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CATALYTIC SLOW PYROLYSIS OF SUGARCANE STRAW USING ALKALINE CATALYST

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Abstract. *The use of biomass carried out by the pyrolysis process has the potential to produce biofuels with high energy density. Biomass pyrolysis is the process of thermal decomposition in an inert medium generating three products, namely: a solid (biochar), a liquid (bio-oil) and a gas (pyrolytic gas). Catalytic pyrolysis has shown improvements in the quality of pyrolysis products. The pyrolysis of sugarcane straw is an option for energy use. The results have shown an increase in biochar yield and in the pH of the bio-oil. The bio-oil yield remained almost constant.*

Keywords: *Catalytic pyrolysis, sugarcane straw, 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 source of energy in the world and has been found to be a potential source of renewable energy, since it can simultaneously solve the problems of energy demand and reduce GHG emissions (Saidur et al., 2011; Tinwala et 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 biofuels with high energy density from non-food 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., 2016). The most studied types of pyrolysis are fast pyrolysis and slow pyrolysis.

Slow biomass pyrolysis is intended primarily to produce biochar (Russell et al., 2017). Biochar can have several applications, such as in agriculture, water treatment and in catalytic chemical processes (Tan et al., 2015; Lee et al., 2017). In the process of slow pyrolysis, 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 the low calorific value) being 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 heat source 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 rapid catalytic pyrolysis, there is great interest in the use of catalysts in the slow biomass pyrolysis as it can increase the yield of the 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 performance of this process.

The literature presents several works that discuss the study of the slow thermal pyrolysis of several biomasses, however, there are few studies on the effect of the use of catalysts in the process of slow biomass pyrolysis. 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 found 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 17.4% share (base year 2017) (EPE 2018). The participation of sugarcane should increase due to the improvement in its productivity, thus, there will be a greater availability of bagasse. Currently, sugarcane straw has a considerable amount of sugarcane straw in the sugar and ethanol plants, due to laws that prohibit the burning of straw before harvest and the improvement in mechanized harvesting technology (Leal et al., 2013; Centeno 2015; Menandro et al., 2017; Santos et al., 2017). Several studies highlight the potential of straw to produce electricity (Carvalho et al. 2017; Cervi et al., 2019; Go and Conag 2019).

However, its chemical composition limits its use through combustion. Straw has a high ash content, which during combustion causes scale due to the low melting temperature of the ash, one of the main problems of steam generators (Jacome 2014). Due to the availability of sugarcane straw in the state of São Paulo, a study on its use through slow catalytic pyrolysis to produce biofuels (bio-oil) is relevant.

2. MATERIALS AND METHODS

Figure 1a shows a sample of raw sugarcane straw. For experimental test a sample of sugarcane straw was milled until a particle size of 200μm. This granulometry was selected to get an appropriate mixing with the catalyst. Figure 1b. show the catalyst being the calcium oxide (CaO).

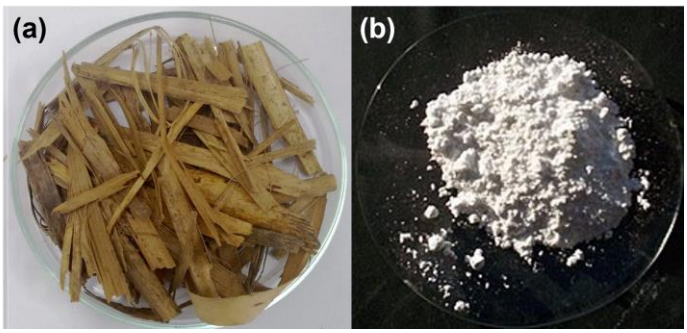

Figure 1. (a) Sugarcane straw; (b) Calcium oxide.

2.1 Experimental setup

Figure 2 exhibit the experimental setup used for the test. For experimental test was considered a temperature of 300°; 400°C and 500°C. The mass fractions of catalyst used are 10%; 20% and one condition using 50%. In all experiments the mass of biomass was 20g. The catalyst (CaO) was previously mixed with biomass being a IN-SITU catalyst pyrolysis. A gas flow rate of 100ml/min of nitrogen gas is used to carrier the material volatile.

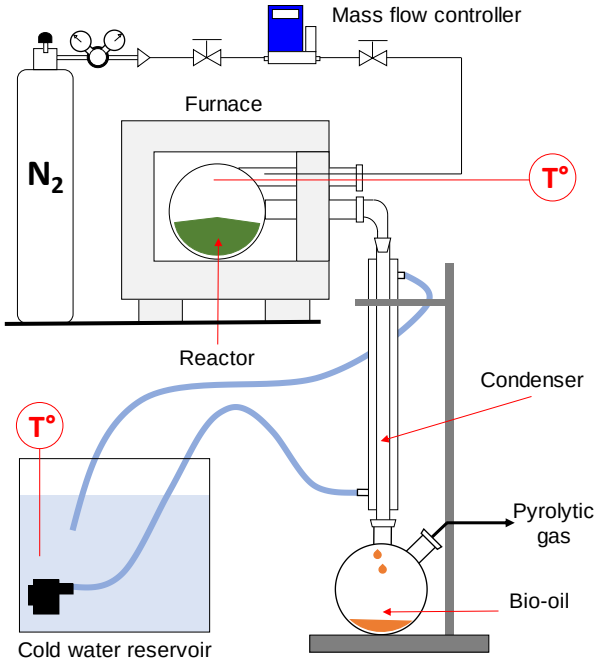

Figure 2. Experimental setup of the catalytic slow pyrolysis.

3. RESULTS AND DISCUSSION

Table 1 shows the results of proximate analysis of sugarcane straw. The high content of volatile material in sugar cane straw suggests a promising capacity to produce bio-oil or pyrolytic gas and the fixed carbon content low productivity of biochar.

Table 1. Proximal composition of sugarcane straw.

Parameter	%
Moisture	8.86
Volatile material	67.33
Fixed carbon	16.49
Ash	7.32

Figure 3 shows the TG / DTG thermogravimetric curves of sugar cane straw in an inert atmosphere. The TG (green line) curve indicates the loss of mass as a function of temperature, analyzing this curve it can be seen that sugar cane straw loses around 68%, this would correspond to the volatile material released, this result is correlated with immediate analysis, where the volatile material content was 67.33%. The DTG curve (blue line) indicates the temperatures and thermal decomposition events of the components of sugar cane straw. The first event corresponds to the decomposition of hemicellulose, the second to the decomposition of cellulose, the third and last, in the range between 400 and 500 ° C, is associated with the decomposition of lignin, and after 550 ° C there is no significant decomposition of sugar cane straw. The DTG curve suggests that 400 ° C would be a temperature sufficient to extract much of the volatile material.

Figure 4 shows the bio-oils obtained in the experimental tests. Figure 4a represents the bio-oil without the use of a catalyst, regardless of the temperature, presented the same qualitative characteristics (color and smell). Figure 4b represents the bio-oil with the use of catalyst, regardless of the temperature and quantity of catalyst, the bio-oil showed a much lighter color. This qualitative characteristic indicates a clear change in the chemical composition.

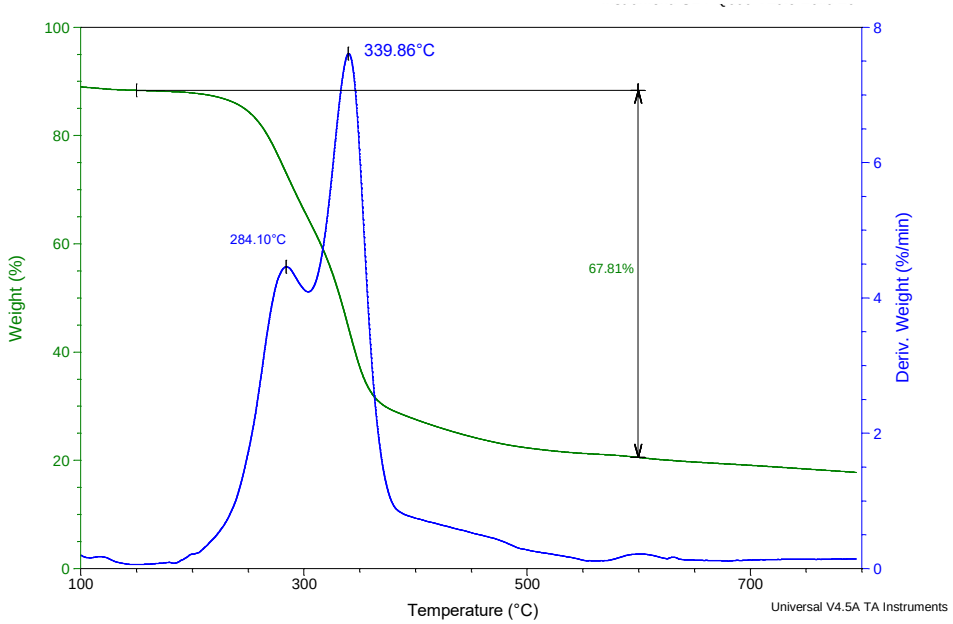

Figure 3. TG/DTG curves of sugarcane straw in inert atmosphere (N_2)

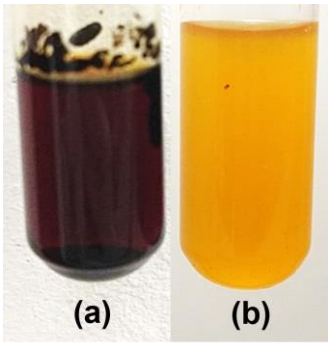

Figure 4. Bio-oil (a) without catalyst; (b) using catalyst.

Pyrolysis experiments without catalyst were performed to serve as a point of comparison. The results show the effect of catalyst (Figure 5). As the pyrolysis temperature increases, the amount of bio-oil is reduced. An increase in the production of pyrolytic gas is observed as the concentration of catalyst increases. The amount of biochar increases progressively due to the presence of the catalyst. At 500 °C and 10% catalyst, the largest amount of pyrolytic gas was obtained. The pH of bio-oil without catalyst was 3. The use of 10% and 20% of catalyst increase the pH until 4. The test carried out at 500 °C and 50% catalyst resulted in a bio-oil with a pH of 5, but it had the lowest yield of bio-oil and pyrolytic gas.

Considering a thermal pyrolysis, the highest yield of biochar was obtained at 300 ° C and as the temperature increases there is a reduction in yield. In catalytic pyrolysis at 300 °C, adding 10 and 20% of catalyst, an increase in the biochar yield is observed, maintaining very similar yield values. If there was a significant reduction in bio-oil yield, however, the amounts of pyrolytic gas remained almost constant.

In catalytic pyrolysis at 400 °C, an increase in the yield of biochar with the addition of catalyst is observed, although to a lesser extent than pyrolysis at 300 °C. This can be explained by the fact that at 400 °C there is a more intense decomposition of the components of biomass, especially cellulose. Under catalytic conditions, the bio-oil yield decreases, but the yield values were kept close in both catalytic conditions. The yield of pyrolytic gas at 400 ° C increases significantly when compared to 300 °C, resulting in similar values in both thermal and catalytic pyrolysis.

At 500 °C, the yield of biochar increases proportionally with the amount of catalyst, however the yield of bio-oil shows a significant reduction when compared to the yield of thermal pyrolysis. In the case of pyrolytic gas, it exhibits a considerable reduction when 20% of catalyst is used. Using 50% catalyst, the biochar yield increased significantly, a significant reduction in pyrolytic gas was obtained, the bio-oil content had a yield like that of other catalytic pyrolysis.

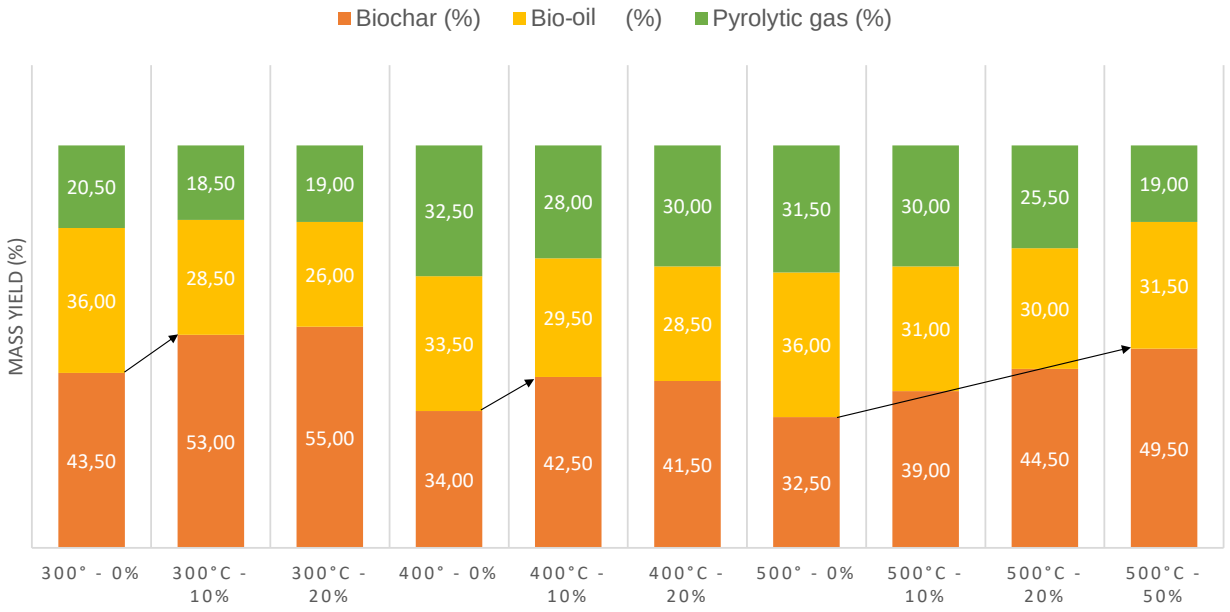

Figure 5. Mass yield of products from catalytic slow pyrolysis.

4. CONCLUSIONS

In this work, it was demonstrated that the addition of CaO significantly impacts the slow pyrolysis of sugarcane straw. The use of CaO in the slow catalytic pyrolysis promoted the formation of biochar proportionally with the increase in temperature and catalysts. The bio-oil yield remained on average 30%, however, under catalytic conditions there was a reduction in the pH content. From the results it is understood that 10% of catalyst is already enough to cause changes in the yields of the products of the sugarcane straw catalytic slow pyrolysis.

5. ACKNOWLEDGEMENTS

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