellets that were close to the pyrolysis reactor. This can somehow explain the reduction in the bio-oil yield, since the deposition of substances on the surface of the pellets would mainly be substances of high molecular weight. The formation of this layer can significantly reduce the action of the catalyst, however the carbon present on the surface of the material can react with the volatile material resulting in its recovery, however, further studies are needed.

Figura 6. Catalyst pellet after process.

4. CONCLUSIONS

The ex-situ catalytic pyrolysis has the advantage of preserving the yields and qualities of the produced biochar, however the bio-oil yield is penalized, due to deposition of substances on the catalyst surface. The calorific value of the bio-oil increased significantly, demonstrating the beneficial effect of the catalyst. The high temperature CaO pellets caused a significant increase in the pyrolytic gas yield, which can be understood as a decomposition of the substances that would form the bio-oil.

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