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Slow Pyrolysis as a Method for Biochar Production from Carob Waste: Process Investigation and Products' Characterization

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Abstract: The zero-waste city challenge of the modern society is inevitably addressed to the development of model's waste-to-energy. In this work, carob waste, largely used in the agro-industrial sector for sugar extraction or locust beangum (LBG) production, is considered as feedstock for the slow pyrolysis process. According to the Food and Agriculture Organization of the United Nations (FAO), in 2012, the world production of carobs was ca. 160,000 tons, mainly concentrated in the Mediterranean area (Spain, Italy, Morocco, Portugal, and Greece). To evaluate the biomass composition, at first, the carob waste was subjected to thermo-gravimetric analysis. The high content of fixed carbon suggests that carobs are a plausible candidate for pyrolysis conversion to biochar particles. The thermal degradation of the carob waste proceeds by four different steps related to the water and volatile substances' removal, degradation of hemicellulose, lignin and cellulose degradation, and lignin decomposition. Considering this, the slow pyrolysis was carried out at three different temperatures, specifically, at 280, 340, and 400 °C, and the obtained products were characterized. Varying the processing temperature, the proportion of individual products' changes with a reduction in the solid phase and an increase in liquid and gas phases, with an increase in the pyrolysis temperature. The obtained results suggest that carob waste can be considered a suitable feedstock for biochar production, rather than for fuels' recovery.

Keywords: slow pyrolysis; carob waste; biochar



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1. Introduction

In recent years, an increasing number of studies have been focused on the conversion of waste, biomass, and various residues into energy, fuels, and other useful materials that should otherwise be disposed of, with the aim of achieving a circular economy and, above all, a zero-waste society. One of the ways to valorise waste, obtaining energy, in terms of fuel and gas, is the pyrolysis process. Pyrolysis is the oldest known method to process biomass [1], with the waste streams coming from agriculture and food industries being its main source of feedstock. Essentially, it is possible to describe pyrolysis as a thermal decomposition that produces three different new resources: synthetic gas (a mixed gas phase of hydrocarbons), oil (mixed of heaviest hydrocarbons), and biochar. Varying the temperature range, pressure, and residence time, the proportion of individual products changes [2,3]. In fact, fast pyrolysis is the most efficient method to produce biofuel, whereas gasification is the most efficient method to produce syngas, and thus is used to generate energy and heat [4]; instead, slow pyrolysis tends to yield higher proportions of biochar owing to the slow heating rates and longer residence time [5–7]. Anyway, as fast pyrolysis is a cost-intensive process in terms of energy, maintenance of equipment, and safety, owing to the rigid process condition, considerable research effort is going into the development of slow pyrolysis for fuel and biofuel production [1,5,8]. There are many studies on the possibility to obtain biofuels via biomass slow pyrolysis [6,7,9–11]. The produced gas fraction can be upgraded in order to obtain syngas or gaseous fuel [12]. Regarding the

solid fraction, some studies focus on the possibility to apply biochar to soil in order to enhance its fertility [13]. J. Gaunt and J. Lehmann studied the implications for greenhouse gas (GHG) emissions of a slow pyrolysis-based bioenergy system for biochar and energy production [8].

Biochar is a carbon-rich material, used nowadays as a renewable fuel or as an additive for improvement of soil quality [2,3,13]. Biochar is essentially composed of carbon, hydrogen, oxygen, nitrogen, sulphur, calcium, and silicon; the proportion between these elements depends on the nature of the biomass used for the pyrolysis process, as well as on the temperature used in the process. Sizerici et al. [2] report how the carbon and calcium concentration in the final biochar increases with increasing pyrolysis temperature; on the other hand, oxygen and hydrogen contents decrease. Biochar is characterized by a higher proportion of aromatic C and condensed aromatic structures, in different forms including amorphous C, turbostatic C, and graphite C [14]. Moreover, in the last years, biochar has attracted attention as a filler for the formulation of bio-composites thanks to its ability to improve mechanical and thermal stability, as well as barrier properties of the polymer system [15–17]. Moreover, the presence of functional groups, able to interact with the polymer matrix, improves the compatibility and final adhesion of the biochar particles.

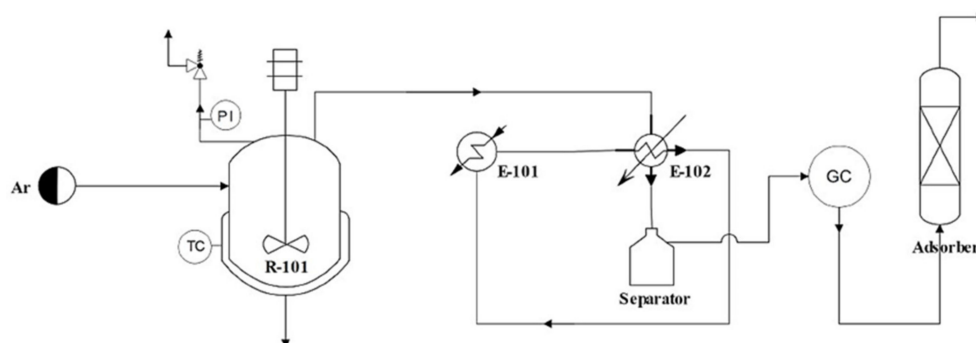
The employment of biochar as a filler for bio-based composites is of great importance in connecting the circular economy and bioeconomy models. The agriculture and food industry generate a waste flow that is usually transformed into biofuel and syngas by means of slow pyrolysis. On the other hand, this process results in a biomass waste product that is typically lost; in this work, we propose to recover this biomass as a value-added char to be used as reinforcement material for bio-composite applications. Particularly, carob waste, after syrup extraction for carob candy production, was subjected to slow pyrolysis at three different temperatures of 280, 340, and 400 °C in order to convert the biowaste in value-added biochar. Feedstock and pyrolysis products, i.e., solid phase, oil, and gas, were characterized to optimize the process conditions and to maximize the production yields.

2. Materials and Methods

Carob waste, after sugar extraction process aimed at the production of carob candies, was used as feedstock.

2.1. Experimental Apparatus and Procedure

The thermal cracking of carob waste was carried out in a semi-batch reactor under atmospheric pressure and inert atmosphere of argon. The piping and instrumentation diagram (P&ID) of the apparatus is shown in Scheme 1.



Scheme 1. P&ID of the experimental apparatus used for slow pyrolysis of carob waste. Reprinted with permission from ref. [11]. 2021 Elsevier.

The reactor R-101 is an autoclave stirred one with a volume of 500 mL. It was flushed with argon in order to remove air from the system and avoid oxidation phenomena. The reactor was heated by electric heating bands. For each cracking experiment, about 20 g of carob waste was placed in the reactor, which was heated with an average heating rate

of 10 °C/min from room temperature to 280 °C, 340 °C, and 400 °C, depending on the experiment. The produced gas stream was sent to the E-102 condenser and cooled with a water–glycol mixture in order to collect the heavier and condensable species inside the separator. The temperature was kept constant at 20 °C by the chiller unit E-101. Thus, the gas fraction was sent to the gas chromatograph (GC) for composition analysis. The adsorption column with activated carbon is necessary to significantly reduce the content of dangerous compounds from the gas stream before venting. All of the experiments were carried out at least twice.

2.2. Analysis of Feedstock

Proximate analysis and thermogravimetric study on carob waste were carried out by means a Netzsch STA 449 F1 Jupiter thermogravimetric analyser. About 90 ± 5 mg of the considered sample was crushed in order to reduce carob waste to powder and transferred in the crucible of the analyser. Each analysis was repeated at least in duplicates and the sample was heated with a heating rate of 10 °C/min from room temperature to 600 °C. Regarding the proximate analysis, in this case, 100 ± 5 mg of the sample was heated from room temperature to 900 °C in a nitrogen atmosphere. In this case, air is sent to the sample in the last part of the analysis in order to oxidize it and to determine the ash content.

2.3. Analysis of Thermal Cracking Product

Liquid fractions were analysed by a Fourier transform infrared spectroscopy (FTIR) Cary 630 Spectrometer (Agilent Technologies, USSanta Clara, CA, US) in the range 4000–650 cm^{-1} with a resolution of 1 cm^{-1} , in order to have a qualitative composition analysis of the samples at each pyrolysis temperature. About 100 μL of the liquid samples was mixed and crushed in a mortar together with 90 ± 5 mg of potassium bromide (KBr) to made sample discs with a hydraulic press (CrushIR, PIKE Technologies, Madison, WI, US). For the characterization of carob waste and the obtained biochar at each pyrolysis temperature, a Spectrum One (Perkin Elmer, Shelton, CT, USA) was used to record IR spectra using eight scans at a resolution of cm^{-1} , on attenuated total reflectance (ATR) mode in the range 4000–450 cm^{-1} . Measurements were performed both on carob and on the three temperature solid fractions.

Solid fractions' HHVs were determined with *Parr 6200* calorimeter. In this case, 1 g of the sample was introduced in *Parr 1108* style oxygen bomb and each analysis was repeated in duplicates.

The microstructure of biochar particles obtained after pyrolysis treatment was investigated using a scanning electron microscope (SEM, Quanta 200 ESEM, FEI, Hillsboro, OR, USA). Prior to SEM analysis, biochar particles were sputtered (Scancoat Six Edwards, Crawley, UK), with a thin layer of gold under argon atmosphere for 90 s, in order to avoid electrostatic charging under electron beam.

3. Results and Discussion

3.1. Carob Waste Characterization

To evaluate the suitability of the carob waste as feedstock for pyrolysis conversion to biochar, the proximate analysis (air-dried basis) was performed by means of thermogravimetric analysis, and the obtained trend is shown in Figure 1. As known, the content of fixed carbon is related to the solid yield, while the volatile content is related to the gas and liquid yields [18]. Carob waste is characterized by a relatively low moisture content, which is 5.1 %wt. (air-dried basis); see Figure 1. The volatile matter and fixed carbon represent more than of 50% of the initial sample weight, 38.3 %wt. and 52.8 %wt., respectively. Further, the final ash value is 3.8 %wt. Therefore, the high value of fixed carbon suggests that the carob waste can be considered suitable feedstock for biochar particles' production.

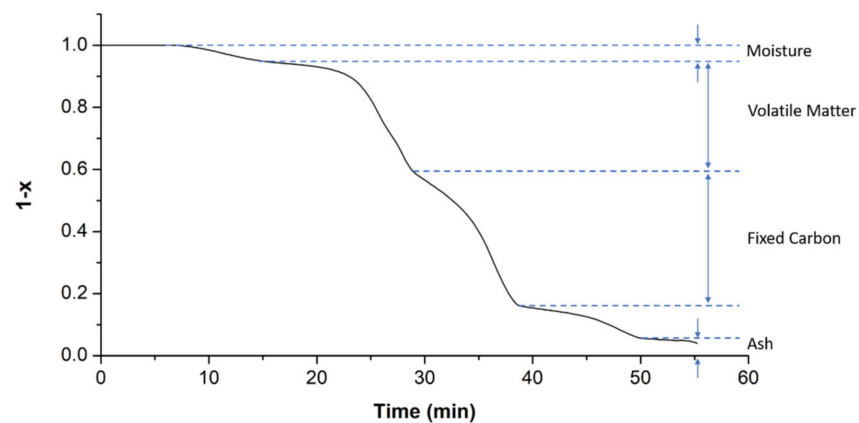


Figure 1. Thermogravimetric curve for proximate analysis of carob waste.

To investigate the thermal degradation of the carob waste, an accurate thermogravimetric analysis was carried out and, in Figure 2, TG and DTG curves of considered carob waste are shown. It is possible to notice that the carob waste has a wide thermal degradation range that begins at ca. 95.6 °C and ends at ca. 525.0 °C with a weight loss of 61.9%. As it can be seen in Figure 2, the DTG trend shows four different well distinguished peaks, suggesting that the thermal degradation of carob waste is a complex process, that occurs by four different degradation steps. Particularly, the first DTG peaks, at about ca. 105.0 °C, are related to the removal of moisture and very high volatiles components. According to the literature, the lignocellulosic biomass degrades upon thermal stress by three different steps, which are (i) degradation of hemicellulose, (ii) lignin and cellulose degradation, and (iii) lignin decomposition [9]. In agreement with the literature, the carob waste shows that the degradation of hemicellulose occurs at 274.5 °C, while the lignin and cellulose structure degradation and the lignin decomposition take place at 336.3 °C and 464.5 °C, respectively. On the basis of the DTG curve, carob waste was pyrolyzed at three different operative temperatures, which are 280, 340, and 400 °C; the temperatures at 280 °C and 340 °C were chosen in order to maximize the rate of decomposition, while the temperature at 400 °C was chosen as a compromise between the need of high weight loss and the need of energy saving with respect to 464.5 °C.

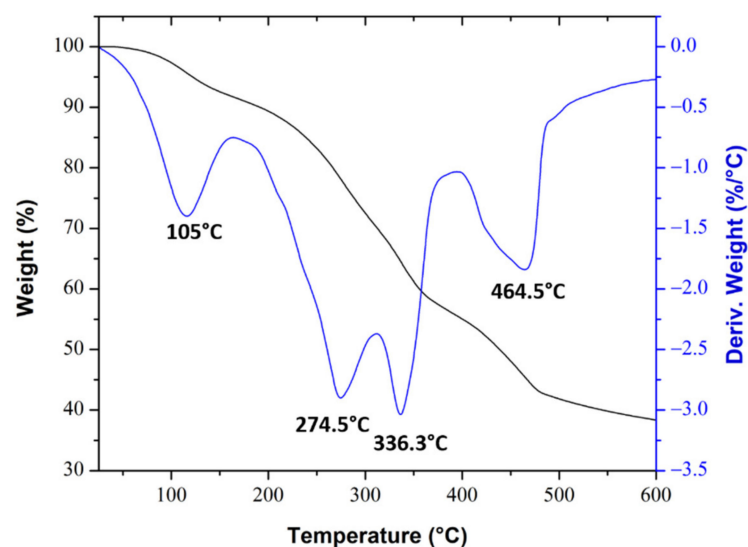


Figure 2. TG and DTG curve of carob waste.

3.2. Pyrolysis Experiments

To study the effect of the operative temperature on the process and on the pyrolysis products' yields, the pyrolysis of carob waste was carried out at three different temperatures:

280, 340, and 400 °C, as discussed above. The obtained temperature profiles during pyrolysis experiments in the laboratory-scale reactor are shown in Figure 3. The reactor was heated with an average heating rate of 10 °C/min from room to the final temperature and each experimental test lasted 105 min. The reaction volume was also stirred at 150 rpm in order to maintain a constant temperature gradient and keep solid in motion. Based on the trends shown in Figure 3, it can be noticed that the temperatures of the reactor were about 200 °C after about 15 min of the pyrolysis beginning, and they were reached setting values up to next 15 min. It is clear that the temperatures inside the reactor was maintained almost constant during the carob waste treatment, suggesting that the pyrolysis processes occur successfully.

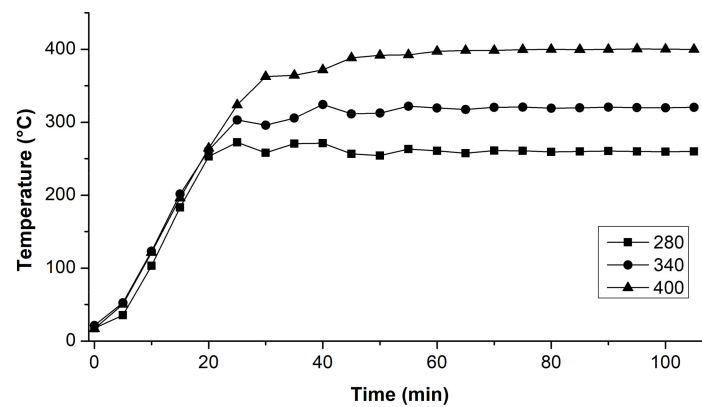


Figure 3. Temperature profiles for each pyrolysis temperature.

Regarding the products' mass yield, the mass of the produced gas phase was calculated from the mass balance on the system as follows:

$$m_{\text{gas}} = m_{\text{biomass}} - m_{\text{liquid}} - m_{\text{biochar}} \quad (1)$$

Figure 4 shows a comparison between the obtained yields for each experimental test, considering the three different pyrolysis temperatures, i.e., 280, 340, and 400 °C. The liquid phase and the biochar were collected at the end of each pyrolysis experiments, when the temperature of the system was low enough, and thus weighed.

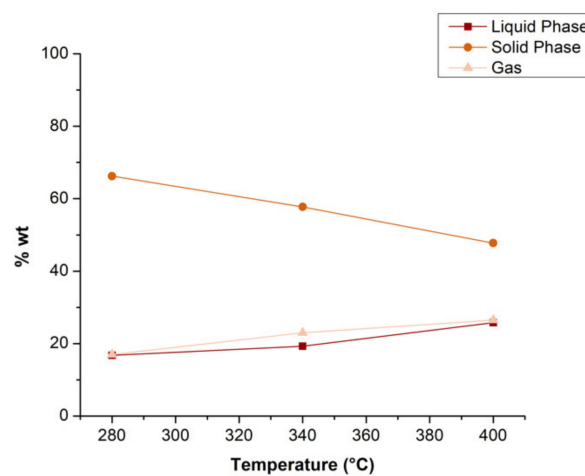


Figure 4. Products' yields at each pyrolysis temperature.

As one can see in Figure 4, the liquid phase yields increase with increasing temperature from 17 %wt. at 280 °C to 27 %wt. at 400 °C. The obtained liquid phase was an aqueous phase with traces of pyrolysis oil. For this reason, it was not possible to measure liquid fractions' HHVs. The solid phase is the predominant fraction and the mass yields decrease

with increasing temperature from 67 %wt. at 280 °C to 48 %wt. at 400 °C, as is typical for biomass slow pyrolysis [5,19]. Solid fractions' HHVs are 23.5 MJ/kg at 280 °C, 25.1 MJ/kg at 340 °C, and 28.6 MJ/kg at 400 °C, and increase with increasing temperature. Regarding the gas phase, in this case, the mass yields slightly increase with increasing temperature from 17 %wt. at 280 °C to 27 %wt. at 400 °C. The obtained results can be understood considering that the slow pyrolysis regime maximizes the production of the solid fraction, also according to the literature [20]. Moreover, as mentioned above, the proximate analysis of the carob waste shows a high value of the fixed carbon that typically leads to a greater solid yield.

3.3. Oil Characterization

Figure 5 shows the FTIR spectra in the range 4000–650 cm^{-1} and some details in the range 1800–1140 cm^{-1} of the liquid fractions collected at each pyrolysis temperature. The obtained liquid phase was an aqueous phase with traces of miscible pyrolysis oil. This is confirmed by the presence of large peaks in the range 3650–3150 cm^{-1} in all the spectra shown in Figure 5, which can be assigned to -OH stretching vibrations, related to the presence of free H_2O molecules. The peaks in the range 1740–1640 cm^{-1} represent $>\text{C}=\text{O}$ stretching vibrations and $-\text{C}=\text{C}-$ stretching vibrations, related to the presence of carboxylic acids and alkenes, respectively. The peaks at 1390 cm^{-1} can be attributed to C-H bending vibrations, related to the presence of aldehydes, whereas the peaks at 1270 cm^{-1} are related with nitrogen compounds such as amine and represent C-N stretching.

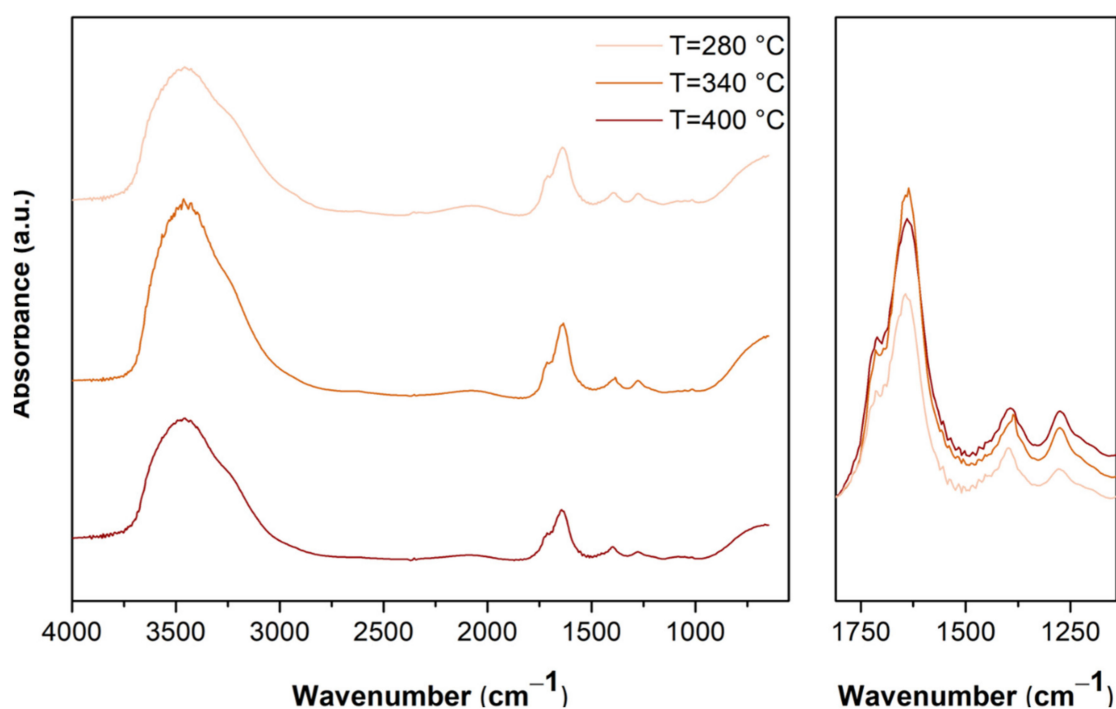


Figure 5. FTIR spectra of the liquid fractions at each pyrolysis temperature (**left**); detail of the FTIR spectra in the range 1800–1140 cm^{-1} (**right**).

3.4. Solid Phase Characterization

In Figure 6a, ATR-FTIR spectra of carob waste before pyrolysis process and of biochar obtained at the three different process temperature are shown. The ATR-FTIR spectra highlight the reduction of typical lignocellulosic peaks with the increase in the pyrolysis temperature. In fact, the ATR-FTIR spectrum of carob waste shows a broad band between 3300–3600 cm^{-1} due to ν_{OH} , which already significantly decreases for BC280, and even more for BC340 and BC400.

Moreover, consistent with the DTG curve, the signals of saturated symmetrical and asymmetrical peaks of ν_{C-H} at 2930 and 2850 cm^{-1} start to disappear for BC340, the temperature at which maximum degradation rate of hemicellulose runs, and no signal for BC400 is detected. Moreover, $\nu_{C=O}$ (1732 cm^{-1}) and $\nu_{C=C}$ between 1680 and 1480 cm^{-1} , usually attributed to the presence of aromatic structures, still remain also for BC400, considering that the lignin decomposition occurs at a higher temperature, according to the DTG curve. Thus, with the increasing temperature, more carbonaceous particles are obtained, losing the predominant functional group related to hemicellulose structure and part of the lignin structure. This result is also noticeable in the following SEM micrograph. In fact, Figure 6b, the micrograph of BC280, highlights a typical lignocellulosic structure, whereas Figure 6d, the micrograph of BC400, appears as a carbonaceous particle; additionally, the morphology of BC340 in Figure 6c shows an intermediate structure.

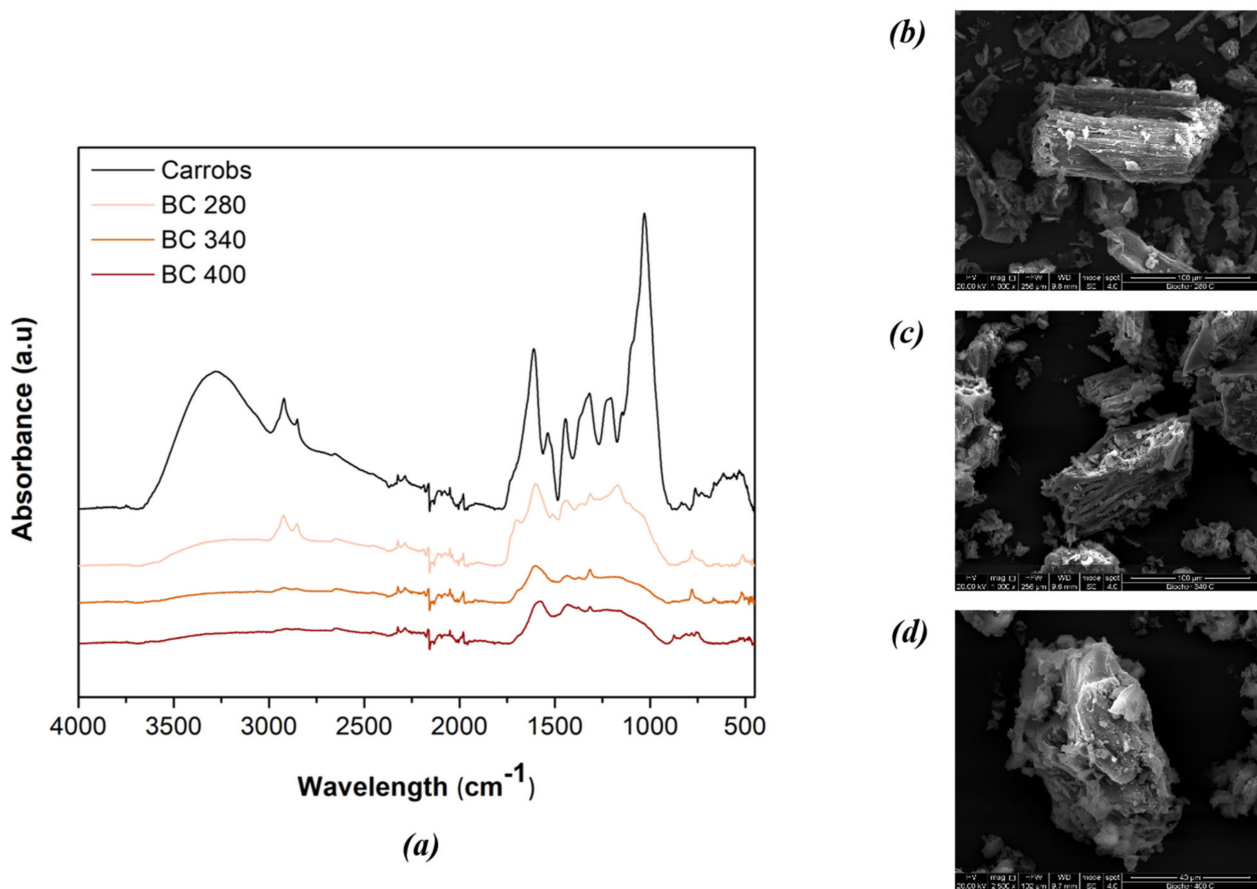


Figure 6. (a) ATR-FTIR spectra of carob before pyrolysis treatment and solid fractions at each pyrolysis temperature and SEM morphologies of (b) BC280, (c) BC340, and (d) BC400.

4. Conclusions

Carob waste, after sugar extraction, was subjected to slow pyrolysis, and the collected gas, liquid, and solid phases were characterized in order to optimize the process conditions and to maximize the products' yields. The thermogravimetric analysis shows a gradual degradation of lignin structure that occurs through four different steps. The first one is related to the moisture and volatile matters' removal, and the other three are related to the structure changes: (i) degradation of hemicellulose, (ii) lignin and cellulose degradation, and (iii) lignin decomposition. Based on this, the slow pyrolysis process was performed at three different temperatures, i.e., 280, 340, and 400 °C, obtaining different proportion in the composition of gas, liquid, and solid phases. The obtained gas fractions are not useful as syngas, and the liquid fractions have non-detectable HHVs. Based on the obtained results

by proximate analysis, the carob waste has a high amount of fixed carbon that makes this feedstock suitable for conversion to value-added biochar for reinforcement of biocomposite applications. The work shows that a cheap agricultural waste could be used as a suitable feedstock for biochar production, rather than for fuels' recovery.

Therefore, a future work will be focused on the production of biocomposites by employing obtained biochar particles.

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Conflicts of Interest: The authors declare no conflict of interest.

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