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EVALUATION OF DOLOMITE AS A CATALYST IN THE IN-SITU CATALYTIC PYROLYSIS OF SUGARCANE BAGASSE

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Abstract. Energy is synonymous with development, and the world's energy demand is currently increasing exponentially. In order to meet this need, biomass can be an important ally. The biomass pyrolysis process holds great potential for the production of biofuels with high energy content. In general, biomass pyrolysis requires the thermal decomposition of biomass in an inert or oxygen-deficient atmosphere, resulting in three products, namely: a liquid (bio-oil), a solid (biochar) and a gas (pyrolytic gas). However, the bio-oil obtained has certain undesirable characteristics, such as a high water content, oxygenated compounds, low pH and a highly variable chemical composition. All these characteristics make it difficult to use as a biofuel. However, these problems can be solved by using a catalyst during the pyrolysis process, which is then called catalytic pyrolysis. Catalytic pyrolysis aims to improve the quality of the bio-oil through chemical reactions such as deoxygenation, dehydration and hydrogenation. One potentially applicable catalyst is dolomite ($\text{CaMg}(\text{CO}_3)_2$), which is one of the main carbonate minerals, composed of calcium carbonate (CaCO_3) and magnesium carbonate (MgCO_3). Compared to most synthetic catalysts, it offers the advantages of being inexpensive and abundant in nature, as it is easily found in limestones. In Brazil, the largest dolomite deposit is located in the north of the country. There, as in some southeastern regions, the use of dolomite as a catalyst for the catalytic pyrolysis of sugarcane bagasse is an established process that enables the production of high-quality and cost-effective biofuels. In this work, the in-situ catalytic pyrolysis of sugarcane bagasse using dolomite as catalyst in a fixed bed reactor is studied. For comparison, the same experiments were also carried out without a catalyst. Preliminary results from the literature demonstrate that the use of dolomite as a catalyst has a significant impact on the quality and yield of the pyrolysis products, causing a reduction in the amount of water, oxygen and the acidity of the bio-oil, thus ultimately leading to an increase in its calorific value.

Keywords: renewable energy, catalytic pyrolysis, lignocellulosic biomass, sugarcane bagasse, bio-oil upgrading.

1. INTRODUCTION

The world is facing a growing energy demand while at the same time ongoing global warming necessitates a reduction in the emission of greenhouse gases, especially carbon dioxide. This has led to an increased interest in the investigation of sustainable resources capable to replace fossil fuels. In this process, biomass appears as one of the most promising renewable sources for future energy generation (Saidur et al., 2011; Tinwala et al., 2015; Kim et al., 2017). Generally defined as organic material originating from plants and animals that has potential for energy production, biomass is already the fourth most widely used energy resource in the global energy mix (MAKENDRY, 2002). In Brazil, one of the main producers of sugarcane, which serves not only as a raw material for the production of sugar, but also the biofuel ethanol, sugarcane bagasse as a biomass-based by-product of these processes is of particular relevance. It was found that the processing of 1 t of sugarcane approximately generates 250 kg of sugarcane bagasse (CONAB 2019; Miranda et al., 2021), which is a lignocellulosic biomaterial that consists of the three macromolecules cellulose,

hemicellulose and lignin (SANTOS, 2012; ARNI 2017). Subjecting biomass like this to thermochemical conversion processes finally allows for the generation of renewable energy. Among the various types of thermochemical processes, pyrolysis is of particular importance due to its potential for the production of biofuels with high energy densities, as well as the simultaneous generation of chemicals that are used on a large scale worldwide, such as benzene, toluene and xylene compounds (Chavez et al., 2019; Zadeh et al., 2020; Bakar and Titiloye, 2012). In general, the pyrolysis process involves the thermal decomposition of the biomass in an inert medium and at a given temperature and reaction time. The three main products of this process are called bio-oil, biochar and pyrolytic gas (SUALI, 2012; PAN et al., 2010; ANAND et al., 2017; Hu and Gholizadehb, 2019).

However, bio-oil exhibits some characteristics that are not compatible with its intended use as a biofuel, such as a high water and oxygen content. It was found that these characteristics can be improved by the use of a catalyst in the pyrolysis process (VENDERBOSCH and PRINS, 2010; YANG et al., 2016; Chávez et al., 2019).

Catalytic pyrolysis has the same set-up as conventional (thermal) pyrolysis, but a catalyst is used during the process (ADAM, 2006). There are two different types of catalytic pyrolysis: *ex-situ* and *in-situ*. In the *in-situ* configuration, the biomass is mixed with the catalyst and then filled into the reactor, so that the catalyst has direct contact with the biomass. In the *ex-situ* configuration, the catalyst and the biomass are placed in different reactors, and it is only the volatile material released by the biomass that comes into contact with the catalyst (YILDIZ et al., 2016).

Dolomite is a mineral that is easy to obtain and less expensive compared to the most commonly used synthetic catalysts such as zeolite, and moreover, some studies show that dolomite can be just as efficient as other catalysts (Tursunov, 2014). Charusiri and Vitidsant (2017) investigated the effect of calcined dolomite as a catalyst on the yield and quality of bio-oil during the catalytic pyrolysis of sugarcane straw. The adverse results showed that the use of dolomite significantly influenced the chemical composition of the bio-oil during carbonylation, and the cracking of the vapors of the volatiles generated a bio-oil with low oxygen content, higher calorific value and lower acidity. Wang and Shen (2022) performed a study comparing the kinetics and products of the catalytic pyrolysis of cellulose and chitin using dolomite as a catalyst. The kinetic analysis showed that the activation energy of chitin was much lower than that of cellulose due to differences in the chemical structure. Calcined dolomite has a high catalytic activity, which aids to reduce the activation energy of biomass pyrolysis, especially in cellulose pyrolysis. The presence of dolomite promoted the conversion of anhydrous sugars into lower molecular weight components (ketones, alcohols, aldehydes, light hydrocarbons). Moreover, calcined dolomite showed a good performance in cracking high molecular weight components into lower molecular weight components during pyrolysis. Buyang et al. (2023) investigated the activity of crude dolomite as a catalyst in the catalytic pyrolysis of RTO. The dolomite used had not been calcined or treated before. The results demonstrate that increasing the pyrolysis temperature improves the bio-oil production with minimal biochar formation. The presence of dolomite increased the proportion of heavy hydrocarbons, thus contributing to an increase in the flash point, thermal stability, and calorific power of the bio-oil, which moreover showed a lower viscosity. Thus, this research aims to evaluate dolomite as a catalyst and its effects on the products of the catalytic pyrolysis of biomass in order to complement the selection of catalysts already present in the literature.

2. MATERIALS AND METHODS

2.1 Materials

In these experiments, ground sugarcane bagasse with a grain size of less than 250 μm (Figure 1(a)) was used in order to achieve a better homogeneity of the BCA-catalyst mixtures. Figure (b) shows the dolomite powder ($\text{CaMg}(\text{CO}_3)_2$) that was used as the catalyst.



Figure 1. (a) Sugarcane bagasse; (b) dolomite.

2.2 Experimental Set-up of the Pyrolysis

Figure 2 shows the experimental set-up of the thermal and catalytic pyrolysis experiments. These two processes are distinguished by the use of a catalyst in catalytic pyrolysis. There are two types of catalytic pyrolysis: *ex-situ* and *in-situ*. In the first configuration, the biomass has no direct contact with the catalyst, but only the released volatiles. In the *in-situ* configuration used in this work, however, the biomass is mixed with the catalyst before being added to the reactor. The reactor is then filled with N₂ gas at a volumetric flow rate of 100 ml/min (measured by a rotameter) in order to create an inert environment. The samples are heated inside a muffle furnace and four condensers, through which chilled water circulates at a constant temperature of 5 °C, are used to condense the condensable fraction of volatiles and thus obtain the bio-oil. The pyrolysis process was examined at temperatures of 300 °C, 400 °C, and 500 °C, which were kept constant for 30 minutes each. The proportion of the catalyst was 10% by weight.

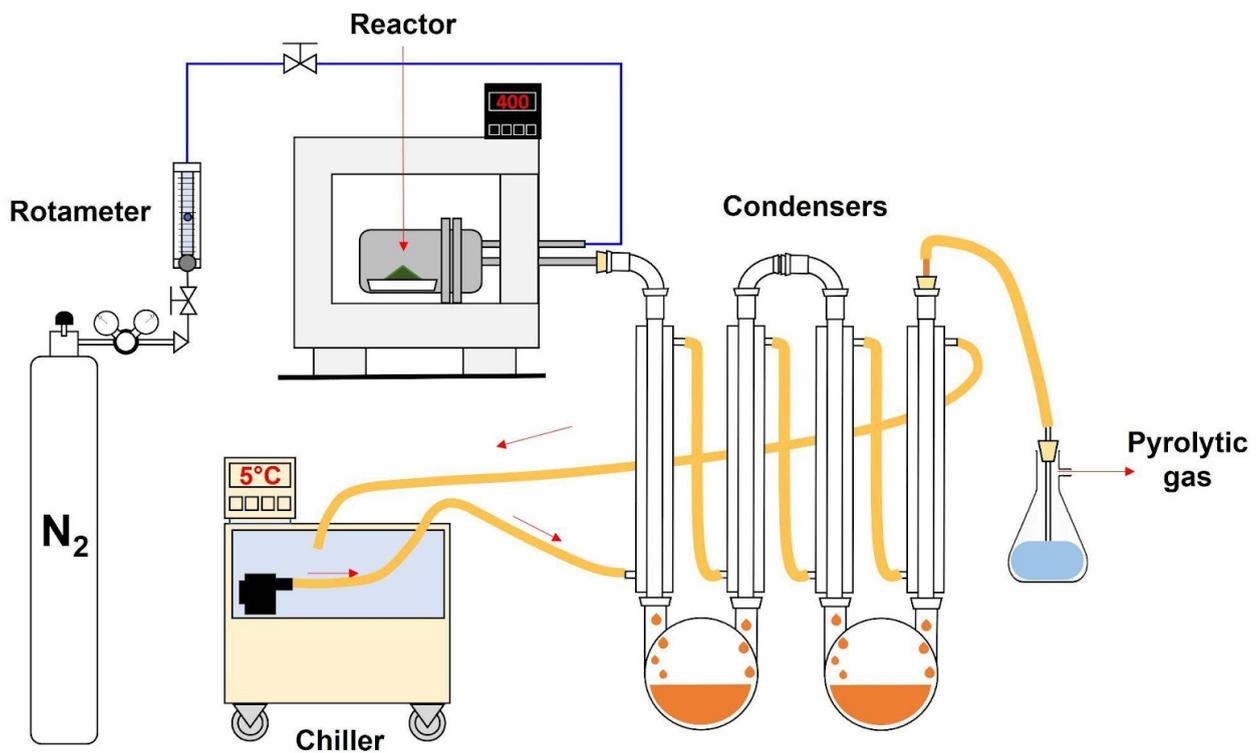


Figure 2. Experimental set-up for biomass pyrolysis.

2.3 Pyrolysis Evaluation Parameters

The reaction yields were calculated using the following equations:

$$\% \text{ (Bio-oil)} = [\text{MB} \cdot 100] / \text{BM} \quad (1)$$

$$\% \text{ (Biochar)} = [\text{MChar} \cdot 100] / \text{BM} \quad (2)$$

Pyrolytic gas:

$$[[\text{MOil}] + [\text{MChar}] + [\text{MG}] = 100\%], \quad (3)$$

where:

MOil = Bio-oil mass

MChar = Biochar mass

MG = Gas pyrolysis

2.4 Characterization Techniques

Compositional analysis was applied to determine the amounts of hemicellulose, cellulose, and lignin in the sugarcane bagasse, following the TAPPI standard procedure. Immediate analysis was used to determine the contents of moisture, volatiles, ash, and fixed carbon. The pH of the bio-oil was measured by means of a pH meter (AK 151). An IKA C500 calorimeter was used to determine the calorific value of the biochar and bio-oil products from the thermal and catalytic pyrolysis experiments. XRF (X-ray Fluorescence) was used to determine the elemental composition of dolomite. All assays were performed in triplicate.

3. RESULTS AND DISCUSSION

3.1 Characterization of Sugarcane Bagasse and Dolomite

Table 1 shows the determined chemical composition as well as the results of the immediate analysis of sugarcane bagasse in comparison to the literature. The experiments verified the expected high cellulose content (41.64%) of the material and the amounts of the other components are within the literature range. The slight variations in the concentration levels are most likely due to the location of cultivation and harvesting of the biomass. However, in the pyrolysis process, higher concentrations of cellulose and hemicellulose imply a greater amount of the liquid fraction (bio-oil), whereas a high concentration of lignin favors the production of the solid product (biochar).

Immediate analysis is used to explore the combustion properties and the quality of sugarcane bagasse as biomass. The experimentally determined moisture content of the SCB is 5.5%, which is in good agreement with the corresponding literature value of 5.40%. The moisture of the biomass can lead to a large formation of acid extract, which leads to a decrease in the calorific value of the bio-oil. Thus, the process may become impracticable as it would require more energy and time (SILVA, 2013). Apart from that, the contents of fixed carbon and volatile material are also found to be within the literature range. The large percentage of volatile material is due to the high amounts of cellulose and hemicellulose and therefore indicates a viable production of bio-oil and gases through pyrolysis. On the other hand, the fixed carbon is due to the presence of lignin in the sample and hence influences the generation of biochar. Finally, the obtained ash content is also in accordance with the limits of the literature that is referred to in this study. In order to carry out pyrolysis aiming at the production of bio-oil, a low ash content is of interest, as it can cause energy losses and reduce the conversion rate of the process, in addition to the formation of 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

XRF (X-ray fluorescence) spectroscopy was used to determine the elemental composition of the dolomite used as catalyst. The main constituents are found to be CaO and MgO, with proportions of 38.187% and 15.032 % m/m, respectively. According to the literature, both magnesium as well as calcium have positive effects on the outcome of the pyrolysis process. Therefore, the investigated dolomite has great potential to serve as an efficient catalyst for the aspired biomass pyrolysis.

Table 2. XRF analysis - elemental composition of the dolomite.

Oxides	% m/m
MgO	15.032
Al ₂ O ₃	0.22
SiO ₂	2.945
P ₂ O ₅	0.116
SO ₃	0.069
K ₂ O	0
CaO	38.187
TiO ₂	0.026
Fe ₂ O ₃	0.233
Y ₂ O ₃	0.001
ZrO ₂	0.003
Nb ₂ O ₅	0.002
In ₂ O ₃	0.394
La ₂ O ₃	0.006
CeO ₂	0.004
Yb ₂ O ₃	0.032

3.2 Pyrolysis Yield

Figure 3 shows the mass yields of the thermal pyrolysis products of SCB obtained at 300 °C, 400 °C, and 500 °C. The results reveal that the bio-oil yield is similar at all the temperatures studied and is always above 40%. The biochar yield was greater than 20% under all conditions, with the highest yield being achieved at 300 °C. It is observed that the biochar yield decreases with increasing temperature, due to a greater thermal decomposition of the biomass. By contrast, the pyrolytic gas yield increased with temperature, reaching a maximum of 7% at 400 °C and a slightly lower value of 6% at 500 °C.

Thermal

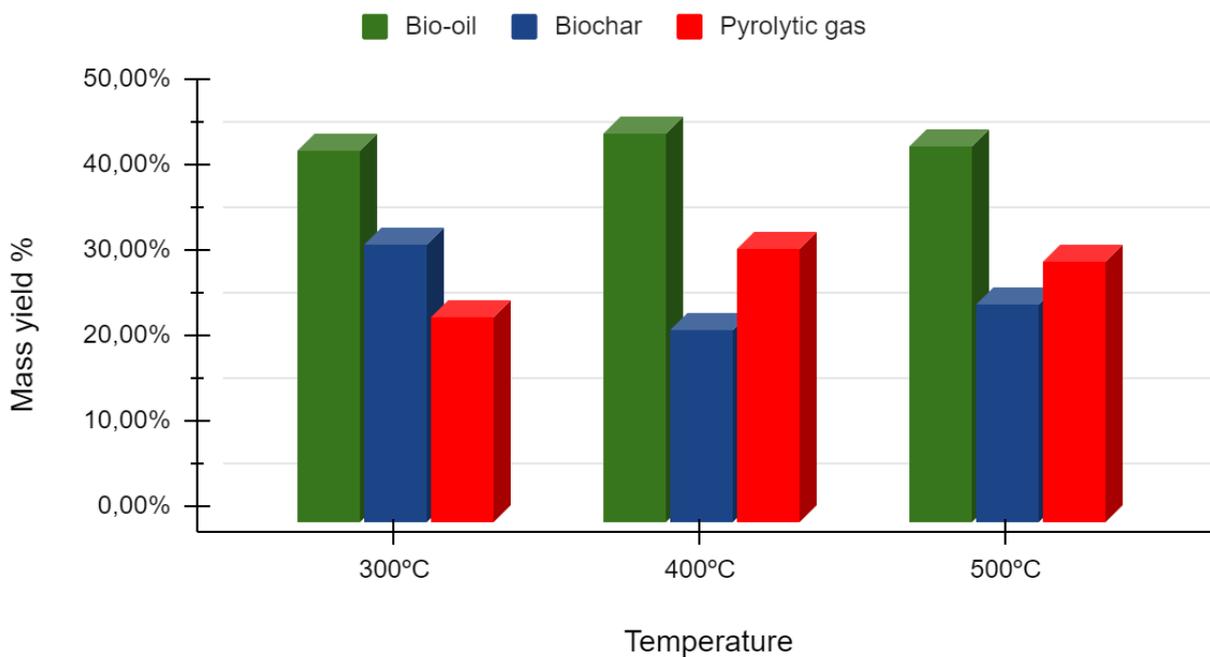


Figure 3. Thermal pyrolysis yields.

Figure 4 shows the yields of the *in-situ* catalytic pyrolysis products of SCB at all temperatures studied. It was found that the bio-oil production drops drastically compared to the uncatalyzed process, reaching the highest mass yield of 20% at 500 °C and the lowest value of 11% at 300 °C. By contrast, biochar production increased significantly, with yields ranging from 50% (500 °C) to 56% (400 °C). The pyrolytic gas outcome remained at approximately 30% for every given temperature.

Catalytic

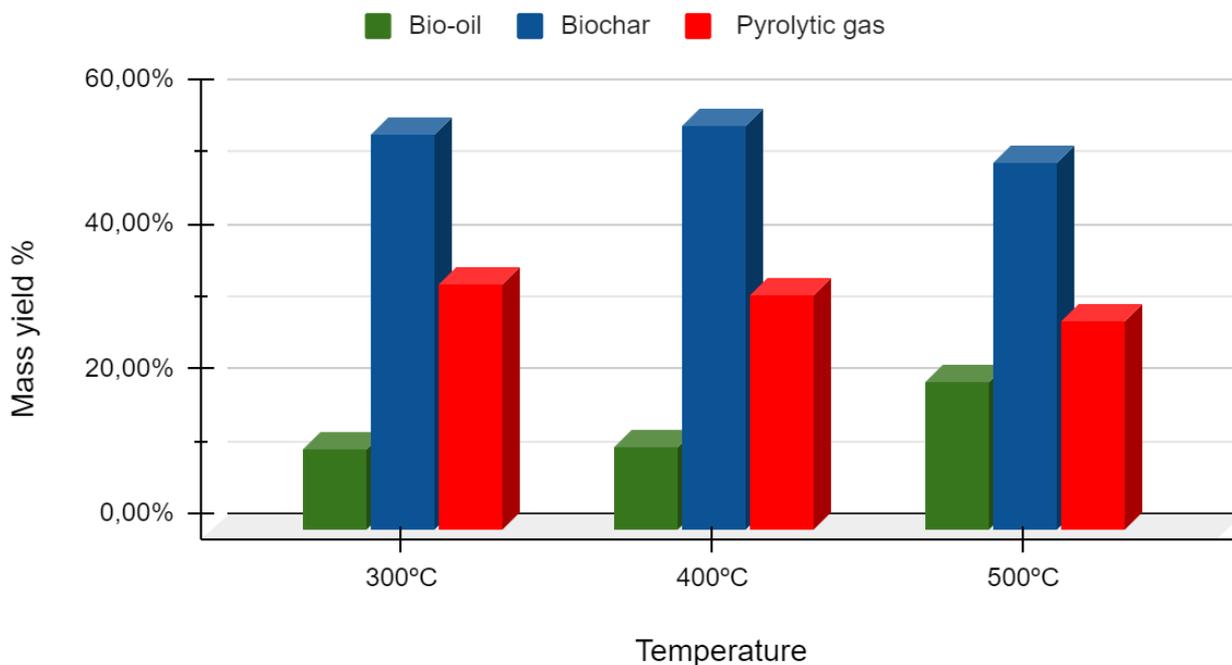


Figure 4. *In-situ* catalytic pyrolysis yields.

3.3 Characterization of the Pyrolysis Products

Figure 5 shows samples of the biochar obtained from the thermal and *in-situ* catalytic pyrolysis of SCB using dolomite as the catalyst. While the former process always produced a black material, regardless of the applied temperature, the latter also yielded some gray particles within the otherwise black biochar.

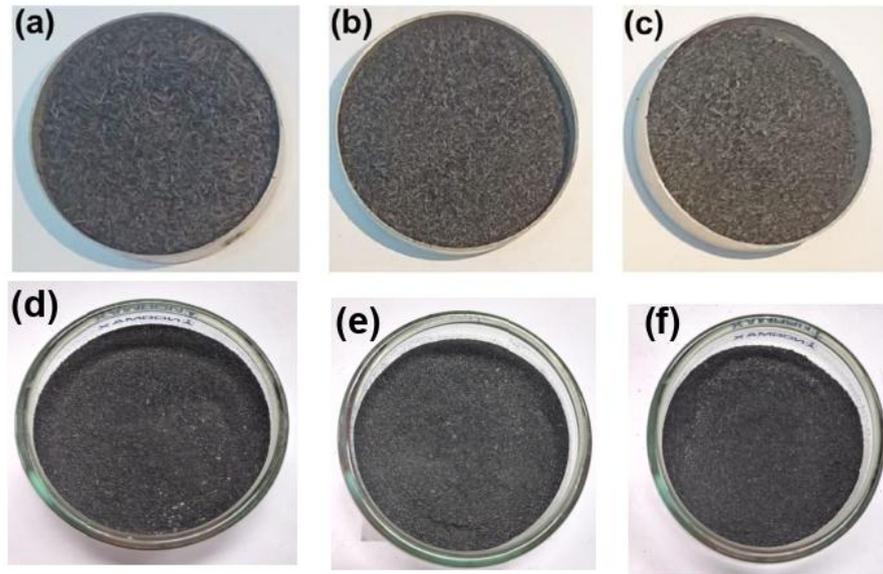


Figure 5. Biochar produced during the pyrolysis of SCB. Upper row: thermal pyrolysis products, obtained at (a) 300 °C, (b) 400 °C, (c) 500 °C. Lower row: *in-situ* catalytic pyrolysis products, obtained at (d) 300 °C, (e) 400 °C, (f) 500 °C.

Figure 6 shows samples of the bio-oil obtained from the thermal and *in-situ* catalytic pyrolysis of SCB. In both cases, the bio-oil exhibits a black color, regardless of the applied temperature. However, in the catalyzed reaction, the amount of bio-oil produced was much lower than under thermal conditions, as shown in Figure 6(b).

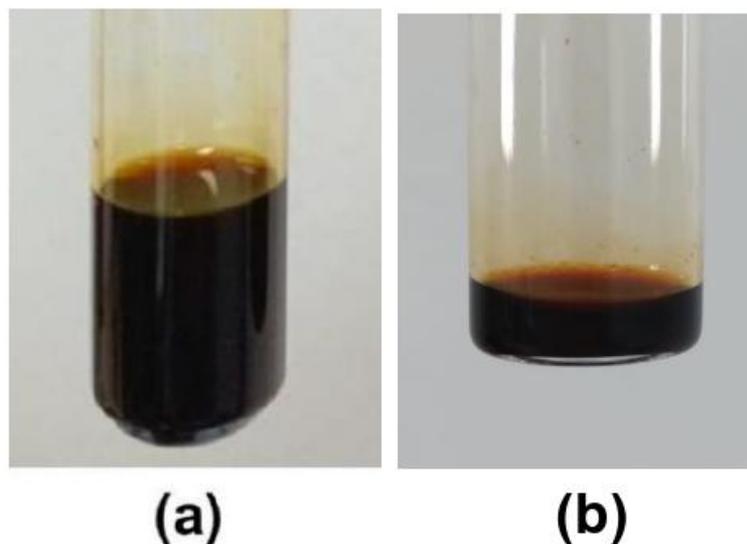


Figure 6. SCB bio-oil produced at 400 °C. (a) Without a catalyst, and (b) *in-situ* catalyzed.

Table 3 displays the calorific values of the biochar obtained under thermal and catalytic conditions. The results demonstrate that for every given temperature, the thermal process led to higher calorific values than the catalytic one. This is due to the presence of the catalyst dolomite, which increases the mass fraction of inorganic substances, thereby significantly reducing the calorific value. Thus, the biochar obtained under the applied catalytic conditions would not be

suitable for use as a solid fuel. However, this biochar could potentially be used in other applications, e.g. in biochar-concrete composites (Akhtar and Sarmah, 2018).

Table 3. PCS (MJ/kg) of the biochar samples.

Conditions	300 °C	400 °C	500 °C
Thermal	25.70	22.30	23.18
Catalytic	14.47	9.73	11.81

Table 4 displays the calorific values of the bio-oil obtained during the thermal and *in-situ* catalytic pyrolysis processes. It is observed that generally, the calorific values are very similar at any given temperature for both the thermal as well as catalytic conditions. However, the latter always led to slightly higher calorific values of the bio-oil, which might be due to the reaction between dolomite and volatile material released during the process.

Table 4. PCS (MJ/kg) of the bio-oil samples.

Conditions	300 °C	400 °C	500 °C
Thermal	7.05	8.52	8.05
Catalytic	9.62	9.39	9.39

Lastly, the pH of the bio-oil samples was examined and the results are summarized in table 5. It was found that, whereas the bio-oil obtained from the thermal pyrolysis processes always had a pH of 3, the addition of the dolomite catalyst only led to a slightly increased pH value of 3.05 when the experiment was carried out at 500 °C. At 400 °C and 300 °C, by contrast, the pH even decreased to 2.73 and 2.53, respectively.

Table 5. pH-values of the bio-oil samples.

Conditions	300 °C	400 °C	500 °C
Thermal	3	3	3
Catalytic	2.53	2.73	3.05

4. CONCLUSION

The experiments carried out in this study revealed that the usage of raw dolomite as a catalyst for the *in-situ* catalytic pyrolysis of sugarcane bagasse does not lead to a significant improvement of the mass yield, calorific value, and pH of the generated bio-oil and biochar in comparison to those obtained from the thermal process. First, the mass yield of the bio-oil produced in the catalyzed reaction (20.52%, 500 °C) is less than half of the mass yield achieved by thermal pyrolysis (45.50%, 400 °C). Moreover, the calorific value of the bio-oil from the catalytic process is only slightly higher than that of the oil from the uncatalyzed reaction, and the catalyst was also unable to enforce the desired significant increase in the pH of the bio-oil.

Regarding the produced biochar, the maximum calorific value of 25.70 MJ/kg was achieved at 300 °C and under thermal conditions. For comparison, the highest calorific value that was determined for the biochar gained from catalyzed pyrolysis was 14.47 MJ/kg (300 °C). Therefore, the biochar produced under catalytic conditions is not suitable to be used for the purpose of energy production. However, it may be applied in other solid biomaterial-based products, such as fertilizers or soil conditioners.

In conclusion, raw dolomite was found to lack the ability of significantly improving the energetically relevant characteristics of the liquid and solid products generated in the catalytic pyrolysis of sugarcane bagasse, and therefore cannot be considered a viable catalyst for improving this process.

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