

Valorization of Cherry and Date seeds residue towards valuable bio-based fuel via thermal pyrolysis approach

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Abstract

Valorization of Cherry and Date seeds residue towards valuable bio-based fuel via thermal pyrolysis approach are rethinking the ways of producing, distributing and consuming energy, as sustainable development must be increasingly incorporated in industrial, commercial and domestic centres. Sustainable processes, use of residues from biomass and its processing, synthesis of new materials and production of biofuels residue towards valuable bio-based fuel via thermal pyrolysis approach are niches that can be fully correlated. This work brings this correlation, focusing on even more integrated production chains. Production of biofuels from residual biomass can also create by-products, even on the basis of sustainability and resource use, as in the case of the gasification procedure, in which biting and incrustations of the equipment can lead to a decrease in the performance by-product, consisting mainly of polycyclic aromatic hydrocarbons. There are therefore two parts of this work: the first is to get a liquid (bio-oil) phase by thermal cracking the tar, and the other, to produce a solid (coal) phase; and, the second, to utilise beer bagasses to obtain charcoal by pyrolysis. In order to include the sulphontate group in their structures, both solid products were submitted for a sulphonation procedure. Several methods for Valorization of Cherry and Date seeds residue analysis, including elemental testing, have shown sulphonation effectiveness and have shown up to a hundred times the amount of sulphur compared with the pre-operation material. As a heterogeneous catalyst, sulphonated tar coal was then used in the esterification and transesterification of oleic acid. With both alcohols, both methods achieved a 100% transformation (methyl and ethyl alcohol).

Keywords: Valorization of Cherry , Date seeds residue , valuable bio-based fuel via thermal pyrolysis approach

1.0 Introduction

Fossil fuel depletions and climate change have led to the development of renewable and alternative sources of energy that can satisfy global energy demands, while lowering greenhouse gas emissions, reducing pollution and keeping the world's temperature constant (Abbas, et al., 2019). One of the downsides of alternative energy sources is that it interferes (solar, hydro or wind power, for example), therefore other choices, such as biomass, that do not present this problem, have to be considered. Because of its great diversity and availability. All biodegradable organic materials from plants, animals and microbes can be determined by bio-mass (Mahmood et al., 2018). This term also covers goods, by-products, agricultural leftovers, and non-fossil organic waste created by industrial and municipal trash. Kazem et al., (2012) highlighted that the shift from oil to biomass is the key to the development of a sustainable society, energy independence and the management of

greenhouse gas emissions. Organic catalysts based on cheap raw materials are under experimentation and have shown good results. Biodiesel means a residue towards valuable bio-based fuel via thermal pyrolysis approach liquid fuel consisting of long-chain alkyl esters of carboxylic acid generated from fatty materials or esterification from vegetable and livestock oils or fats. The conversion of biomass into higher value-added products is key to consolidating this resource. Some well-established processes such as the Valorization of Cherry and Date seeds production of ethanol from sugarcane and thermochemical processes such as pyrolysis and gasification for the production of fuels and energy are already widely known and applied. The biodiesel production process from vegetable oil is also an example of a well-known and widespread production chain, already integrated with the main fuel suppliers around the world, such as Iraq, which sells diesel with biodiesel additions.

Carbonaceous solids obtained from the heat treatment of cellulose, starch, glucose and sucrose, and subsequent sulphonation, have shown high conversion and reuse rates, making their use on a large scale feasible. These catalysts have great potential to be substitutes for conventional sulphuric acid used industrially in homogeneous media, and can also be used not only for transesterification and esterification of fatty materials, but also in cellulose hydrolysis, nitration, among other reactions, acting as acidic solids. Methods for its preparation still need to be improved in order to increase activity, stability and reuse, methods that have already been explored in other studies. This work aims to develop acidic carbonaceous materials from Valorization of Cherry and Date seeds residue towards valuable bio-based fuel via thermal pyrolysis approach their processing, in order to apply them as heterogeneous catalysts in the production of biodiesel. In this way, we seek to integrate more sustainable energy production technologies with a focus on their efficiency and optimization, through the care and management of their waste, reducing industrial costs and, thus, spreading the production of ecologically friendly fuels.

2.0 Material and Methods

2.1 Materials: All the chemical used in this study are AR category purchased from Lab Chem, Sd fine chemicals, Sigma Aldrich with purity of 95-99%. [Sulfuric acid; Oleic acid; Analytical Synthetic Air 5.0 (99.999%), White Martins; KBr, NaCl, 99.5% pure ethyl alcohol, 99.8% pure methyl alcohol, analytical nitrogen 5.0 (99.999%), Glacial Acetic Acid, Glacial Acetic Acid, Isopropanol, Toluene, White Martins, Soybean oil, Magnesium sulphate heptahydrate, Thermal cracking reactor (three-way balloon, heating mantle, thermometer, condenser and balloon to collect condensed liquid).].

2.2 Gasification: The gasification system used was carried out following the methodology proposed by Rahman(2015), where eucalyptus wood residue (*Eucalyptus* spp.) was gasified in a counter current fixed bed reactor. In the gas outlet system, two 1 L kit-assets were coupled, with isopropanol for condensing the by-products of the process (tar) and thus cleaning the gas obtained. Thus, this isopropanol solution with the residues was submitted to the evaporation procedure to remove the solvent, water and dissolved light acids to obtain only the tar and application in the next experimental stage (thermal cracking). The tar obtained was characterized by infrared spectroscopy and thermogravimetry.

2.3 Obtaining coal from tar by thermal cracking: 100 g of tar were used for the thermal cracking process in which the reaction temperature ranged from 260 to 450°C. After the

procedure, the charcoal produced was removed from the balloon, dried and stored in a desiccator. For its later use in the sulphonation process, the charcoal was crushed by maceration. The name of the derived samples are Tar derived from the gasification of Eucalyptus wood (AE) and Coal produced from the cracking of Tar (CA). After the procedure, the charcoal produced was removed from the balloon, dried and stored in a desiccator. For its later use in the sulfonation process.

2.4 Preparation of sulphonated materials: The coal produced from the cracking of tar (CA), as well as the coals produced from the pyrolysis of bagasse of 100% barley malt (CBC), cellulose (CC) and starch (CAm) were submitted to the sulphonation process. The coals were subjected to reaction with sulphuric acid at 80 °C and under constant agitation for 1 h. The system used was a stainless steel reactor with a Teflon container and heating controlled by electrical resistance. After the procedure, the sulphonated materials (sulphonated carbons) were then filtered and washed with distilled water to remove all excess sulphuric acid (pH measurements were taken of the filtrate to attest to the effectiveness of the washing). Then, the materials were dried at 105 °C to remove moisture and stored in a desiccator. The samples after the sulphonation process of the respective coals were Sulphonated Coal from CA(CsA); Sulphonated Coal from CBC (CsBC); Sulphonated Coal from CC(CsC) and Sulphonated Coal from CAm(CsAm).

Stages of the beer production process until the separation of spent grains from the beer or malt bagasse adopted from the method developed by Mussatto et al., (2006)

2.5 Characterization techniques: The characterization techniques for the sulphonated carbons were Elemental analyzes of Carbon, Hydrogen and Nitrogen (C,H,N) were carried out in the Perkin Elmer 2400 Series II CHN/S equipment (the oxygen was obtained by difference together with the residue of the TG analysis, as well as the percentage of hydrogen where it was taken into account the amount of water) and energy dispersive X-ray fluorescence (XRF/EDX), using a Shimadzu spectrometer, model EDX-720, with X-ray tubes with a rhodium (Rh) target. Fourier transform infrared (FTIR) spectra were obtained on a VARIAN 640-IR spectrophotometer. Measurements were performed using KBr pellets and wavenumber readings between 400 and 4000 cm^{-1} . The TG/DTG curves were obtained in a Shimadzu equipment, model DTG-60H, using synthetic air (99.999%) and nitrogen (99.999%) as purge gases (30 mL min^{-1}). Analyzes were performed from room temperature (~26 °C) to 800 °C at 20°C min^{-1} . Platinum pans with a mass between 15 and 20 mg were used for each analysis and SEM –EDS analysis by Fei Quanta 450 equipment and a radiation current of 5-10 kV and 90 mA also coupled to a Dispersive Energy System (EDS)).

2.6 Reactions for biofuel production

For the reactions tested in this work, sulphonated coal derived from the cracking of tar was used as catalyst. Fatty acid esterification and oil transesterification reactions were tested.

2.6.1 Esterification Reaction: The esterification reaction was carried out with P.A. oleic acid using 10% catalyst (in relation to the amount of oleic acid). It was activated at 200 °C in a muffle for 1h before application in the reactions. The reaction system used is described by Macedo⁹⁷, in which 5 mL mini-reactors were used. Methanol and ethanol were used in a 1:6 ratio (oleic acid:alcohol), and the reactions were tested in 1, 2, 3 and 4h. All reactions were carried out at 100 °C with an average agitation of 400 rpm. After being removed from the

reaction system, the product was centrifuged to remove the catalyst and then washed with water. After separating the water, MgSO_4 (24h) was added to remove the aqueous solution residues in the produced esters.

2.6.2 Transesterification Reaction: The transesterification reaction was carried out with commercial soybean oil (LIZA brand), being also tested with methanol and ethanol. The reactions followed the same parameters for the esterification, being 10% catalyst, 1:6 ratio (oil:alcohol), 100°C with 400 rpm of agitation, being tested in 1,2,3 and 4h of reaction. The product of the reactions was centrifuged to remove the catalyst and added a 10% NaCl solution (w/w). To the product after separation was also added MgSO_4 (24h).

2.6.3 Malt bagasse from beer production: Four types of malt bagasse were used, three of them with a mixture of barley malt and adjuncts (unmalted cereals) and one with 100% barley malt. The 100% malted barley bagasse. The other bagasse has a mixture of malt with barley, corn (45.0 % m/m), millet (45.0 % m/m) and buckwheat (40.0 % m/m) in their formulation and were collected from developed productions. Two samples were also used as reference for the analysis and for the process, microcrystalline cellulose and starch. The names of the samples and the respective abbreviations used to name them in this work are presented as 100% barley malt bagasse (BC); Barley malt bagasse (55.0% m/m) + corn (45.0% m/m) (BM); Barley malt bagasse (55% m/m) + millet (45% m/m) (BMT); Barley malt bagasse (60% m/m) + buckwheat (40.0% m/m) (BS); Microcrystalline Cellulose (CM) and Starch (Am). The biomass used for the physicochemical analyses was obtained with a particle size between 20 and 50 mesh for the samples from the first crushing process and between 50 and 100 mesh for the samples from the second processing. The bagasses were characterized by immediate analyses (moisture, volatiles, ash and fixed carbon), as well as their composition in terms of lignin, holocellulose and extractable in order to study the composition of the plant structure present in these samples. In addition, the following characterization techniques were used: X-Ray diffraction (XRD), in order to verify the crystal structures in the samples, comparing them with their respective standards, thermal analysis (TG/DTG/DTA) with the objective to evaluate the thermal decomposition and elemental analysis of Carbon, Hydrogen, Nitrogen and Oxygen (CHNO), as well as X-Ray fluorescence analysis by energy dispersive (XRF/EDX) that characterizes its elemental composition.

In order to compare the pyrolysis results of the studied samples with some of their main structural components, two standards were submitted to the pyrolysis process, microcrystalline cellulose P.A. (CM) and starch P.A. (Am). These two compounds present in biomass (more complex matrix), when subjected to the same process as the samples studied, help to elucidate the process of formation of carbonaceous material. In addition, coals produced from such inputs are already reported in the literature, which were later submitted to the sulphonation process (main purpose of the application of such coals in this work) and, thus, help as a comparative basis for sulphonated coals from samples of this work, in this case tar and bagasse from beer production.

3.0 Results and Discussion

3.1 Thermal Cracking of Tar Derived from Biomass Gasification

3.1.1 Characterization of the tar cracking product: The tar derived from the gasification of eucalyptus (EA) as well as the product derived from its cracking (CA) were characterized

by infrared in order to observe the differences when the thermal process was applied, observing the main predominant organic functions (spectra shown in Figure 1). Tar has a very heterogeneous composition and may contain several species of long-chain hydrocarbons, as well as the characteristic polycyclic aromatic groups present in this by-product.

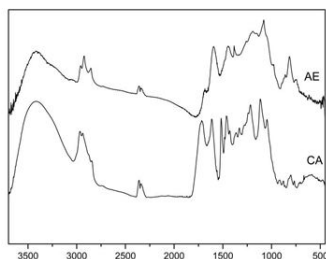


Figure 1 - Infrared spectrum of tar from eucalyptus gasification (AE – Eucalyptus tar) and coal derived from cracking (CA – Coal derived from tar).

The main bands observed in the AE spectrum were: 3400 cm^{-1} attributed to OH stretch (which could be water or phenolic and carboxylate compounds), CH stretch from 2963 to 2845 cm^{-1} (associated with alkyl and aromatic groups), 1700 cm^{-1} corresponding to the C=O stretch, band in 1612 cm^{-1} associated with the angular deformation of the water, band in 1451 cm^{-1} associated with the angular deformations of $-\text{CH}_2$ and CH_3 groups, and between 750 and 900 cm^{-1} corresponding to the deformation of aromatic ring; C-O stretch at 1257 cm^{-1} and C-O-C deformation at 1103 cm^{-1} (may be associated with long-chain ethers and esters); in addition, the presence of stretches at 1450 and 1600 cm^{-1} indicate the presence of a C=C group characteristic of aromatic species present in biomass-derived tar. In CA, the following bands are observed: 3417 cm^{-1} corresponding to the stretching of the O-H group; 2960 , 2924 and 2854 cm^{-1} from the C-H stretch; 1595 and 1444 cm^{-1} associated with C=C stretch, 1192 and 1082 cm^{-1} may be related to C-O stretch (present in phenols) and 815 cm^{-1} attributed to C=C stretch of aromatic rings with substitutions. The reduction of stretch by 1700 cm^{-1} in CA, in relation to AE, demonstrates that the cracking process was able to considerably decarboxylate the structure. Furthermore, even with the presence of stretching in the region of 1000 to 1100 cm^{-1} in CA, the sample's “deoxygenation” can be attributed, considering that these bands become phenolic compounds or water, instead of ethers and long-chain esters attributed to AE accompanied by the presence of signals at 1200 and 1300 cm^{-1} . In Figure 2, the TG and DTG curves for AE and CA are presented. There is a considerable difference in the thermal degradation profiles of AE and AC. AE has three main mass losses, at $195\text{ }^\circ\text{C}$, $370\text{ }^\circ\text{C}$ and $508\text{ }^\circ\text{C}$. As an extremely heterogeneous material (in terms of the various types of hydrocarbons present), it is difficult to predict exactly what is degraded in each phase through this analysis, but it is possible to infer that the mass losses may be related to compounds of lower molecular weight, such as water, remnants of the solvent in which the tar was collected (isopropanol), organic acids and lighter hydrocarbons. At $307\text{ }^\circ\text{C}$ and $508\text{ }^\circ\text{C}$, the second and third mass loss occurs, resulting from the thermal degradation of medium and high molecular weight compounds. The last loss may possibly be associated with the breaking of polycyclic aromatic groups, characteristic of this by-product, and which have higher thermo-resistance due to the maintenance of a resonant structure with stronger carbon bonds. As for CA, 3 losses are identified from the DTG. The first two of lesser intensity at $70\text{ }^\circ\text{C}$ and $185\text{ }^\circ\text{C}$, related to the loss of physically and chemically adsorbed water. The third and

most expressive mass loss has its maximum reached at 472 °C, due to the thermal decomposition of the more thermally stable carbonaceous structure as a result of the consequences of thermal cracking. Making a parallel with the AE thermal cracking process, the temperature used for the process reached approximately 400 °C, and it can be observed that the compounds that would be degraded after this temperature remain in the formed coal (observed by the proximity of the peaks in the DTG at 508 °C for AE and at 472 °C in CA). Thus, the thermal process (cracking) applied in EA was able to degrade the lower molecular weight compounds, as well as the output of oxygenated compounds (as inferred by the IR analysis), letting the higher molecular weight compounds form a structure more stable carbonaceous in CA (degradation starts around 400 °C), the main objective of the procedure to form a more cohesive carbonaceous structure.

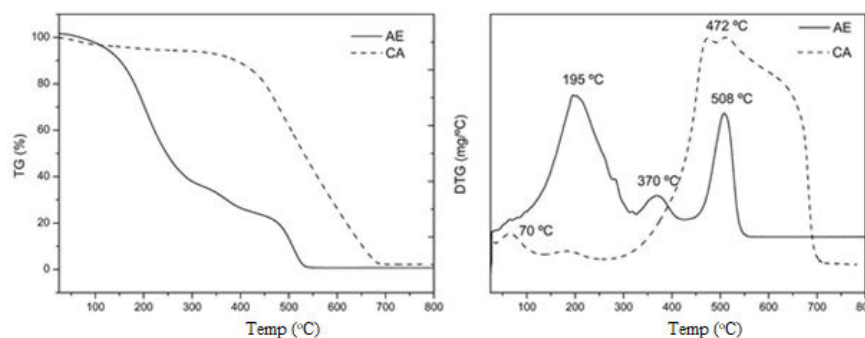


Figure 2: Thermogravimetric curves (TG) and Derivatives of thermogravimetric curves (DTG) in Synthetic Air from tar and coal derived from tar cracking.

The process of using tar through thermal cracking is one of the possibilities for the destination of this by-product, which creates major problems for gasification processes. The alternative of forming new materials from waste enables the integration of technologies, considering that the gasification of biomass already has the objective of producing gaseous biofuel, the route of converting its residue to form another product (which will assume different functions in other processes) adds value to the entire production chain through gasification. In addition, cracking enabled the production of a liquid co-product (bio-oil), which has the potential to be also investigated as to its use (in the production of by-products or in their refining and direct use), with these topics being perspective for future deepening in this investigation. The process enabled the formation of a solid product with characteristics of the formation of a stable aromatic carbonaceous network, considering the spectroscopic and thermogravimetric analyses.

3.2. Step-2: Bagasse from Beer Production: Characterization and Pyrolysis for Charcoal Production

3.2.1 Characterization of Bagasse from Beer Production: Infrared is not able to clearly elucidate the specific composition of the compounds present in the biomass, but through the organic functions it is possible to infer the presence of some components and other techniques should complement the characterization of the biomass. In this work, the use of bagasse from beer production from beers produced only with barley malt and with the addition of some adjuncts was explored. Its derivatives (in this case, in the pyrolysis products). In Figure 3, the IR spectra for the 4 bagasses used are presented. All had a very similar profile with very close band values, except for the intensity of some specific bands.

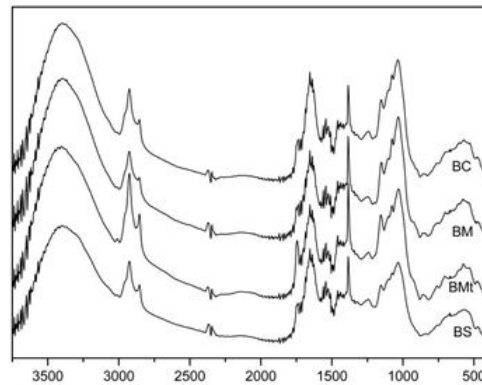


Figure 3 - Infrared spectrum of brewing

The main bands observed in the four spectra were: 3394 cm^{-1} , associated with O-H stretch (water, phenolic compounds and alcohols); 2925 and 2854 cm^{-1} , corresponding to the >C-H stretch; 1745 cm^{-1} low intensity band that can be attributed to >C=O; 1654 and 1542 cm^{-1} , attributed to the C=C stretch (may be related to the presence of aromatic compounds such as phenols and carboxylates present in organic acids and lignin that make up the biomass structure); 1382 cm^{-1} , associated with symmetric folding of $-\text{CH}_3$; 1033 cm^{-1} , associated with C-O stretching (present in ethers, esters, carboxylic acids and alcohols) and 1245 cm^{-1} , corresponding to C-O-C stretching (present in ethers and esters); 574 cm^{-1} to C-H folding. This profile follows what was found for the analyzed bagasse Candido, et al (2019). Table 1 shows the values of the elemental analysis for bagasse (BC, BM, BMt and BS) and for CM and Am.

Table 1- Elementary analysis of bagasse from beer production

Elements(%m/m)*	Microcrystalline Cellulose	Starch	100% barley malt bagasse	malted barley bagasse + corn	malted barley bagasse + millet	malted barley bagasse + buckwheat
	41.8	37.7	44.7	43.5	44.9	45.2
Carbon	6.0	6.6	6.9	6.6	6.9	6.4
Hydrogen	0.2	0.1	3.2	3.4	2.9	2.9
Nitrogen	50.1	55.6	40.7	43.4	42.7	41.9
Oxygen	-	-	0.5	0.6	0.3	0.5
Sulphur	1.9	-	4.0	2.5	2.3	3.1

*Data presented is on a dry basis.

The bagasse samples had a similar carbon content with an average of $44.6\% (\pm 0.8)$, as well as the hydrogen content with an average of $6.7\% (\pm 0.2)$, differing from the levels found for CM and Am (the result of a compositional difference already expected for these reference samples and the biomass samples of plant origin). For nitrogen and oxygen contents there is a notable difference. Biomass have nitrogen content around 3%, while for CM and Am this is close to zero. Such result is to be expected considering that both were used from P.A reagents and it is expected that for such compounds they do not contain nitrogen. The oxygen content was higher for CM and Am (50.1 and 55.6%, respectively) in relation to biomass that was around $42.2\% (\pm 1.2)$. The sulphur contents for BM, BMt and BS were close to between 2 and

3%, standing out only for BC whose value was 4%. The composition in “others” represents the inorganic material present in the samples. The bagasse in this composition contains Ca, P, K, Si, Fe and Zn, elements also present in the cereals that give rise to the bagasse. Ulbrich et al. (2017) performed elemental analyses for bagasse from beer production (the type not specified), reporting the contents of CHNS are close to the bagasse studied in this work, taking into account the variability of the raw material used as the origin of the cereal used in beer and the conditions of the brewing process, it is also worth emphasizing the presence of adjuncts that can modify this profile. Data from immediate analyses (moisture, volatiles, ash and fixed carbon) for bagasse are shown in Table 2.

Table 2 - Data from the immediate analysis of the studied beer production bagasse

Composition (% m/m)	100% barley malt bagasse	malted barley bagasse + corn	malted barley bagasse + millet	malted barley bagasse + wheat Saracen
Moisture	77.67	78.78	71.1	75.75
Volatiles*	81.1	81.61	81.71	80.3
Ashes*	3.64	2.53	2.42	3.33
Fixed carbon*	16.26	16.87	16.87	17.37
Dice of composition of two bagasse from beer production studied				
Extractives	18.89	25.35	18.69	9.19
Cellulose	11.72	8.89	8.28	17.68
Hemicellulose	32.83	30.40	32.42	42.72
Lignin	22.93	20.30	22.73	30.70
insoluble	11.41	8.28	8.59	8.79

* The values are presented on a dry basis.

In various work or process of drying, it is necessary to prepare the raw material for the adequacy of the operational conditions for its transformation, which by consequence will lead to obtaining a product with a higher added value than the original malt stock. Comparing the data (Table 2) between the actual samples, a quantitative variation is not large, observing that two adjuncts have no significant effects on these parameters. These data are important, they can predict the behaviour of biomass against thermal degradation processes, such as the pyrolysis process. A high volume of flipping, for the pyrolysis process, for example, provides higher yields in bio-oil production, while higher fixed carbon values are preferred for bio char production. In Table 2, the composition values of two studies of beer production are presented. The theoretical data of extractive stayed are heterogeneous among themselves, varying from 25.1% for BM to 9.1% for BS. The extractives are essentially minor organic compost, such as carboxylic acids and alkalis. No process, it occurs, also, to extraction of some free acids that may be present (normally reported as lipid theory, more or same day extraction process). As it was varied to the composition of two attachments, these contribute to the modification of this profile. Santos et al. (2015) report on the analysis of beer bagasse in five main analyses. The cellulose (mean of 11.5% (\pm 4.3)) and hemicellulose (mean of 34.3% (\pm 5.5)) theories remain close to values for BC, BM and BMT, while for or BS these values increased, cellulose for 17% and hemicellulose for 42%. Such a change is the fruit of

the structural composition of buckwheat whose vegetative fibres from large hulls are in a large quantity and provide an increase proportional to the mixture as the bagasse of malt.

XRD analysis assists in the elucidation process of the matrix in terms of its structure. Especially for vegetative species, some structures have crystalline phases capable of diffraction, like cellulose in its crystalline phase. The diffractograms of the images show forms superposed as microcrystalline cellulose, following a scale presented provided hairs given from an analysis of the equipment, being presented in Figure 4.

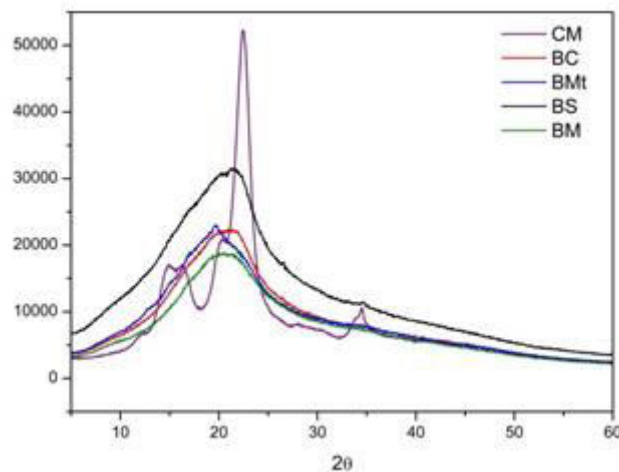


Figure 4 - X-Ray Diffractograms of bagasse

Thus, biomasses will show the following values of 2θ with higher intensity: BC(21.5°), BM(20.5°), BMt(19.6°) and BS(21.6°). Pradhan, et al (2020) characterize the bagasse of malt for its insertion in the production of biodegradable forms, and use the non-working XRD to compare the insertion of another matrix in the form composition. It is reported a value of 2θ of 20.9° attributed to crystalline cellulose, a value close to two found for the bagasse in this work. The BS angle a little before two more goes than found in composition analysis, where this has a higher quantity of cellulose. Pradhan, et al states that it peels the presence of proteins and oligosaccharides not bagasse, for this reason it has a very complex, difficult, and difficult three-dimensional removal or crystallization process. Looking at Figure 4, it is possible to see that the peak of the 002 plane present in our range is close to the same peak for CM, which has a crystallinity of 80%. In this way, it is verified that crystalline cellulose is present in the studied biomasses, and the same contribution of amorphous cellulose is a component that is combined with other composites that have higher thermostability (lignin) for the process following heat treatment.

Another analysis of extreme importance for the characterization of biomass and its thermal degradation profile. Following in Figure 5 are shown the curves of TG and DTG in synthetic Ar of BC, BM, BMt and BS, and CM and Am, respectively.

Analysing the bagasse composition data and the thermogravimetric curve data (Figure 5), a correlation can be made between the weight loss values and the composition values for each component. This comparison is a little delicate considering that the mass loss ranges of each component are not precisely delimited, considering that some components degrade over a wider temperature range. Making this parallel, a range of thermal decomposition where we

can make a more accurate comparison is between 500 °C and 800 °C, where the remaining lignin in the biomass is degraded (the most thermally stable component and the last to be degraded). Analyzing the losses in this range for BC, BM, BMt and BS, the corresponding values are 22.7%, 22.6%, 24.7% and 28.2%, respectively. These values are close to the compositional analysis for insoluble lignin where the percentages obtained for the samples were 22.7%, 20.1%, 22.5% and 30.4%, respectively.

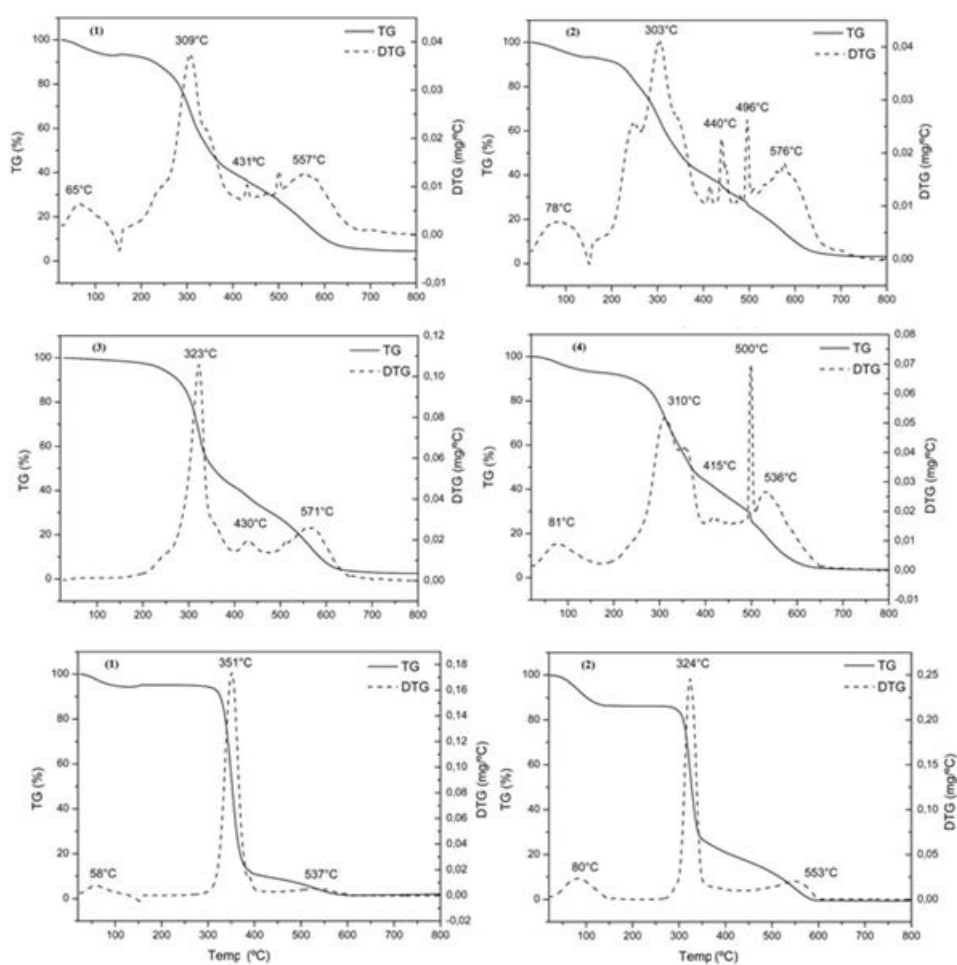


Figure 5 - Thermogravimetric curves (TG) and derivatives of thermogravimetric curves (DTG) in Synthetic air of bagasse and Synthetic Air of the reference samples

Faced with the objective of carrying out a thermochemical process with the studied biomass, knowing their thermogravimetric profile is extremely important to understand their behavior under the desired operating conditions for the process. As an example of the production of charcoal in pyrolysis, which is directly related to the amount of lignin in the sample, some authors attribute lignin as the main component of controlling the rate of the pyrolysis reaction, as well as the conversions and composition of the products

Superior calorific value tests (SCV) were carried out for all bagasse. SCV values are shown in Table 3. In order to produce a carbonaceous material through the pyrolysis process of these biomasses, it is important to know the amount of stored energy, which can be used during the

process. The bagasse had very similar SCV values, on average 20.24 (± 0.8) MJ/Kg. Balogun (2017) performed the same type of analysis for malt bagasse (MBr) in their study, reporting a value of 21.917 MJ/Kg, pointing out that this value is relatively high among lignocellulosic biomasses and that such resource is great for thermal decomposition processes. This analysis points out that bagasse can be used and used in other thermochemical conversion processes and that, in a suitable reactor, not only the coal can be separated, but also the gaseous fraction and the liquid fraction (bio-oil).

Table 3 - Superior calorific value (SCV) values for beer bagasse samples

Bagasse samples	Superior calorific value(MJ/Kg)
Bagasse 100% barley malt	19.897
Barley malt + corn bagasse	19.493
Barley malt bagasse+ millet	19.998
Bagasse of barley malt + buckwheat	19.897
malt bagasse (MBr)	21.917

4.0 Conclusions

The prepared materials showed Valorization of Cherry and Date seeds residue towards valuable bio-based fuel via thermal pyrolysis approach. The high acid density is a favourable characteristic for an acid heterogeneous catalyst, allowing smaller amounts of catalysts to be used for high conversion values, in addition to reuse possibilities without loss of activity. As a perspective, there is an analysis of the surface areas of the prepared materials, in order to make a correlation with the acid density and prove their better performance against the works described in the literature on similar materials. In addition, the perspective of Valorization of Cherry and Date seeds residue towards testing other sulphonated materials in front of esterification and transesterification reactions, testing the reaction kinetics by temperature, alcohol:fatty material molar ratio and amount of catalyst. The recycling of catalysts under the most optimized experimental conditions and the consequent evaluation of their leaching are also perspectives of this work. The towards valuable bio-based fuel via thermal pyrolysis approach can still be incorporated into other reaction systems that use acid catalysis, given the acid density results found. The hydrolysis of lignocellulose materials is one of the application perspectives for these catalysts.

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