PROPERTIES OF CHARS OBTAINED WITH PYROLYSIS OF CASTANEA SATIVA BY PRODUCT

by

Eylem PEHLIVAN

Chemical and Process Engineering, Faculty of Engineering, Bilecik Seyh Edebali University, Bilecik, Turkey

> Original scientific paper https://doi.org/10.2298/TSCI160406174P

The application of biomass derived energy is gaining importance due to the decreasing supply of fossil fuels and growing environmental concerns. This study described the possibility of utilizing Castanea sativa's by-product as biofuels by producing char via pyrolysis. The process was carried out in a fixed-bed reactor at different heating rates of 10 °C, 100 °C, and 200 °C per minute at temperatures ranging from 400 °C to 700 °C, and a nitrogen flow rate of 100 cm³ per minute. The produced chars were characterized by proximate and elemental analyses, Brunauer-Emmett-Teller surface area, nuclear magnetic resonance, scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, and X-ray fluorescence analyses. The char yield was found to decrease as both pyrolysis temperature and heating rate increases. The carbon content of char ranged from 68 to 87 wt.%, which correspond to approximately 43% of carbon in the biomass. The char obtained at 700 °C had high fixed carbon content (79.90%) as well as high heating value, and hence, it could be used as a solid fuel or as a precursor in the activated carbon production with its 268 m^2 per gram surface area.

Key words: fast pyrolysis, Castanea sativa, char, characterization

Introduction

Due to the necessity for environmentally friendly-alternative fuels, researchers have been seeking for new and straightforward techniques for the last decades. Biomass being an environmental friendly and cheap material, is an alternative solution for these problems and it is the most important energy source for many developing countries. It also plays an important role in industrialized countries that meet the Kyoto protocol requirements, and can reduce the countries' dependency on crude-oil [1]. Pyrolysis is defined as the thermochemical degradation of organic materials in the absence of oxygen, and it is used to convert biomass into valuable products such as biofuels. If biomass is pyrolyzed in itself, the liquid products obtained contain significant amounts of water and other organic chemicals such as organic acids, alcohols, aldehydes, ketones, phenols, and ethers, which are unfavorable in terms of their utilization [2]. Therefore, most of the studies focus on char, the solid, residual product of biomass pyrolysis, which could be harnessed for energy production like coal or for the production of adsorbents. At moderately high temperatures in an inert atmosphere, pyrolysis thermally decomposes the carbohydrate structure of biomass into carbonaceous solid residue (char), and

Author's e-mail: eylem.onal@bilecik.edu.tr

into condensing and non-condensing vapors of various molecular weight compounds. Char can be produced from various waste biomass sources, including woody biomass, municipal waste, and agricultural residues. According to the International bio-char initiative, an estimated 80% of all crop and forestry residues may be converted to bio-char, for use as soil conditioners and for energy production by the year 2050 [3].

Char is a value-added product which can be used for several purposes. The solid char, similar to fossil coal, is a useful product that can be used as biofuel. It is highly carbonaceous with a high energy content compared to high rank coals. Char also has a large microscopic surface area due to the micro-pores developed during pyrolysis, therefore, char can be used for the filtration and adsorption of pollutants. Such features of char can be further enhanced by physical or chemical activation, of which the final product becomes adsorbent, which is also referred to as a substitute for activated carbon. Another way to utilize char is the addition into the soil which is an effective way of improving soil quality. Blending char with the soil could increase the soil's nutrient retention and water holding capacity, crop yield and ameliorate soil pH value [4, 5].

Turkey has high agricultural potential as various agricultural residues are available. One of the most important biomass sources in Turkey is food processing waste. The production of chestnut ranges from 47,000 to 49,000 tons [6]. Turkey produces a large amount of chestnut shell and leaf waste annually, since the chestnut candy industry is dominant and successful especially in the western part of the country. Establishing the effective use of chestnut by-product would help to resolve the problems of pollution caused by the chestnut waste disposal [7]. Low cost and abundantly available renewable biomass sources highly recognized as valuable feedstock are used to get energy in the char form from biomass. Agricultural wastes such as wheat straw [8], flax straw [9], rice husk [4], industrial wastes such as sugarcane bagasse [5], castor bean [10], and forest biomass residues such as elm sawdust [4], umbrella tree [6], and palm oil tree [11] were studied for char production with different pyrolysis methods. In the present investigation, the slow and fast pyrolysis of *Castanea sativa* by-product for its utilization as a solid fuel-char was performed. The chars obtained were characterized using physico-chemical and spectroscopic methods in order to enhance the benefits of char technologies for their usage as biofuels.

Experimental

Raw material

Chestnut shell, which is the by product of *Castanea sativa* (CBP), consists of leaf (inner shell) and shell (outer shell) that surround the edible nuts. It was supplied from a chestnut factory located in Bursa, Turkey. Air dried biomass samples were ground and screened to give an average particle size of 1.094 mm for individual characterization and pyrolysis experiments.

Pyrolysis experiments

The pyrolysis experiments were conducted with three different heating rates of 10, 100, and 200 °C per minute, at 400, 500, 550, 600, and 700 °C final temperatures, under nitrogen atmosphere (100 cm³ per minute) using laboratory scale reactor with a length of 90 cm and an inner diameter of 2.5 cm made of 310 stainless steel. A schematic diagram of the reactor can be found elsewhere [12]. The reactor was heated directly by an AC voltage to enable rapid heating and cooling. During the experiments, heating rate and pyrolysis temperature were controlled

with a proportional-integral-derivative (PID) controller. For the fine control of the nitrogen flow rate before entering into the reactor, a rotameter was used. Temperature measurements were taken above the bed, with the thermocouple in the middle of the reactor, in order to control the reactor temperature. The experiments were conducted under atmospheric pressure.

Analysis of biomass and char

The proximate analysis of raw biomass and chars was based on the ASTM standards (moisture content: ASTM E871-82, ash: ASTM D1102-84, volatile matter: ASTM E872-82, and fixed carbon is calculated by the difference). The ultimate analysis was performed in an elemental analyzer (Leco CHN628, S628). The heating values are very important thermal properties for the design and the evaluation of thermal conversion systems. Higher heating values (HHV) were calculated using the Dulong formula:

$$Q_{\rm HHV} [\rm MJkg^{-1}] = 33.83C + 144.3(\rm H-O/8)$$
(1)

where C, H, and O represent the mass fractions of carbon, hydrogen, and oxygen, respectively.

The pH values were measured by adding char to de-ionized water at a mass ratio of 1:20. The solution was then hand shaken and allowed to stand for 5 minutes before measuring the pH with a pH meter, Mettler Toledo AG SevenGo. Surface areas and pore volumes of the chars were determined by the application of the Brunauer-Emmett-Teller (BET) and t-plot analysis software available with the instrument Micromeritics Asap 2020. Surface morphology of the samples was confirmed using the Zeiss Supra 40 VP scanning electron microscope. Energy-dispersive X-ray (EDX) analysis was also carried out with the same microscope when working distance was adjusted by 10 mm. The structure of char obtained was examined by a diffractometer (Panalytical Empyrean). For chemical characterization, ¹H-NMR spectra were acquired with an Agilent VNMRS 500 MHz. FT-IR spectra of samples were recorded using Perkin Elmer Frontier FT-IR LR64912C in order to get further information on the chemical structure of the samples in the infrared region 4000-400 cm⁻¹ by preparing KBr pellets. XRF analysis of char was acquired with a Panalytical axios.

Results and discussion

Biomass characterization

Properties of CBP are given in tab. 1. The CBP sample contained 14.42% moisture, 59.70% volatile matter, and 1.90% ash. The CBP with its low ash content could be an appropriate biomass sample for producing chars that have little ash content and high calorific values. The volatile matter to fixed carbon ratio was 2.50, which is in a typical range for lignocellulosic biomass. The calculated HHV was 13.96 MJ/kg, which is similar to the value (13.45 MJ/kg) estimated by Lee *et al.* [13] The lignin content of the sample was 23.0%. Lignin, which is composed of aromatic rings with various branches, decomposes over a wide range of low to very high temperatures, with a very low mass loss rate. Therefore, the sample with high lignin content might have relatively higher char yields [11].

Char yields

Figure 1 shows the effect of pyrolysis temperature and heating rate on the char yield. The char yield under the HHR and LHR conditions decreases from 31.23% to 26.22% and from 52.26% to 37.48% with increasing pyrolysis temperature from 400 °C to 700 °C, respectively. The decrease in char yield with a rise in temperature could result from either greater

Pehlivan, E.: Propertie	es of Chars Obtain	ed with Pyrolys	is of
THERMAL SCIENCE,	Year 2017, Vol. 21	, No. 2, pp. 108	3-1092

	wt.%		wt.%		wt.%		
Moisture ^c	14.42	C ^a	43.14	Р	4.42		
Ash ^b	1.90	H ^a	5.77	Mg	0.97		
Volatile matter ^b	59.70	N ^a	1.41	Si	0.72		
Fixed carbon ^b	23.98	O ^a	49.68	Mn	1.36		
Cellulose ^c	19.48	H/C	0.86	Fe	1.40		
Acid-insoluble lignin ^b	32.53	O/C	1.60	Ca	25.47		
Oil ^c	0.86			K	10.93		
Alcohol-benzene solubles ^b (extractives)	10.59						
Raw protein ^a	2.78						
CBP – empirical formula – CH _{1.60} N _{0.028} O _{0.86} ; higher heating value –13.96 [MJkg ⁻¹]; bulk density – 220 [kgm ⁻³]							

Table 1. Properties of CBP

1086

^a Dry-ash-free basis. ^b Dry basis. ^c As received



Figure. 1. Effect of pyrolysis temperature and heating rate on biochar yields



primary decomposition of CBP at elevated temperatures or the secondary decomposition of the char residue. By using a slow heating rate and low operational temperature, it is possible to maximize the char production in the pyrolysis process [14]. It can be clearly observed that the char yield in the LHR condition is higher than that in the HHR condition. Relation between H/C and O/C during pyrolysis is presented in fig. 2.

Characteristics of char

Properties of chars and the results of characterization analyses of chars are listed in tab. 2. The CBP had a high volatile matter content of 59.70% which reduced remarkably to 4.26% with increasing pyrolysis temperature to 700 °C. The fixed carbon content of chars increased by 1.83-3.33 times compared with that of the biomass, indicating the carbon stability of char. The CBP helps to preserve carbon as was discovered by Lee, Y., *et al.* for Geodae-Uksae [13]. In addition, fuel ratio is a ratio of fixed carbon against volatile matter and is a characteristic value demonstrating the property of a solid fuel and classifying coal rank according to ASTM 388. The increasing fuel ratios imply elevated combustion efficiencies and diminished pollutant emissions during char combustion [15]. Carbon, as the primary element in all of the produced chars (69-87 wt.%), occurs in considerable greater amounts in the chars than in the dried biomass. In comparison with the raw biomass, the O and H contents

Heating rate			10 °C	er m	inute		100 °C per minute 200 °C pe			C per n	per minute					
	Temp. [°C]	400	500	550	600	700	400	500	550	600	700	400	500	550	600	700
Proximate analysis [wt.%] FC ^a Ash	Moisture	4.13	4.18	3.71	3.66	3.20	4.56	3.75	3.62	3.33	2.88	4.29	4.94	4.32	3.21	2.66
	VM	40.44	31.95	27.97	15.01	6.58	33.01	31.76	26.2	17.38	9.98	43.07	32.22	22.17	15.69	4.26
	FC^{a}	45.27	52.7	57.28	69.88	75.06	51.88	53.26	58.73	67.41	73.4	43.95	52.89	63.26	69.9	79.9
	Ash	2.74	3.79	3.85	4.07	6.66	3.72	3.77	4.25	4.85	5.79	2.38	3.37	3.45	4.14	5.87
Ultimate analysis [wt.% daf] C H N O ^a H/C O/C	С	69.67	75.35	70.72	79.75	87.14	68.87	71.94	76.66	79.75	86.51	68.55	71.62	78.81	81.51	85.06
	Н	3.82	3.89	4.04	3.12	2.36	3.94	3.61	3.42	3.12	2.45	4.01	3.81	3.72	3.45	2.82
	Ν	0.92	1.04	1.08	1.15	1.39	1.09	1.07	1.06	1.15	1.21	0.94	1.31	1.07	1.18	1.27
	O^{a}	25.59	19.72	24.16	15.98	9.11	26.10	23.38	19.92	15.98	9.83	26.5	23.26	16.4	13.86	10.85
	H/C	0.657	0.619	0.685	0.469	0.324	0.686	0.60	0.535	0.469	0.338	0.701	0.64	0.57	0.51	0.397
	O/C	0.275	0.196	0.256	0.150	0.078	0.284	0.243	0.194	0.150	0.085	0.289	0.243	0.156	0.13	0.095
HHV [MJkg ⁻¹]		24.47	27.55	25.39	28.60	31.24	24.28	25.33	27.28	28.60	31.03	24.19	25.53	29.07	30.05	30.89
Carbon yield [wt.%]		84.39	77.98	69.16	75.35	75.70	73.16	70.61	72.99	75.72	71.29	69.10	64.56	67.65	64.26	64.69
pН		7.42	7.38	7.19	7.38	8.50	6.83	7.46	7.20	7.03	7.95	6.31	6.58	6.80	7.06	7.31

Table 2. Properties of chars

^a By difference

decreased in all char samples due to dehydration and decarbonylation/decarboxylation reactions [11]. These results are consistent with others presented in the literature for various agricultural residues. Losses in the amount of hydrogen and oxygen correspond to the scission of weaker bonds within the char structure favored by higher temperature [16]. The C, H, and O composition of the raw biomass and char were compared on a van Krevelen diagram shown in fig. 2. As can be seen, the H/C and O/C atomic ratios gradually decreased with rising pyrolysis temperature, implying that the chars become increasingly more carbonaceous in nature due to the loss of O-containing species, and substitution groups [10]. Several studies have reported the content of oxygen and hydrogen in char decrease while content of carbon in char increase with increasing pyrolysis temperature [10, 17, 18]. The HHV is a very important property necessary in characterizing biofuels. The chars produced from pyrolysis of CBP have high HHV, between 21-31 MJ/kg, which is comparable with those of solid fuels, ranging from lignite to anthracite, suggesting that chars have potential usage as solid fuels.

The pH values of the chars obtained under different pyrolysis temperature and heating rate are given in tab. 2. Pyrolysis heating rate did not have a significant effect on pH values, but the pH values of the chars increased from 6.31 to 8.50 with increasing pyrolysis temperatures. This trend concurred properly with values reported for char produced from rice husk, elm sawdust and wheat straw [19, 20]. From the carbon content and mass yield, the carbon yield representing the amount of carbon remaining in the char was calculated. Chars had carbon yield values in the range of 64-84%.

Like other physical and chemical characteristics, the BET surface area of char is important because it may strongly affect the reactivity and combustion behavior of the char. The

higher surface areas are probably due to the opening of the restricted pores [20]. Imam and Capareda [21] studied the pyrolysis of switchgrass and showed that thermal treatment develops porosity in the chars resulting in macro-microporous structure particles. Table 3 presents the surface areas of char samples obtained at 700 °C. The BET surface area of char was found higher than that of obtained from rice straw, hickory wood, rapeseed bagasse, hornbeam shell, bamboo, apricot stone, hazelnut shell, grape seed [6, 22-24]. At 700 °C, the HHR char has a lower surface area compared with the LHR char (137.49 and 227.13 m²/g for micropore surface area and 164.71 and 268.03 m^2/g for total surface area, respectively). This is because if heating rate is too high, a higher temperature is reached inside the raw material and a partial graphitization with the formation of graphene structures occurs. This graphitization is not in favor of the development of a large surface area [22]. Similar results were obtained by Brown et al. [25] mentioning in their study that higher pyrolysis temperatures and lower heating rates favor the formation of porosity by increasing the surface area of the chars. It is striking that reaching 270 m²/g surface area with pyrolysis is quite a good result. However, it is not sufficient to be used as active carbon. Favorable conditions which are used for the production of activated carbon as an adsorbent of pollutants with its physical and chemical methods can be determined, when the surface areas of the solid products are taken into consideration. The large surface area stemming from the microporous structure, which constitutes approximately 85% of the total surface area, is considered to be an effective property of the chars [25].

	10 °C per minute	100 °C per minute	200 °C per minute
$S_{BET} [m^2 g^{-1}]$	268.0269	252.227	164.7116
$V_{\rm total} [{\rm cm}^3 {\rm dk}^{-1}]$	0.126	0.121	0.078341
$V_{\rm micro} [{\rm cm}^3/{\rm dk}^{-1}]$	0.105601	0.095	0.063843
$S_{ m micro} \left[{ m m}^2 { m g}^{-1} ight]$	227.1329	204.36	137.4902
$S_{\rm meso} \left[{ m m}^2 { m g}^{-1} ight]$	40.894	47.86	27.2214
Average pore diameter [n Å]	223.858	237.881	364.273

Table 3. Surface area analysis of chars produced at 700 °C at different heating rates

As fig. 3 shows the presence of a large, intense band of intermolecular hydrogen bonds of OH, with a stretching vibration at 3.400 cm⁻¹ can be assigned to hydroxyl functionalities for CBP. And the absorption band around 1.700 cm⁻¹ could be as a result of the presence of carboxylic acids, while the absorption between 900 and 1.300 cm⁻¹ could be due to C-O vibrations. The unsaturated carboxylic acids could be indicated by the absorbance peak of the C = O band between 1.700 cm⁻¹ and 1.725 cm⁻¹ and the C = C or C = O stretching at 1600 cm⁻¹. The carboxylic group, carbonyl group, C-O bonds and hydroxyl group were also found in CBP. However, the absorption intensities of the carbonyl group, carboxylic group, and hydroxyl group in char significantly decreased compared to the raw feedstock.

To evaluate the structural variations in char particles after different thermal treatments, SEM has been used. The results of the SEM analysis of raw material and chars obtained at six different temperatures and 100 °C min⁻¹ heating rate are shown in fig. 4. As demonstrated in fig. 4, noticeable structural differences had taken place during the pyrolysis process. A carbonization process which is carried out at high temperatures results in the destruction of raw materials. Pores open when volatile substances in the raw material goes off

1088

during this process. The increase in pyrolysis temperatures leads to the amorphous and heterogeneous structure of CBP chars. Chars particles showed several cavities of different sizes and of irregular shapes, while the surface of CBP was flat with fewer cavities. The vesicles occurred through a melt phase of cellular components. From a phenomenological point of view, a gradual release of different volatile compounds occurs as the temperature increases during devolatilization [26, 27]. The EDX spectrum on the surface of the resulting char is also shown in fig. 4. It can be seen that the peak in carbon is more severe as well as in other elements including potassium, calcium, magnesium, aluminum and chlorine in solid products.

The XRF analysis was performed for char prepared by means of slow pyrolysis at 550 °C. Ca (37.30%) is dominant. Other inorganic elements in the char are K (17.96%), Fe (8.39%), P (2.505%), Mn (1.97%), Si (1.59%), and Mg (1.27%).



Figure 3. The FT-IR spectra of CBP and its chars obtained at different temperatures

The ¹H-NMR analysis was used to investigate chemical composition of biomass and char which has important influences on the pyrolytic characteristics and then, the percentage hydrogen distributions calculated from the chemical deviation values were determined from the ¹H-NMR spectra, are presented in tab. 4. The results demonstrated that a large quantity of aliphatic structures exists in the biomass. Analysis of char were quite different from those of feedstock indicating the thermal decomposition of biomass during pyrolysis. Reflected aro-matic structures and the protons in the CH₂ and CH attached to naphthenes were indicated as the majority in the pyrolysis char of CBP. The aromaticity content of char was higher than bi-omass, which is due to the progressive dehydration, decarbonylation and decarboxylation re-actions [28]. The most distinguished signal in char is a sharp peak at 2.0-1.5 ppm, which is at-tributed to CH₂ and CH attached to naphthenes.

Hydrogen type	Chemical shift [ppm]	CBP [%]	Char [%]
$CH_3 \gamma$ or further from aromatic ring and parafinic CH_3	0.5-1.0	6.26	5.33
CH_3 , CH_2 , and $CH \beta$ to aromatic ring	1.0-1.5	26	15.58
CH ₂ and CH attached to naphthenes	1.5-2	42.76	30.90
CH_3 , CH_2 , and $CH \alpha$ to aromatic or acetylene	2.0-3.0	7.50	17.44
Total aliphatics	0.5-3	82.51	69.25
Hydroxyl. ring-joining metylene, methine or methoxy	3.0-4.0	1.31	1.64
Phenols. non-conjugated olefins	4.0-6.0	2.26	1.92
Aromatics. conjugated olefins	6.0-9.0	13.83	27.09

Table 4. Results of ¹H-NMR for CBP and char (600 °C and 100 °C per minute)



Figure 4. The SEM and EDX analysis at 100 $^{\circ}C$ per munte heating rate (a) raw material, (b) 400, (c) 500, (d) 550, (e) 600, and (f) 700 $^{\circ}C$

The X-ray diffraction method was applied in order to analyze the char obtained at 550 $^{\circ}$ C and 10 $^{\circ}$ C per minute. The XRD pattern of char sample obtained from CBP is shown

in fig. 5. This XRD analyses showed that char sample contains several mineral (or inorganic) species, such magnesium oxide (MgO), calcium (Ca), silicon (Si), coesite (SiO₂), (CaHO₂), and stishovite (SiO₂).

Conclusions

The production of char from the pyrolysis of CBP was investigated using a fixed



Figure 5. XRD-diagram of char obtained from CBP(■ CaH₂O₂, □ SiO₂, ○ Mg0 ▲ Si , △Ca

bed reactor, under various reaction conditions, such as pyrolysis temperatures and heating rates. The most important factor affecting the yield of chars produced is the pyrolysis temperature. CBP pyrolysis at 400 °C maximized the char yield. The volatile matter, hydrogen, and oxygen contents of the char decreased as the pyrolysis temperature increased from 400 to 700 °C, but the fixed carbon, ash and carbon content, pH, surface area and higher heating value increased. This was due to the increased devolatilization rate during pyrolysis resulted in the char being predominantly carbon. This study also demonstrates the effect of heating rate on the surface area of char. The increase in heating rate lead to a significant decrease in BET areas. As a result, low temperature and heating rate encourage the potential to obtain solid fuel-char from waste biomass via pyrolysis. Being an environmental friendly raw material, CBP seems to be a promising feedstock candidate for application in the nearest future.

Acknowledgments

The author would like to gratefully acknowledge The Scientific and Technological Research Council of Turkey for the support of this work through the project 2209.

References

- Duman, G., et al., The Effect of Char Properties on Gasification Reactivity, Fuel Process Technol., 118 (2014), 1, pp. 75-81
- [2] Ates, F., et al., Comparison of Real Waste (MSW and MPW) Pyrolysis in Batch Reactor over Different Catalysts, Part I, Product Yields, Gas and Pyrolysis Oil Properties, *Bioresource Technol.*, 133 (2013), 1, pp. 443-454
- [3] Kolodynska, D., et al., Kinetic and Adsorptive Characterization of Biochar in Metal Ions Removal, Chem. Eng. J., 197 (2012), 1, pp. 295-305
- [4] Wang, Y., et al., Characterization of Biochar from Fast Pyrolysis and Its Effect on Chemical Properties of the Tea Garden Soil, J. Anal. Appl. Pyrol., 110 (2014), 1, pp. 375-381
- [5] Lee, Y., Production and Characterization of Biochar from Various Biomass Materials by Slow Pyrolysis, Energy Systems R&D Group, Korea Institue of Industrial Technology, Cheona, http://www.agnet.org/ files/ lib articles/20150108114134/tb197.pdf
- [6] Ozcimen, D., Ersoy-Mericboyu, A., A Study on the Carbonization of Grapeseed and Chestnut Shell, Fuel Process Technol., 89 (2008), 11, pp. 1641-1646
- [7] Braga, N., et al., Castanea Sativa By-Products, a Review on Added Value and Sustainable Application, Nat. Prod. Res., 29 (2015), 1, pp. 1-18
- [8] Weng, X., et al., Char Characteristics from the Pyrolysis of Straw, Wood and Coal at High Temperatures, J. Biobased Mater. Bio., 7 (2013), 6, pp. 1-9
- [9] Tushar M. S. H. K., et al., Production, Characterization and Reactivity Studies of Chars Produced by the Isothermal Pyrolysis of Flax Straw, Biomass and Bioenerg., 37 (2012), 1, pp. 97-105
- [10] Angin, D., Effect of Pyrolysis Temperature and Heating Rate on Biochar Obtained from Pyrolysis of Safflower Seed Press Cake, *Bioresource Technol.*, 128 (2013), 1, pp. 593-597
- [11] Shaaban, A., et al., Characterization of Biochar Derived from Rubber Wood Sawdust through Slow Pyrolysis on Surface Porosities and Functional Groups, Procedia Engineering, 68 (2013), 1, pp. 365-371

- [12] Uzun, B. B., et al., Rapid and Catalytic Pyrolysis of Corn Stalks, Fuel Process Technol., 90 (2009), 5, pp. 705-716
- [13] Lee, Y., et al., Characteristics of Biochar Produced from Slow Pyrolysis of Geodae-Uksae 1, Bioresource Technol., 130 (2013), 1, pp. 345-350
- [14] Touray, N., et al., Thermochemical and Pore Properties of Goat-Manure-Derived Biochars Prepared from Different Pyrolysis Temperatures, J. Anal. Appl. Pyrol., 109 (2014), 1, pp. 116-122
- [15] Ozcimen, D., Karaosmanoglu, F., Production and Characterization of Bio-Oil and Biochar from Rapeseed Cake, *Renewable Energy*, 29 (2004), 5, pp. 779-787
- [16] Keiluweit, M., et al., Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar), Environ. Sci. Technol., 44 (2010), 4, pp. 1247-1253
- [17] Demiral, I., Cemrek-Kul, S., Pyrolysis of Apricot Kernel Shell in a Fixed-Bed Reactor, Characterization of Bio-Oil and Char, J. Anal. Appl. Pyrol., 107 (2014), 1, pp. 17-24
- [18] Raveendran, K., Ganesh, A., Heating Value of Biomass and Biomass Pyrolysis Products, Fuel, 75 (1996), 15, pp. 1715-1720
- [19] Xie, T., et al., Characteristics and Applications of Biochar for Environmental Remediation, A review, Crit. Rev. Env. Sci. Tec., 45 (2015), 9, pp. 939-969
- [20] Ioannidou, O., Zabaniotou A., Agricultural Residues as Precursors for Activated Carbon Production A review., *Renew. Sust. Energ. Rev.*, 11 (2007), 9, pp. 1966-2005
- [21] Imam, T., Capareda, S., Chracterization of Bioil Syn Gas and Char Switchgrass Pyrolysis at Various Temperatures, J. Anal. Appl. Pyrol., 93 (2012), 1, pp. 170-177
- [22] Fu, P., et al., Evaluation of the Porous Structure Development of Chars from Pyrolysis of Rice Straw, Effects of Pyrolysis Temperature and Heating Rate, J. Anal. Appl. Pyrol., 98 (2012), 1, pp. 177-183
- [23] Angin, D., Sensoz, S., Effect of Pyrolysis Temperature on Chemical and Surface Properties of Biochar of Rapeseed (*Brassica napus L.*), *Int. J. Phytoremediat.*, 16 (2014), 1, pp. 684-693
- [24] Morali, U., Sensoz, S., Pyrolysis of Hornbeam Shell (*Carpinus Betulus L.*) in a Fixed Bed Reactor, Characterization of Bio-Oil and Char, *Fuel*, 150 (2015), 1, pp. 672-678
- [25] Brown, R. A., et al., Production and Characterization of Synthetic Wood Chars for Use as Surrogates for Natural Sorbent, Org. Geochem., 37 (2006), 3, pp. 321-333
- [26] Guerrero, M., et al., Pyrolysis of Eucalyptus at Different Heating Rates, Studies of Char Characterization and Oxidative Reactivity, Mater. Lett., 74 (2005), 1-2, pp. 307-314
- [27] Liu, Z., et al., Characterization and Application of Chars Produced from Pine Wood Pyrolysis and Hydrothermal Treatment, Fuel, 89 (2010), 2, pp. 510-551
- [28] Nishimiya, K., Analysis of Chemical Structure of Wood Charcoal by X-Ray Analysis of Chemical Structure of Wood Charcoal by X-Ray Photoelectron Spectroscopy, J. Wood Sci., 44 (1998), 1, pp. 56-61