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A study on the porosity development for biomass based carbonaceous materials

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ABSTRACT

This study deals with the structural and morphological changes occurring during pyrolysis and activation steps for the production of porous carbons from an arid-land plant *Euphorbia rigida*. A fixed-bed retort was used for slow pyrolysis and for further activation processes. Effect of pyrolysis atmosphere was examined at 550 °C and char yields were calculated to be 22.6, 23.1 and 17.5% under static, nitrogen and steam atmospheres respectively. Solid product obtained under static atmosphere was then impregnated with different chemicals (HCl, KOH, K_2CO_3, H_2SO_4, H_3PO_4, NaOH, $ZnCl_2$) and a second thermal treatment was applied under different activation atmospheres. It was observed that the impregnation material, impregnation ratio and activation technique showed a strong influence on the yield and porous texture of the resulting carbons. On the basis of BET surface areas, most effective chemical agent was selected as K_2CO_3 giving a specific surface area of 1079 m^2/g and microspore volume of 0.443 cm^3/g. The physical–chemical properties of the chars and activated carbons were investigated by proximate and ultimate analyses, FT-IR, SEM, EDX, XRD and iodine number. In addition, surface functional groups were classified by Boehm titration method. Results suggest that chemical activation of *E. rigida* char produces valuable activated carbons under proper conditions.

1. Introduction

In the last decades concerns over the quality of drinking water have resulted in more research activities on the removal of these toxic and unwanted contaminants from waste water. One of the most powerful removal methods is adsorption by activated carbon. Activated carbon (AC) is a porous material with high surface area and has been prepared from various amorphous carbon-based materials like plant biomasses [1]. Due to its chemical nature and porous structure, activated carbon has a great adsorptive capacity, an affinity for a wide variety of dissolved organics and chlorine and an ability to suit specific applications [2,3].

Environmental and economic concerns on the production of AC have led research studies through the selection of production techniques and suitable precursors. Here, biomass being an environmental friendly and cheap raw material seems to be an alternative solution for AC production. The methods for preparing biomass based AC can be divided into two main categories: physical and chemical activation. Physical activation involves two stages: biomass sample is first carbonized at moderate temperatures and the carbonized material is further activated by an oxidizing atmosphere such as steam or carbon dioxide at relatively higher temperatures. On the other hand, chemical activation involves the impregnation of biomass with an activating reagent such as H_3PO_4, $ZnCl_2$, KOH, K_2CO_3 and *etc.*, and the impregnated material is thermally decomposed under an inert atmosphere at moderate temperatures [4]. The combination of the chemical and physical activation processes is a new method and results in the production of AC with specific surface properties [5]. In the preparation of ACs from biomasses, the effects of impregnants, activation conditions and biomass type on the carbon surface chemical structure are important parameters [6]. Several biomasses are used for activated carbon production and for adsorption studies at laboratory level. Agricultural residues such as soybean straw [7], wheat straw [8], corn straw [8], coconut shells [9], cotton stalk [10], sunflower shell [11], nut shells [12], peanut hulls [13]; forestry residues such as pinecone [11], *Eucalyptus camaldulensis* wood [14] eucalyptus [13], radiata pine [13] and industrial biomass wastes such as olive oil residue [11], cotton seed residue [11], grape seeds [12], leather waste [15], almond shells, nut shells, olive stones [16], soybean cake [17] are some examples for biomass based activated carbon production *via* various activation methods.

One group of arid land plants, Euphorbiaceae, are characterized by their ability to produce milky latex, an emulsion of 30wt% terpenoids in water. *Euphorbia rigida* (Euphorbiaceae family) is found around the Mediterranean from Morocco through Portugal to Turkey and Iran. It is known that 80 species of Euphorbia are found in Turkey that

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Table 1
Properties of *Euphorbia rigida* and chars obtained under different atmospheres (pyrolysis temperature: 550 °C; heating rate: 10 °C/min).

Analysis	Method	Results			
		Raw material	Char		
			Static	Nitrogen	Steam
Moisture (wt.%)	ASTM D 2016-74/1762-84	3.0	3.5	3.7	4.4
Ash (wt.%)	ASTM D 1102-84/1762-84	6.4	4.7	4.3	4.6
Volatile matter (wt.%)	ASTM E 897-8271762-84	76.8	1.4	1.3	1.8
Fixed carbon (wt.%)	Calculated from difference	13.8	90.4	90.7	89.2
C (wt.%)	Elemental analyzer	48.53	61.69	62.31	55.27
H (wt.%)	Elemental analyzer	5.67	0.93	0.93	0.92
N (wt.%)	Elemental analyzer	0.96	0.57	0.37	0.67
S (wt.%)	Elemental analyzer	–	–	–	–
O (wt.%)	Calculated from difference	44.84	36.81	36.39	43.13
H/C		1.39	0.180	0.178	0.198
O/C		0.69	0.450	0.440	0.580
Empirical formula		$CH_{1.39}N_{0.02}O_{0.69}$	$CH_{0.180}N_{0.008}O_{0.450}$	$CH_{0.178}N_{0.005}O_{0.44}$	$CH_{0.198}N_{0.010}O_{0.58}$
Higher heating value (MJ/kg)	Calorimetric bomb	16.77	21.06	21.83	19.31
S_{BET} (m^2/g)	Autosorb 1C	0.23	3.16	1.16	1.28
Iodine number (mg/g)	ASTM D4607-94	–	26.97	19.43	20.35

are grown nearly in all regions [18]. Previous studies showed that some species of this family have been identified as promising candidates for renewable fuels and chemical feedstock for the future [19]. These studies include pyrolysis, catalytic pyrolysis and steam pyrolysis at different temperatures and the general objective of them was to produce high yields of bio-oil [19,20]. On the other hand, during the last few years, solid product from pyrolysis of *E. rigida* attracts attention to produce high surface activated carbons. Kılıç et al. [21] studied the chemical activation of raw material with $ZnCl_2$, K_2CO_3, NaOH and H_3PO_4 at different impregnation ratios and at 700 °C activation temperature. Highest surface area was attained when 75% K_2CO_3 impregnation was applied [21]. In another study, *E. rigida* was impregnated with H_2SO_4 (50%) and activated at 850 °C for 30 min. Surface area was detected to be 741.21 m^2/g [22,23]. These studies were focused on the chemical activation of *E. rigida*. However, pyrolysis and further combined physical–chemical activation of *E. rigida* char has not been studied yet. In this manner, to achieve an information on the porosity development during combined pyrolysis and chemical activation processes this work is carried out. The main steps and related objectives followed in this study are:

- Pyrolysis of an arid land plant – *E. rigida*: Determination of the effect of atmosphere on char yield.
- Application of different physical/chemical activation methods on char obtained from static pyrolysis: Determination of the best activating agent according to surface area.
- Characterization of the chars and best featured activated carbon.

2. Experimental

2.1. Raw material

The samples of *E. rigida* were collected from southwest Anatolia during fall time. Prior to the experiments, the sample was air dried, ground in a high speed rotary cutting mill (Retsch) and screen analysis was applied to obtain mean particle size of $0.425 < D_p < 1.25$ mm. Ultimate analysis was carried out using Carlo Erba 1108 elemental analyzer and C, H, N and O percentages were obtained, while the moisture, ash and volatile matter contents were determined *via* ASTM standards (Table 1). Higher heating value of the raw material was obtained as 16.77 MJ/kg using IKA calorimetric bomb. A Bruker Tensor 27 model FT-IR spectrometer was used to obtain FT-IR spectrum of *E. rigida* between 4000 and 400 cm^{-1} wave numbers. Solid state ^{13}C NMR spectrum of *E. rigida* was measured with the CP/MAS method, and spectrum was acquired using the Bruker Ultra Shields Plus 500 NMR spectrometer. To determine the inorganic species XRD patterns of raw material and the ash obtained from *E. rigida* at 650 °C were recorded using a Rigaku Rint 2200 X-ray diffractometer.

2.2. Preparation of char via pyrolysis

For the pyrolysis experiments, 20 g of *E. rigida* samples were placed into a 400 cm^3 stainless steel fixed bed reactor, details of which were given in the previous studies, and heated, with a rate of 10 °C/min, until reaching the final temperature of 550 °C [23,24]. Three different atmospheres were used during pyrolysis to see the effect of static, sweeping gas (nitrogen with a flow rate of 100 cm^3/min) and steam (flow rate of 0.5 cm^3/min) on the char yields and quality. After reaching the final temperature, pyrolysis reactor was taken to cool down till room temperature, char was removed and weighed. Char yield was calculated according to the equation given in the previous study [25].

2.3. Activation

The influence of the chemical reagent and impregnation ratio on activation process was investigated. Chars obtained at static atmosphere were then impregnated with the selected chemicals (HCl, KOH, K_2CO_3, H_2SO_4, H_3PO_4, NaOH, $ZnCl_2$) with a chemical reagent/biomass ratio of 0.5. To obtain the required chemical reagent/biomass ratio, calculated amounts of chemicals are dissolved in distilled water and solutions were prepared. The char-liquid mixture was stirred at 300 rpm for 2 h and kept at room temperature for 24 h. Then to obtain the impregnated chars, the slurry was oven-dried at 105 °C for 48 h. Activation of the impregnated chars was carried out in the same reactor described in pyrolysis. 5 g of sample was placed in the reactor and was heated to 550 °C at a rate of 10 °C/min under either nitrogen or steam atmospheres. Following the heating period, the sweeping gas changed to steam or nitrogen during 30 min isothermal time. After activation, the samples were cooled in nitrogen atmosphere, removed from the reactor and weighed. Then they were washed with hot distilled water until reaching a stable pH of around 7. Prior to characterization wet activated carbon samples were dried at 120 °C in oven for 24 h.

2.4. Characterization of chars and activated carbons

Chars obtained under different atmospheres and best featured activated carbons were characterized by various methods.