

Study on Pore and Surface Development of Activated Carbon Produced from Iranian Coal in a Rotary Kiln Reactor

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Abstract

Coal is widely used in activated carbon production as an important precursor. Product properties of the coal gasification are as functions of coal type and operating conditions, so processing of any coal to produce activated carbon follows a different approach. In this study, a coal sample from Goltoot mine, one of the important coal mines in Iran was selected. Pre-oxidation, charring and activation of the coal were carried out in a rotary kiln reactor at different operating conditions. The results showed excellent potential of the coal for producing high quality activated carbon with controllable pore structure. Steam activation of the char at temperature 860 °C for 3 hr produced an activated carbon with surface area around 1300 m²/gr and yield %20 wt. The effects of operating conditions such as activation time and temperature and reactant gas type were studied to develop the tailored properties in the product.

Keywords: *Activated Carbon, Coal Activation, Iranian Coal, Pore Size Distribution, Rotary Kiln Reactor*

1. Introduction

Activated carbons can be produced from virtually any carbonaceous precursor. Coal and lignite [1,2], wood [3,4], agricultural wastes such as coconut shells [5], almond shells [6], hazelnut [7], stone of olive [8] and industrial wastes [9,10] are raw materials widely used to produce activated carbons.

Activated carbons are prepared by physical activation, gasification of a char in oxidizing gases, or by chemical activation, carbonization of carbonaceous materials impregnated

with chemical reagents [11]. Any cheap material with high carbon content can be used as a raw material for producing activated carbon. Nowadays, coal is one of the most important carbonaceous precursors to produce activated carbon. It is generally accepted that the properties of the activated carbon are a function of the coal properties as a raw material of activation process. Thus different coals (based on type, rank and analysis) reacting in different condition of activation produce activated carbon with

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different properties (such as surface area, porosity and pore size distribution). Therefore, there have been numerous attempts to produce activated carbon from different coal origins such as coal from the U.S. [11-14], Canada [15], Spain [16], Australia [17], Indonesia [18], Brazil [19] and France [20]. In these experimental studies, the activation process of the coal char was studied and the results show a variety in the activated carbon properties even in the same operating condition.

Iran is the 39th coal producer in the world and has about 2 billion tons of coal. Coal mines are spread throughout several regions of the country. There are different coal mines in each region with different specifications. Comparison of the coal from the point of surface area development was studied and the results indicated the coal sample of Goltoot coal mine in the Kerman region has good potential to develop high surface area and pore volume. In addition, individual kinetic parameters were determined in the kinetic study of the coal activation [21]. Therefore, in this work the effects of main operating conditions such as temperature, activation time and oxidizing gas on the pore structure, surface area and yield of product were studied.

2. Material and methods

2-1. Raw material

The selected coal sample was a bituminous coal from Goltoot mine which is located in the Kerman coal area. The proximate analysis of the as-received coal sample is shown in Table 1. The proximate analysis was carried out with LECO instrument model

MAC-400 and sulfur analysis was performed with LECO instrument model SE-32.

Table 1. Proximate analysis of as-received and cleaned coal sample.

Components	As-received Coal	Clean Coal
Volatile Matter	%16	%31
Fixed Carbon	%25	%59
Free Moisture	%2.5	%1.5
Ash	%56.5	%8.5
Total Sulfur	%1	%1
FSI*	n.a.	5.5

*Free swelling Index determined as ASTM D720-91

2-2. Characterization of the activated carbon

The parameters such as the BET surface area, pore size distribution and yield were determined for characterization of the activated carbon product. The adsorption isotherm, BET surface area and pore size distribution analysis were measured by nitrogen adsorption at the temperature of 77 K with Autosorb AP-1 apparatus (Quantachrome Corp.). Yield is defined as the amount of activated carbon obtained for a given amount of the raw material fed. This parameter is calculated as the percent of W_1/W_0 . Where W_0 is the original weight of the precursor on a dry basis and W_1 is the weight of the ending product.

2-3. Charring study

Heating of the coal powder sample from room temperature to 800°C under nitrogen gas flow and then holding at this temperature for 15 min, gave a firm and foamy body with %21 weight loss. When the pre-oxidation of the same powder sample was carried out and air at 225°C for 30 min with air flow rate of 20 cc/min initially and then the above heat

treatment was repeated, an agglomerated char without swelling was produced with weight loss of 17%. With extension of the pre-oxidation time to 60 min (which increases oxidation degree of the coal) and repetition of the heat treatment, the char particles shape did not change and the weight loss of the samples was around %15. Increasing the pre-oxidation time decreased both the agglomeration problem and the weight loss. This shows rule of amount of oxygen functional groups which were inserted in the coal during oxidation.

The experiments showed that coal treatment at the temperature of 225°C for 4hr in air flow rate 20 cc/min is proper for pre-oxidation. The charring step (containing carbonization and volatilization) was carried out by heating the pre-oxidized coal at the temperature of 450°C for 1.5hr in the nitrogen atmosphere, which these conditions are good enough to generate a char without softening and swelling at high operating condition of the activation process [21]. Carbonization of the pre-oxidized char produces a nongraphitizable char and generates cross-links between the carbon atoms of char with the oxygen functional group. In addition, the volatilization liberate volatile matter and also most of the non-carbon elements, mainly hydrogen, oxygen and nitrogen in the form of gases and vapors from the char. Result of the volatilization is leaving behind a rigid, low porous carbon skeleton formed by aromatic sheets and strips.

2-4. Experimental setup

Figure 1 shows the experimental setup used in this work. The reactor was a quartz glass

tube with a 50 mm diameter and 150 mm length heating zone. For entering and exiting the gas both sides of heating zone were equipped with smaller tubes with a diameter of 25mm. The rotational speed of reactor as 10 RPM was controlled by an electromotor. The tube was fitted with a perforated gas distributor to ensure uniformity of the temperature and gas concentration profiles inside the reaction zone. The temperatures inside and on the wall of the reactor were recorded with a K-type thermocouple. Temperature of the reactor was controlled by temperature controller (Advanced, series TMB).

The process of pre-oxidation, charring and activation of the coal sample was carried out in a rotary kiln reactor.

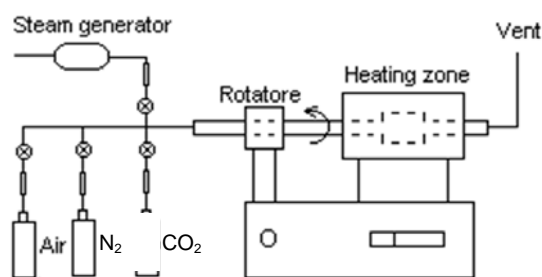


Figure 1. The schematic of rotary kiln reactor.

2-5. Procedure

After grounding and sieving of the coal sample, the coal with particle size of 0.35-0.7 mm (mesh size 24 to 45) was selected as raw material for the experiments. Because of the high ash content of the coal sample, it should be cleaned to reduce its ash content. Washing in heavy media was used for ash washing and coal cleaning in the laboratory.

In this method, several solutions with different ZnCl₂ content (which generate different solution density) were made. At

first, the coal was washed with the medium density 1.6 and then the floated portion was washed with the medium density 1.5 and the washing was repeated with the density solution 1.4 and 1.3. In each step the weight of floated and submerged portions was measured. The results are shown in Fig. 2.

The low ash coals were washed with distilled water several times to remove the zinc chloride.

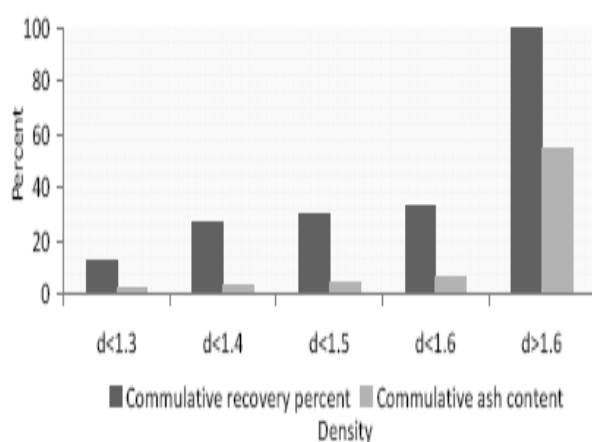


Figure 2. Results of coal washing with Zinc chloride solution.

It is shown in Fig. 2 that at the specific gravity of 1.6, more than 60% of coal sample can be recovered as low ash coal and the ash content of this coal was 8%. These recovery percentages and ash content are good enough from economical and operational view points. Therefore this low ash coal was used as raw material in the experiments. The proximate analysis of this clean sample is presented in Table 1.

Major and minor elements percentages of coal sample were determined by X-ray fluorescence (XRF) presented in Table 2. This analysis shows that more than 90% of SiO_2 and Al_2O_3 , as the main ingredients of coal ash, are removed in the washing step.

3. Results and discussion

3-1. Effect of activation time

The pore structure of activated carbon is mainly a function of the extent of burn-off and consequently the activation time. Effect of this parameter is related to the overall reaction rate of the activation and thus to the sample burn-off. The effect of activation time on surface area and yield in steam and CO_2 activation of the char at different temperatures were studied and the results are shown in Fig. 3. This figure shows yield is decreased but surface area follows a parabolic trend during the reaction progress.

Table 2. The XRF analysis of as-received and clean coal.

The Components (%weight db)	As-received	Clean
SiO_2	36.2	3.2
Al_2O_3	17.0	2.0
Fe_2O_3	2.23	0.44
CaO	0.28	0.21
MgO	0.69	0.12
K_2O	2.9	0.23
Na_2O	0.40	0.06
TiO_2	0.55	0.06
P_2O_5	0.05	0.03
MnO	0.006	0.002
Sr (ppm)	174	114
Ba (ppm)	439	124
Zr (ppm)	120	19

The comparison of pore size distribution (PSD) of the products determined with DA model are more interesting [23]. The N_2 adsorption isotherm and pore size distribution of these products presented in Figs.4 and 5 show rule of the activation time

on the pore development. The figures show that, as reaction progresses, the surface area is increased but the PSD presents wider distribution with lower peak. Up to a medium of burn-off, there is mainly an opening of porosity with a low contribution from mesoporosity that gives a sharp distribution of pore size in the product. Whereas with activation progressing which gives high

burn-off, the activation produces a widening and overlapping of existing micropores to meso and macropores. Therefore the PSD of the product is changed to a wider profile [24, 25]. This behavior was found for activation of the char at different operating conditions. For example, the results for CO₂ activation of the char at 920°C presented in Figs.6 and 7 show the same behaviors.

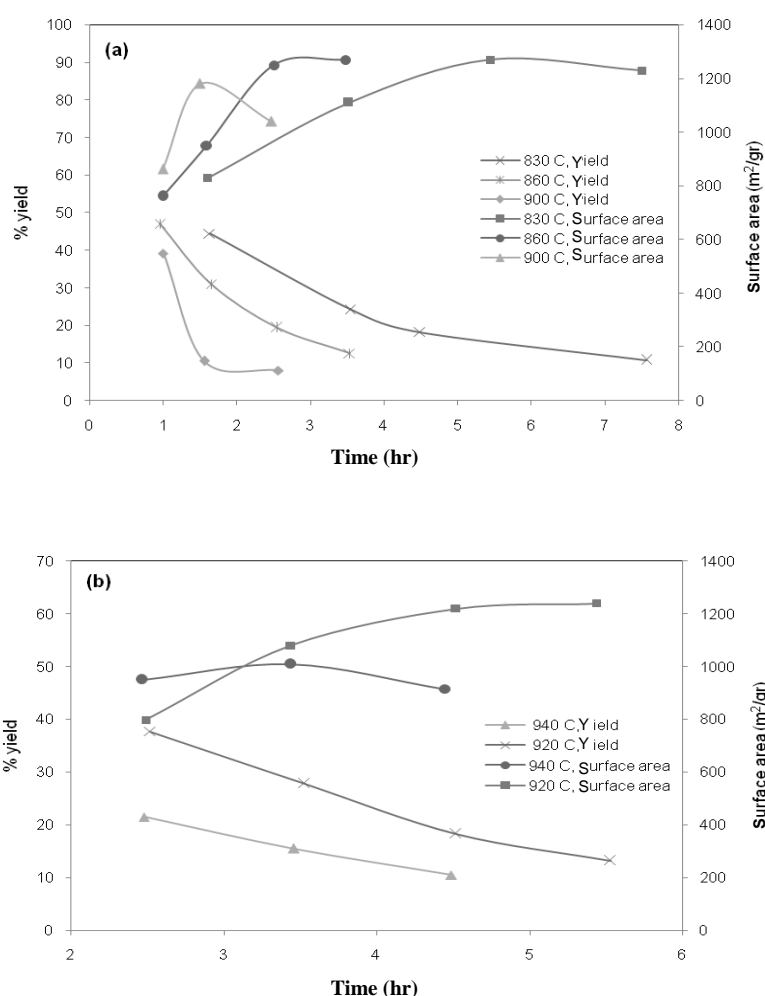


Figure 3. Effect of activation time on surface area and yield at different temperatures in steam (a) and CO₂ (b) activation.

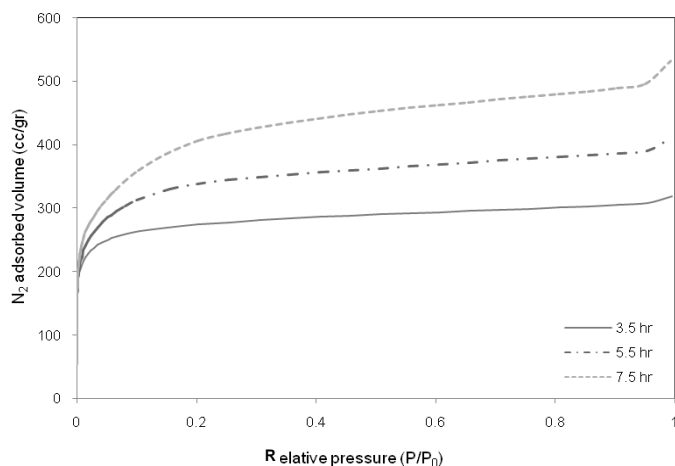


Figure 4. N_2 adsorption isotherm of the activated carbon produced in the steam activation for different times at $T=830\text{ }^\circ\text{C}$.

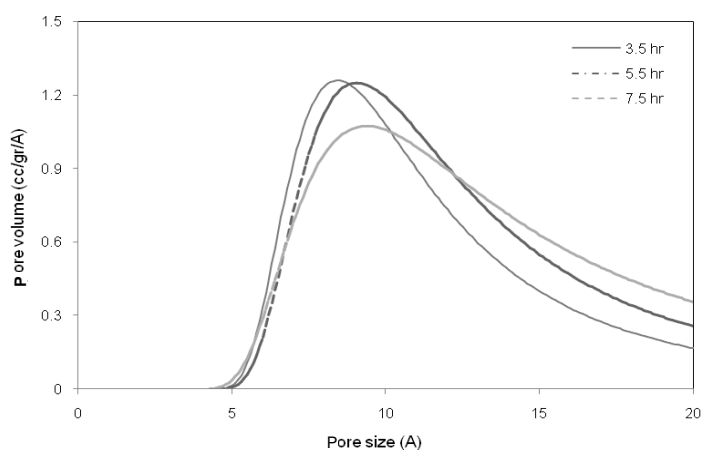


Figure 5. PSD of the activated carbon produced in the steam activation for different times at $T=830\text{ }^\circ\text{C}$.

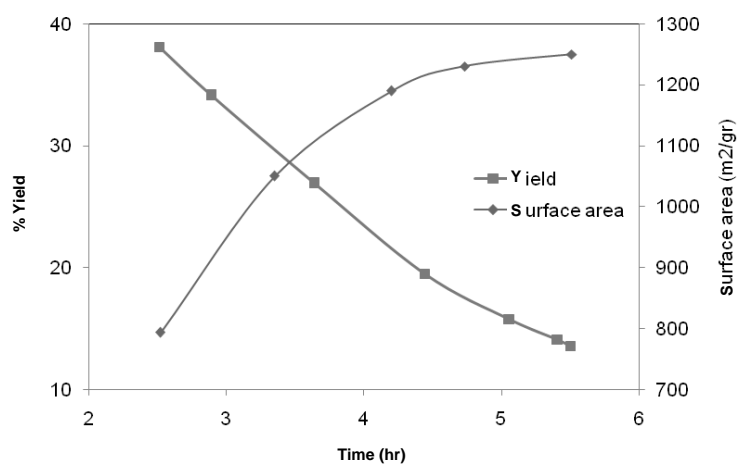


Figure 6. Activated carbon properties produced in CO_2 activation of the char at $T=920\text{ }^\circ\text{C}$.

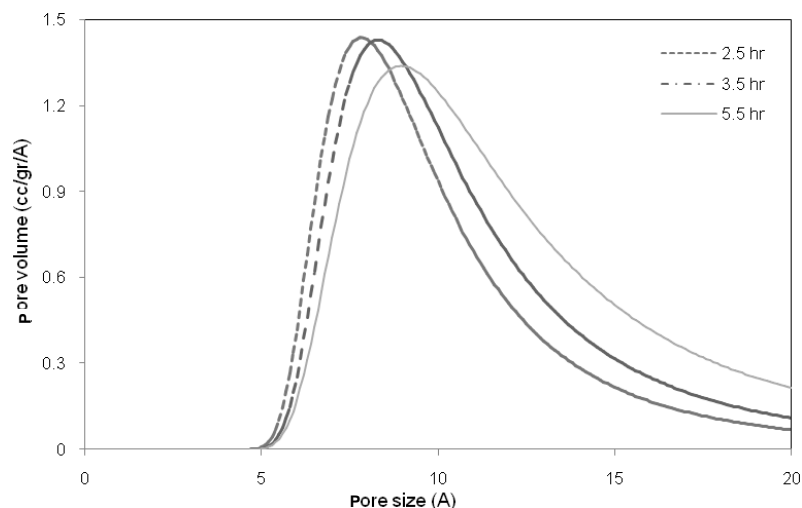


Figure 7. PSD of the activated carbon produced in the CO₂ activation for different times at T=920 °C.

3-2. Effect of activation temperature

The changes in surface area and yield of activated carbon with temperature during the activation are shown in Fig. 8 for the char activation with steam for 1.5 h. The surface area of the products is increased at low temperatures, while at higher temperatures, the surface area is dropped. The effect of activation temperature may be followed by analyzing the relative importance of both chemical reaction and pore diffusivity. At

lower temperatures in which the chemical reaction controls the activation progress, temperature increasing causes improvement of surface area because of faster reaction rate. As the activation temperature increases to around 900°C, the pore diffusion resistance is higher than chemical reaction resistance. In this condition, the C-H₂O reaction takes place predominantly on the exterior on the particle. This causes decreasing of the product surface area [25].

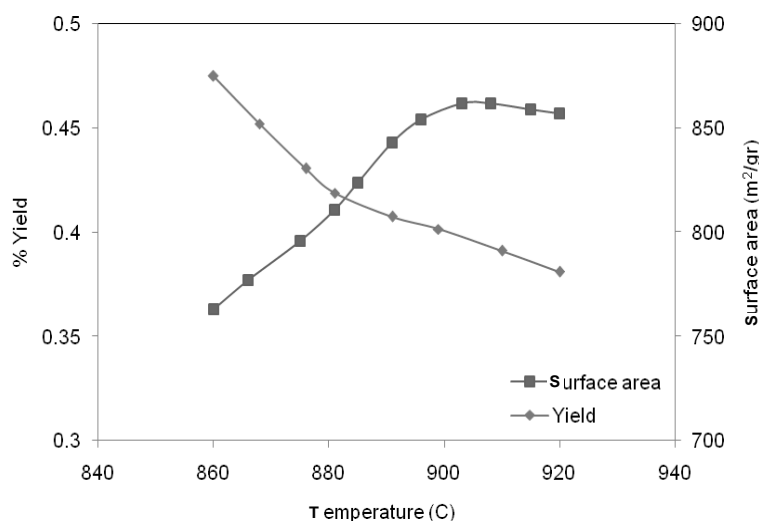


Figure 8. Activated carbon properties produced in steam activation of the char for 1.5 hr.

Regarding the overall reaction control regime, the activation temperature has a direct effect on the development of all ranges of porosities. But the higher temperature on the reaction causes wider size distribution of the pores due to the faster reaction. This effect is shown in Fig. 9 for the char activation with steam for 3.5 hr.

3-3. Effect of reactant gas

Molecular size of reactant gases and kinetic parameters of the reactions are effective

parameters on progressing of char activation and pore development.

Activation of the char with CO₂ and steam in the same overall reaction rate can introduce the possibility to study the effect of gas reactant on pore development regardless of the effects of the reaction rates. As Fig. 10 shows, the char activation with steam at the temperature of 830°C and with CO₂ at the temperature of 920°C gives a similar overall reaction rate with near Thiele modulus.

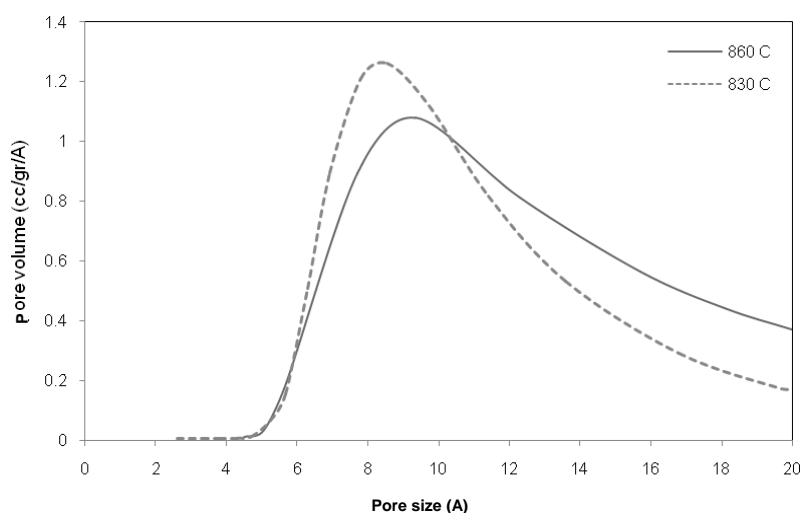


Figure 9. Pore size distribution of the activated carbon prepared in the steam activation for 3.5 h.

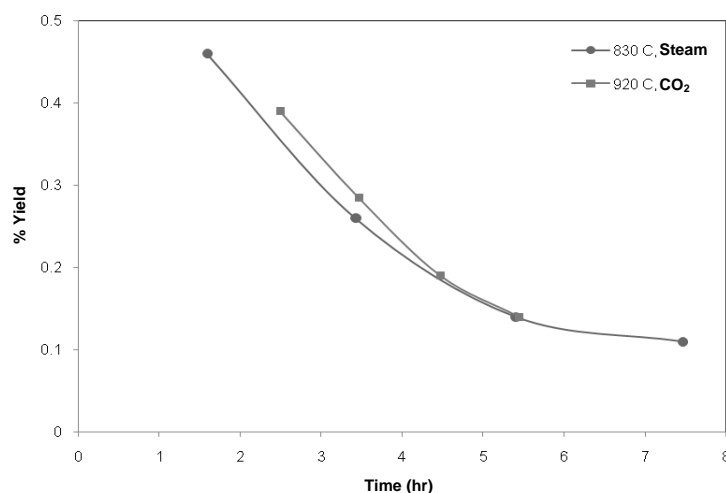


Figure 10. Constant rate of the char activation with steam and CO₂.

This figure also shows that overall reaction rate with both reactant gases at the activation time of 3.5hr are the same. The surface area and burn-off of the products were 1163 m²/gr and 26% for steam activation and 1110 m²/gr and 23% for CO₂ activation.

The activation rate for these two products was approximately constant and equal to 0.35 %/min. The difference in surface area shows the effect of activation with CO₂ in comparison with steam activation. As Fig. 11 shows, in the same reaction rate the surface area in steam activation is more than that in

CO₂ activation because molecules of steam are smaller than CO₂. This causes easier diffusing for steam than CO₂ in the pores. Also, kinetic parameters indicate that the reaction rate of steam with carbon is faster than carbon dioxide [26].

The pore size distribution of these samples is compared in Fig. 12. By comparison of the sample properties, it is shown that although surface area of the samples is approximately the same, pore size distribution of the sample activated by CO₂ is sharper than the other sample.

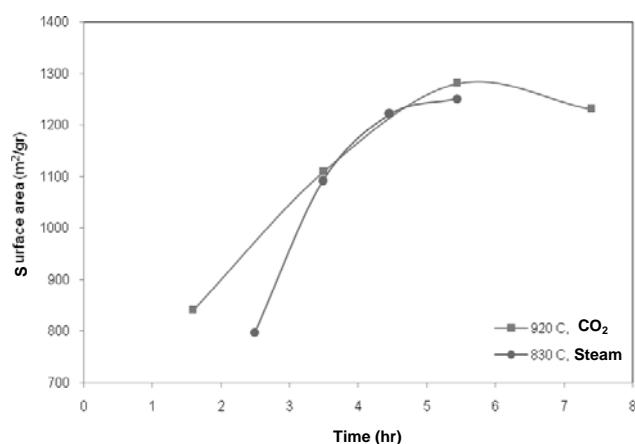


Figure 11. Comparison of the surface area in steam and CO₂ activation at the same reaction rate.

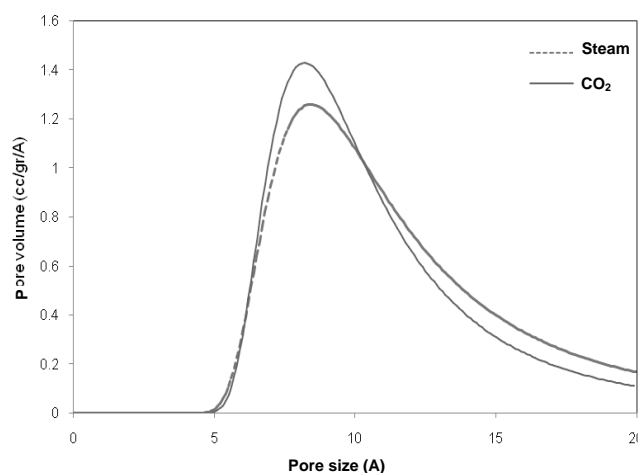


Figure 12. Pore size distribution of the products produced in the same reaction rate.

4. Conclusions

Production of activated carbon from Iranian coal (Goltoot mine) in a rotary kiln reactor with several operating conditions was studied. The experiences showed the main effect of pre-oxidation and charring steps on the final properties of the product. In addition, the potential of this coal mine for activated carbon production was very interesting, hence even the fast reaction condition (such as steam activation at 900°C for 1.0 hr) can produce a relative high surface area product (surface area of 850 m²/gr).

The yield was found to decrease with increasing of activation temperature and time while the surface area followed a parabolic trend. Comparison of the resulting carbons showed that the carbons prepared with steam activation have a greater surface area than those produced with CO₂ activation. The PSD comparison of the product showed the effects of activation time and temperature

and also reactant gas type on the tailored properties of the activated carbon. With increasing of activation time and temperature the PSD presented a wider distribution with lower peak whereas the PSD of the sample activated by CO₂ was sharper than the sample activated by steam.

All experimental data are presented in Fig. 13. Regardless of the conditions of carbon production, all data follow a parabolic trend. It shows that during activation, the burn-off is the key parameter for controlling the surface area development. This figure shows the burn-off around 20% is the optimum point of activated carbon production.

Acknowledgment

The authors are so thankful Professor M. Rostam-Abadi and his staffs in the University of Illinois at Urbana-Champaign (UIUC) to facilitate the experimental setup and the characterization instruments of this study.

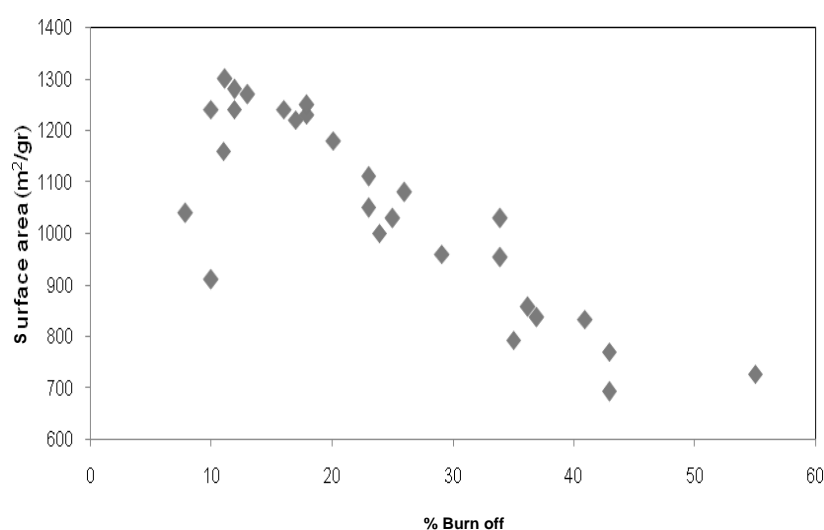


Figure 13. parabolic shape of the curve burn off-surface area.

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