
Production of Activated Carbon from Waste PET' Chars

Mikail Olam

Department of Chemical Engineering, Inonu University, Malatya, Turkey

Email address:

mikailolam@gmail.com

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Abstract: Activated carbon, which is used in many application areas such as gas purification, purification of pollution in water and wastewater, removal of odor and pollution, in the defense industry, in the production of protective clothing and in the health sector, was produced from solid products obtained by waste polyethylene terephthalate (wPET) liquefaction that was carried out under non-catalytic conditions, the reaction time of 15-90 min, and a reaction temperature of 325-425 °C in a batch reactor. The solid products obtained, after grinding, were made in a muffle furnace at 400-700°C in a nitrogen gas atmosphere for 30 min. The solid products obtained in the liquefaction of waste polyethylene terephthalate contain approximately 60% Carbon (C), 4% Hydrogen (H) and 36% Oxygen (O), and are composed of terephthalic acid (C₈H₆O₄) in crystalline form. According to Brunauer–Emmett–Teller (BET) analysis, BET surface area of 313.05 m²g⁻¹ and average pore diameter of 2.71 nm of ZnCl₂ activated carbons were obtained. They have formed largely mesoporous structures. According to Scanning Electron Microscopy (SEM) analysis, it was observed that medium and large porous structures were formed. Produced activated carbons have commercial product potential but there is a need to optimize the process parameters for better results.

Keywords: Activated Carbon, Waste PET, Porous, Surface Area

1. Introduction

Activated carbon is a unique adsorbent that has an extremely porous structure that allows it to effectively capture and hold materials. Widely used throughout a number of industries to remove undesirable components from liquids or gases [1, 2]. It can be applied to a number of applications that require the removal of contaminants or undesirable materials [3], from water and air purification to soil remediation [4], and even gold recovery [5]. Activated carbon is produced by using many materials such as different agricultural waste, coal, polymer, etc [6–9]. Activated carbon is activated by two methods, physically and chemically [10]. While the physical activation process is carried out by giving suitable activating gases (CO₂, inert gas, water steam) to the carbonized product between 800°C and 1000°C [11], chemical activity is a one-stage process in which the biomass is activated directly after pretreatment with a chemical substance such as zinc chloride, phosphoric acid, and potassium hydroxide [12]. In the chemical activation process, since the chemicals used prevent the formation of tar and reduce the volatile substances in the product, activated

carbon with a higher surface area can be obtained at a lower temperature and time compared to the physical activation [13]. Moreover, since the micropore and mesopore development is greatly increased, it enables to adsorb large amounts of gaseous and liquid chemical compounds [14]. Recently, adsorbents produced from waste have been used in many areas. Adsorbents such as activated carbon, clay and zeolite are generally used in wastewater treatment [15, 16]. New adsorbents are needed because of the disadvantages of these adsorbents being difficult to recover, the need for large quantities, and the high cost [17].

In this study, petroleum-derived alternative liquid fuels were produced because of the liquefaction of waste polyethylene terephthalate (wPET). Gas, liquid and solid products were obtained as a result of liquefaction [18]. While liquid and gas products were evaluated as fuel, solid products (chars) remaining from liquefaction were collected as waste. wPET's liquefaction/pyrolysis yield among other polymers is very low [19]. In other words, solid products are obtained at high rates (approximately 50%) in the liquefaction/pyrolysis of wPETs. Within the scope of this study, activated carbon was produced from these solid products containing high carbon (approximately 55%).

2. Experimental Section

2.1. Materials and Equipments

During the liquefaction experiments, tetralin (98%, Sigma Aldrich), nitrogen gas (N_2) and tetrahydrofuran (THF, Merck) were used as the consumption material, and the liquefaction experiments were made in the full stirring batch reactor (Parr 4575, 500 ml). Fourier transform infrared (FTIR, PerkinElmer Spectrum One) was used to observe the chemical bond structure of chars obtained because of liquefaction of wPETs. The spectra were taken in the range of $650\text{--}4000\text{ cm}^{-1}$ at 128 scans and 2 cm^{-1} resolutions. Chemical compositions of chars were analyzed using Rigaku Miniflex 600 computer-controlled X-ray diffractometer and $CuK\alpha$ ($\lambda = 1.5405\text{ \AA}$) source. The scans were recorded in the range of $5^\circ < 2\theta < 80^\circ$ at a step of 0.05° , at a rate of 2° per min. Ultimate analysis of chars was performed on Leco CHNS 932 (Leco Corporation, St. Joseph, MI) device.

During the carbonization experiments, oven (Gemo DT107), Edmund Bühler TH15/KS15), zinc chloride (98%, Sigma Aldrich), nitrogen gas (N_2 gas) and the chars obtained liquefaction of wPETs were used. The characterization of the chars and carbonized residues were analyzed by SEM (LEO-EVO 40) and BET (Micromeritics Instrument Corp., Gemini VII 3.03). The specific surface areas of the chars after carbonization were determined by a BET (Brunauer, Emmett and Teller) surface analyzer with liquid N_2 at 77 K.

2.2. Procedure

wPET bottles were ground in about 0.5 cm in size and then dried for 24 h in atmospheric conditions. The liquefaction processes were carried out under initial pressure of 20 bar, 1/4 wPETs/solvent ratio, at reaction temperature of $325\text{--}400^\circ\text{C}$, and reaction time of 30 min. Tetralin was used as a solvent in liquefaction experiments, but it was recovered by separating it from its liquefied products using the evaporator (Buchi Rotavapor R-100) after liquefaction.

The process was made according to the flow chart shown in Figure 1. They were then carbonized at 400°C for 30 min in inert atmosphere of N_2 at a flow rate of 20 ml/min. The

chars obtained from liquefaction of wPETs, which they were ground to particles $<250\text{ }\mu\text{m}$ in size, were taken from each 5 g. It was made either pre-treatment with $ZnCl_2$ solution or directly carbonizes treatment. To pre-treatment with $ZnCl_2$ solution, it was added to 100 ml of 40% $ZnCl_2$ solution and stirred at 600 rpm for 12 h. The samples were then dried in a 102°C vacuum oven for 12 hours. The dried samples were carbonized in an atmosphere of N_2 gas at a flow rate of 20 ml/min, at 400°C for 30 minutes in an oven.

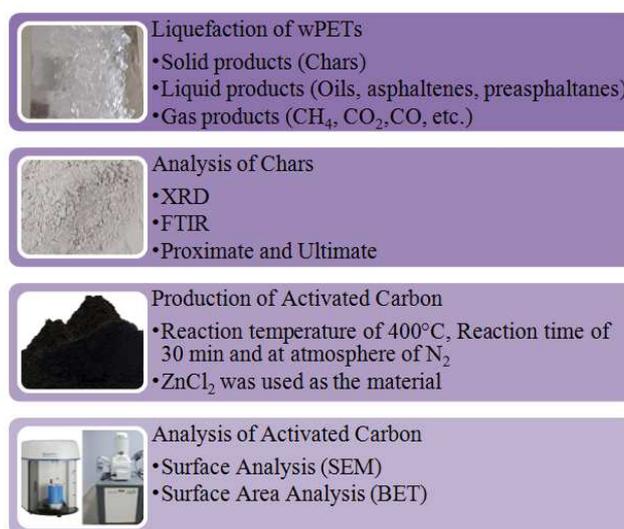


Figure 1. Process design.

2.3. Examining of Chars

The char (solid product) yield was approximately 50% in the liquefaction of wPETs. According to FTIR analysis of the chars, wPET's structure did not decompose enough at liquefaction (Figure 2a), and therefore the char yield has a higher rate. According to XRD analysis of the chars obtained at a reaction temperature of $325\text{--}400^\circ\text{C}$ in the liquefaction process of wPETs, most of them were significantly formed terephthalic acid ($C_8H_6O_4$) (Figure 2b). Furthermore, they consist approximately of 62% C, 4% H and 34% O (Table 1). It can be said that they have content carbon (C) at high rates, and this is enough for activated carbon.

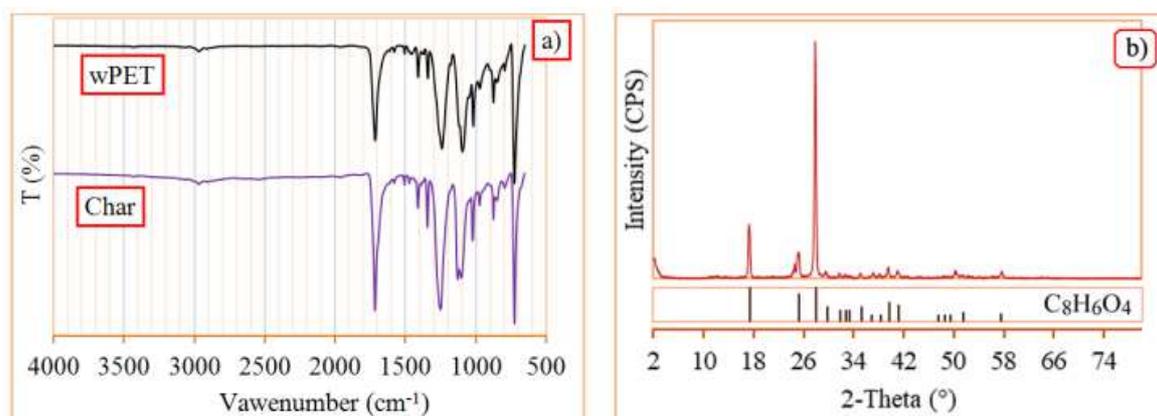


Figure 2. The analyses of chars obtained liquefaction of wPETs; a) FTIR, b) XRD.

Table 1. Ultimate analysis of the chars.

Reaction temperature	Reaction Time (min.)	C (%)	H (%)	O* (%)
325°C	30	64	5	31
350°C	30	64	5	31
375°C	30	62	4	34
400°C	30	58	4	38

3. Results and Discussion

3.1. BET Analysis

As can be seen in Table 2, the BET surface area of the chars obtained by liquefaction of wPETs at 325-400°C was $0.74 \text{ m}^2 \text{ g}^{-1}$ before not carbonized, and the total pore volume was $0.001 \text{ m}^3 \text{ g}^{-1}$, and the average pore diameter was 3.82 nm. As a result of the 700°C carbonizations of the chars obtained by liquefying wPETs at 325-400°C, the BET surface area was $442.60 \text{ m}^2 \text{ g}^{-1}$, and the total pore volume was $0.227 \text{ m}^3 \text{ g}^{-1}$, and the average pore diameter was 2.05 nm. The BET surface area was increased by carbonizing the chars at 700°C under an N_2 environment (Cchar). However, after chemical activation of chars with ZnCl_2 solution (40%), the BET surface area decreased compared to the Cchar in the carbonization process at 400°C (ZnCl325, ZnCl350). With the carbonization of the chars obtained by liquefaction of wPETs at 325°C (ZnCl325), both the BET surface area and the total pore volume were higher than the chars obtained at 350°C (ZnCl350). This may be due to the fact that the conversion at low temperatures is minimal and thus the structure does not degradation significantly. It may be that wPETs undergo more deformation in their chemical structures at high temperatures, and free radicals are formed faster during carbonization, and when they cannot be adequately ventilated with N_2 gas, they form different gaseous compound structures. Increasing the carbonization temperature increased the surface area and total pore volume while reducing the average pore diameter (Cchar). However, although the BET surface area of the Cchar sample that has not been activated with ZnCl_2 is high, the amount of absorption and desorption is very low (Figure 3). This shows how important the activation process is. The adsorbed and desorbed quantity of the chars (solid products) obtained by liquefaction of wPETs at 325-400°C were very little changed (char_a, char_d) (Figure 3). The adsorbed and desorbed quantity did not change significantly after the carbonization process was applied to them in N_2 atmosphere at 700°C (Char_a, Cchar_d). The best-adsorbed quantity was in the ZnCl325 sample.

According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the ZnCl325 and ZnCl350 activated carbons belonged to typical type IV adsorption isotherms with an H1 hysteresis loop characteristic of mesoporous structures (Figure 4) [20]. In addition, as seen in Figure 5, it was observed that the BET surface area increased proportionally with high relative pressure (p/p_0) [21]. Here, it can be said that the presence of macropores contributing to

the high pore volume is low. When the variation of the pore volume in Figure 6 with p/p_0 was examined, it was seen that the pore volume increased almost linearly with the increase of p/p_0 . Therefore, it can be said that ZnCl325 and ZnCl350 activated carbons have mesoporous structures.

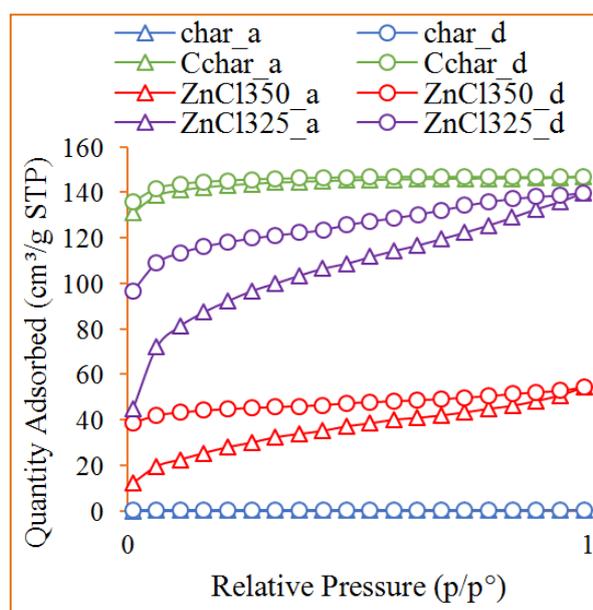


Figure 3. Variaton of relative pressure with quantity absorbed; char_a: adsorption, char_d: desorption, Cchar_a: adsorption, Cchar_d: desorption, ZnCl350_a: adsorption, ZnCl350_d: desorption, ZnCl325_a: adsorption, ZnCl325_d: desorption.

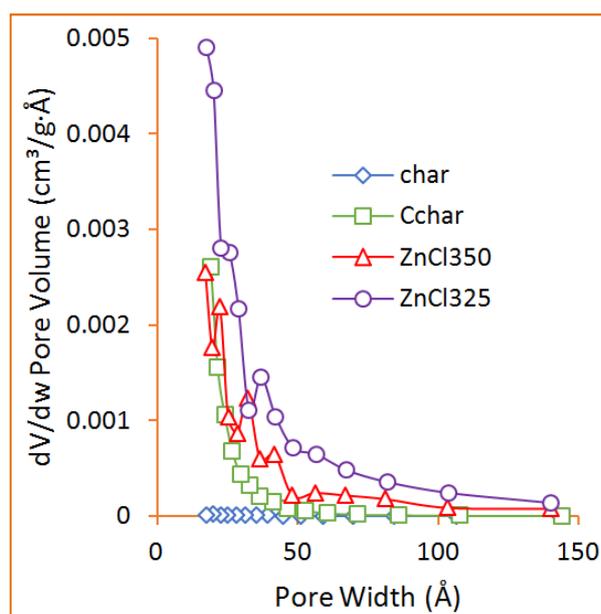


Figure 4. BJH adsorption dV/dw pore volume (halsey: faas correction).

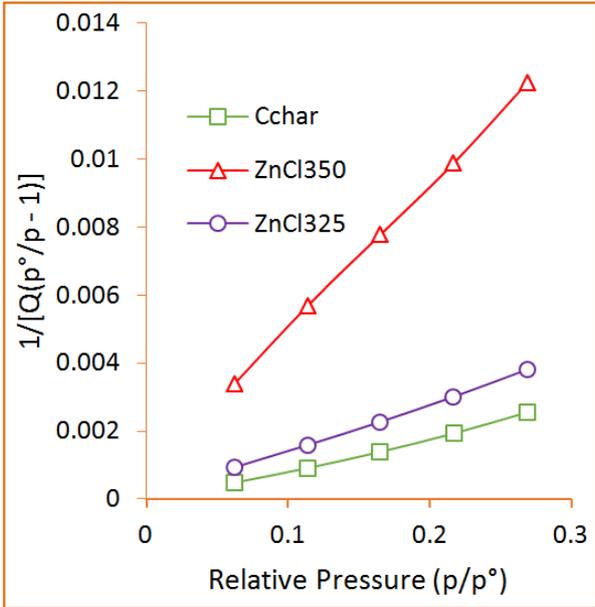


Figure 5. BET surface area plot.

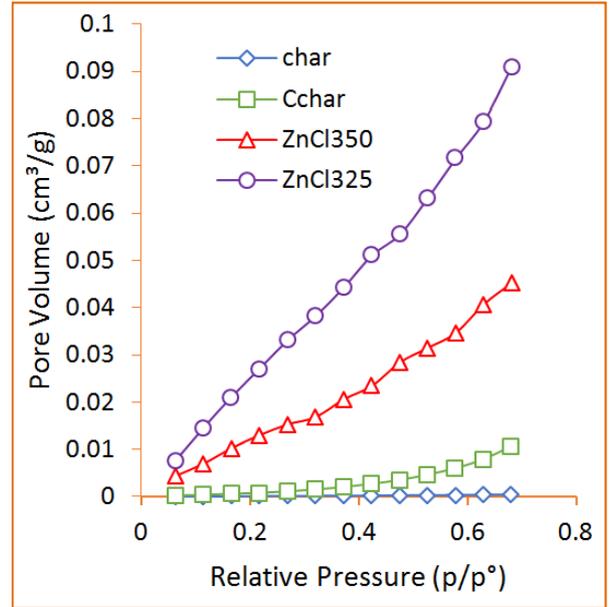


Figure 6. Change of pore volume with relative pressure.

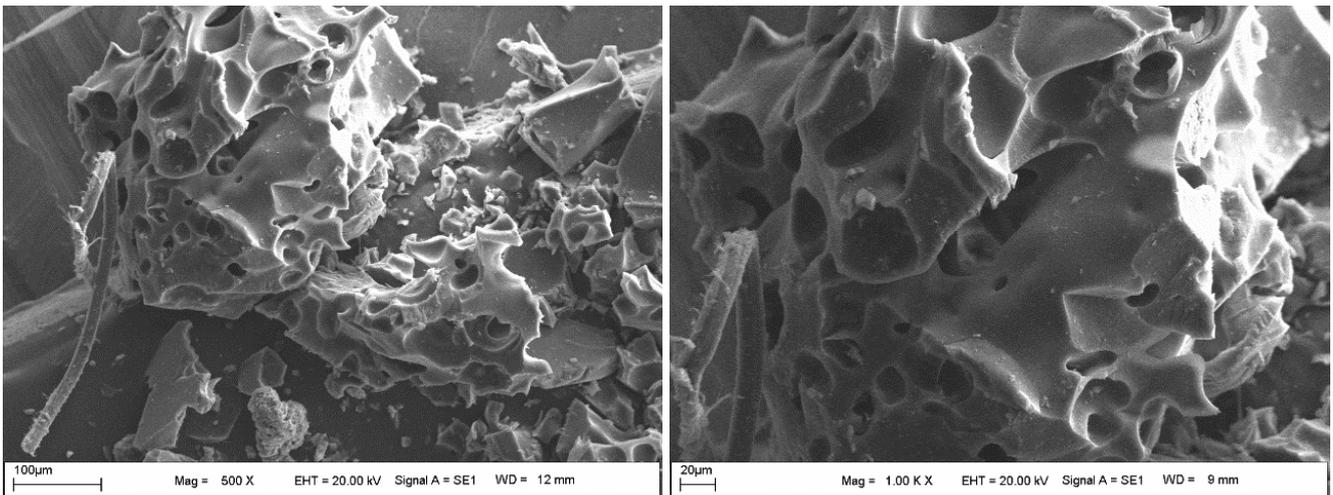


Figure 7. SEM images of activated carbon at 400°C.

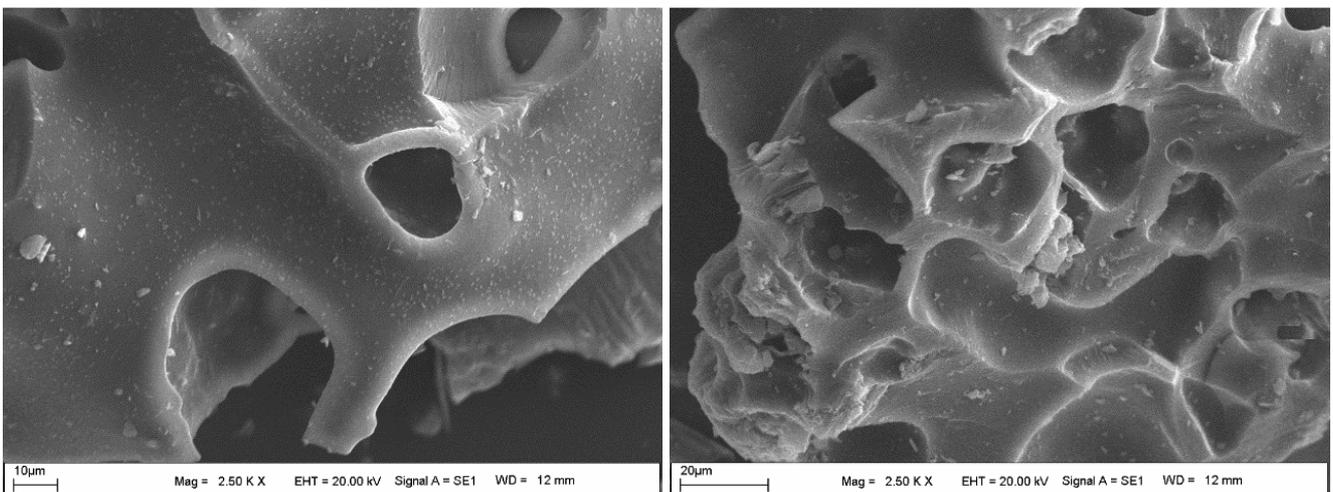


Figure 8. SEM images of carbonized char at 700°C.

Table 2. Results of BET analysis.

Sample Name	Carbonization temperature (C°)	Activated substance	BET surface area (m ² g ⁻¹)	Total pore volume (m ³ g ⁻¹)	Average pore diameter (nm)
char	Non-carbonized	-	0.74	0.001	3.82
Cchar	700	-	442.60	0.227	2.05
ZnCl325	400	ZnCl ₂	313.05	0.212	2.71
ZnCl350	400	ZnCl ₂	100.70	0.080	3.18

3.2. SEM Analysis

The morphology of the surface (activated carbon in Figure 7 and non-activated carbon in Figure 8) after carbonization of solid products (chars) obtained as a result of liquefaction of wPETs with Scanning Electron Microscopy (SEM) was examined. As seen in Figure 7 and Figure 8, the pores on the surfaces of both activated carbons (ZnCl₂) and non-activated carbons (Cchar) were formed in an irregular structure. The surface structure of the samples is porous and irregular. It was observed that a series of coarse and small voids were formed scattered on the surface of the obtained activated carbons. This is mainly due to high-temperature decomposition followed by evaporation of volatile compounds. It can be said that the activated carbons obtained from the wPET chars have a satisfactory pore structure according to the SEM analysis and that they have the absorption ability according to the BET analysis.

Within the scope of this study, solid products (unconverted) obtained as a result of the conversion of waste PETs into liquid and gaseous products by liquefaction method were evaluated as activated carbon. It has been shown that the activated carbons obtained can be used in existing areas of use. However, in order to improve their current performance, optimization of carbonization temperature, activator, residence time and inert gas feed rate is required.

4. Conclusion

In this study, wPETs were converted to alternative fuels by liquefaction process in a batch reactor at 325-400°C, the liquid and gaseous products obtained were evaluated as fuel, and activated carbon was produced from the remaining solid products (which did not turn into liquid and gaseous products). The current potentials of the produced activated carbons were investigated. In the BET analysis, the maximum surface area was 442.60 m²g⁻¹ in the inactivated product at 700°C, and the best absorption/desorption value was obtained by chemically activating with ZnCl₂ and carbonizing it at 400°C. In SEM analysis, coarse and medium porous structures were formed as a result of carbonization. However, the activated carbons produced needed optimization of the activation and carbonization conditions in order to increase the BET surface areas. In addition, the adsorption capacity of this activated carbon is determined.

In the future, the solid wastes remaining at the end of thermal processes (liquefaction, etc.), which are used in the recycling of wPETs and other hydrocarbon wastes

(agricultural wastes, plastic wastes, etc.), can be carbonized together, and they can be examined how to affect the pore structure and surface area.

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