

DEVELOPMENT TECHNIQUE IN THE ACTIVATION PROCESS OF PETROLEUM COKE

Theresia I. Pudiyanto and S. Nurlatifah
PERTAMINA

Petrochemical and Non Fuel Product
Jalan Raya Bekasi KM 20, Jakarta 13920, INDONESIA

1. INTRODUCTION

The manufacture of activated carbon involves two main stages, the carbonization of the carbonaceous precursor and the activation of the resulting char. Process activation is to enhance the pore structure by the partial gasification of the char in steam, carbon dioxide, air or a mixture of these; this is the so-called "physical activation". The term "chemical activation" refers to the carbonization of the precursors after addition of substances that restrict the formation of tar (H_3PO_4 , KOH, etc); in this way, a carbonized product with a well developed porosity (after appropriate washing) may be obtained in a single operation. There is, of course, the possibility of combining these two activation processes. In our experiments, the two principal methods of activation, i.e., that which uses CO_2 and that which uses KOH were chosen and treated to green petroleum coke as starting materials. The properties such as surface area and Iodine adsorption were relatively low in the physical activation. The surface area was reached in the range of 27 to 79 m^2/g and Iodine adsorption 59 to 85 mg/g . The adsorptive power in Iodine solutions increased to the value of approximate 600 mg/g for physical activation of green coke binded with tar pitch. Further more, a well developed in pore, surface area and Iodine adsorption was achieved using KOH activant with appropriate process condition.

2. EXPERIMENTAL

- a). Green petroleum coke was obtained from Dumai oil refinery. The size of particle was +4 mesh. The raw material was carbonized at 400 - 500°C for 2 hours and then proceed to activation process. For activation, temperature was increased to 600 - 700°C and flow of CO_2 after reaching the temperature. After activating with CO_2 for 3 hours, cooling to room temperature was carried out naturally before taking the sample for further analysis.
- b). The green petroleum coke was ground and sieved to sizes of 200 mesh. Afterwards this material was mixed thoroughly with coal tar pitch of known percent weight. The mixed petroleum coke is then extruded to form discontinuously tube in a cylinder press. These moulded forms are then broken into short lengths and sieved to size between 8 - 4 mesh for further carbonization and CO_2 activation. During carbonization, the sample was shielded by calcined coke with size 16 - 14 mesh and gradually heated to 110°C for 2 hours and proceed to temperature 500 - 600°C for 3 hours and cooled to ambient temperature. Before activation, the carbonized material was separated from calcined coke by sieving in order to obtain the required size (2.5 - 4.5 mm). The activation carried out at temperature 900 - 1000°C for

3 hours under flowing of CO₂. For comparison, green coke with the same size was treated directly in the same process condition as mentioned above.

- c). Green coke was ground to -50 mesh and the process under investigation in this study involves the reaction of coke with a substantial proportion of solid KOH (KOH : coke varied from 1 to 4 parts weight). Reactions took place in a nickel boat, within a reaction furnace tube under nitrogen. Reaction mixtures were heated 600 - 900°C for periods up to 1 hour and after reaction the furnace was withdrawn and cooled to ambient temperature. The reaction products were removed from the container and washed with distilled water to remove soluble salts. Other samples were reacted at 450°C for 1 hour and then subjected to thermal treatment up to 850°C and held at this temperature for 1 hour. Each of the solid products was leached with distilled water and vacuum dried at 110°C.

3. RESULTS AND DISCUSSION

Table 1 : Typical Properties of Green Petroleum Coke

Moisture, wt %	0.62
Volatile matter, wt %	14.54
Ash content, wt %	0.34
Fixed carbon, wt %	84.50
Sulphur content, wt %	max 0.5

Table 2 : Preparation Condition of 2 a and Its Properties

Sample	Carbonization & Activation, °C	Iodine Adsorption, mg/g	Surface Area, m ² /g
C1	400	59.73	47
C2	500	59.34	42
C3	400 ; 600	72.52	28
C4	400 ; 700	85.69	79
C5	500 ; 600	69.12	54
C6	500 ; 700	69.59	33
C7	Reference		588

Table 3 : Preparation Condition of 2 b and Its Properties

Sample	Carbonization & Activation, °C	Iodine Adsorption, mg/g		Ash, wt %	
		With binder	Non binder	With binder	Non binder
A1	600 ; 1000	674.76	669.42	0.18	0.19
A2	600 ; 900	698.82	645.72	0.07	0.08
A3	500 ; 1000	662.13	637.36	0.10	0.12
A4	500 ; 900	656.24	626.11	0.04	0.06
A5	Referene	850.23		1.03	

Table 4 : Preparation Condition of 2 c and Its Properties

Sample	KOH Coke	Reaction Temperature °C/time, hour	Heat Thermal Treatment °C/time, hour	Surface Area, m ² /g
B1	1:1	600/1	-	439
B2	4:1	600/1	-	50
B3	1:1	900/1	-	416
B4	4:1	900/1	-	34
B5	1:1	450/1	850/1	177
B6	1:2	450/1	850/1.5	1190
B7	1 3	450/1	850/1.5	1404
B8	1:4	450/1	850/1.5	2054

The activation technique process that was chosen in the experiment 2 a did not indicate the development of adsorptive properties and surface area as can be seen from Table 2. The gasification of carbonaceous materials with CO₂ at 600 and 700°C have no influences to Iodine adsorption and surface area improvement. Its value range from 59.34 to 85.69 mg/g and highest surface area was achieved max 79 m²/g. These value was below expectation compare to the required properties of an adsorbent materials. The obtained surface area was 1/10 from 588 m²/g of reference.

To improve the adsorptive properties, next sample binded with coal tar pitch, moulded and shielded with calcined coke during carbonization up to 600°C. The aim of using calcined coke was to avoid rapid decreasing of particle size due to oxidation. The CO₂ activation which subjected to carbonized product have increased drastically the Iodine solution adsorption and the highest value was 698.82. On the other hand, the non binder activated samples seems to have nearly same value as the binded one. The use of calcined coke in the second experiment act as an inert media during process operation and the higher temperature chosen for activation (900 - 1000°C) lead to the surface affinity improvement of the green petroleum coke.

The Iodine adsorption in the range from 626.11 to 698.82 mg/g for binder and non binder materials. Although these obtained value were less than reference (850 mg/g), this technique reveals that inert condition facilitate the activation process of green petroleum coke. The lower ash content in both samples reflex the higher quality of the starting material and binder. The ash content of reference 1.03 wt % indicated that difference carbon precursor was being used. Since the two previous physical activation techniques did not indicate good results, so the further experiment was carried out by chemical activation. The carbonization of coke with potassium hydroxide is expected to destroy the coking and coking capacities of green coke and to produce a char of high surface area and showed increase in adsorptive capacity. The progress of activation involves the reaction of coke with a substantial proportion of solid KOH from 1:1 up to 4:1 at reaction temperature 450°C for times 1 hour and subjected to

heat treatment at 850°C for times of 1 hour to 1.5 hours could produce an active carbon of high surface area up to 2054 m²/g as can be seen from Table 4 and suitable for further application analysis.

The reaction temperature carried out at 600 and 900°C results nearly same surface area namely 439 and 416 m²/g. On the other hand, the least introduce reactant tend to decrease the surface area of activated carbon to value 34 - 50 m²/g. The process conditions and amount of KOH have influenced the surface area formation of carbon, an important property for adsorbent.

4. Conclusions

- Different preparation technique of activation were greatly influence the pore structure enhancement of green petroleum coke.
- Formation of high surface area active carbon from green petroleum coke was obtained effectively by using KOH activant.