The Secondary Activation of Petroleum (Texaco) Cracked Carbons

The Secondary Activation of Petroleum (Texaco) Cracked Carbons[7]

Hiroshi Yanai

Abstract

The properties of primary activated carbon of Texaco (A and C) and Fauser (B) processes should be different owing to the structure of furnace and operating conditions. These are similar to the cases where were gasified such carbonaceous materials as charcoal, lignite and brown coal by fluidized activation as described before. The operating conditions are conclusively effected on the nature of dusts. Therefore, these effects of a secondary activation on adsorbability and other properties should be influenced by the source of primary products, especially the operating pressure of the previous stage. This paper was discussed the mechanism of gaseous activation, comparing the properties of carbons being examined (petroleum cracked carbons) before and after the secondary activation.

1 Introduction

In recent years, it has been attempted to utilize the carbon that is essentially formed by the cracking of various hydrocarbons under conditions of incomplete combustion in the course of manufacturing a hydrogen gas. Since 1947, the present writers have been developed a series of the commercial plant separating the more activated carbon from the cyclone dust that is produced by the internal heating fluidized furnace from such carbonaceous materials as charcoal, lignite and brown coal as reported before[3]~[6]. In 1948, this process was started with Mitsui chemical Co. Ltd. in its endeavor to pioneer the fluidized bed reactor as a patent process[1][2]. Judging the resulting data by comparison, similar experimental trials had been carried out in a certain Winkler generator. The following conclusion has already been reported in the previous paper[3].

The operating conditions are conclusively effected on the nature of dusts. There are the optimum feed rates according to the scale of furnaces. The optimum conditions for the gasification and for the activation are approximately the same. The operations of all these processes are carried out at an atmospheric pressure. The Texaco and Fauser processes are similar to our process except that feed materials are replaced the carbonaceous solid materials by the hydrocarbon oils. The Texaco process illustrated in this paper is operating under pressure Therefore it has been attempted to activate secondarily these primary activated carbon by the method similar to the ordinary gaseous activation.

2 Experimental apparatus and its procedure

2-1 Sample

In order to solidify, suitable quantity of water is added to the cracked carbon

produced from different operating conditions, corresponding to A, B and C Co. Ltd.. Properties of these primary activated carbon are illustrated in Table 1, where A and C are the products of Texaco process and B is a product of Fauser process.

2-2 Activating apparatus

Diagrammatic apparatus for activation is shown in Fig 1. The reaction tube is made of quartz, being 3.5 cm in diameter, and 1 m in length. For the purpose of preheating, uniform distribution of activating gas and supporting a sample, the rolled stainless wire screen are arranged about 45 cm in length below the sample.

The sample is dried at 105°C for 48 hours and then the sample of about 15 g is charged into a reactor encircled by an electric furnace. The rising rate of temperature is regulated at 5°C/min, N_2 gas passing through, until it reaches to a certain temperature. The activating gas are passed through it at a constant flow rate of 2 1/min for a given time. The quantity and the analysis of generated gas are measured with the wet gas meter and the gas chromatographic procedure respectively. And the secondary activated carbons are estimated for the following items.
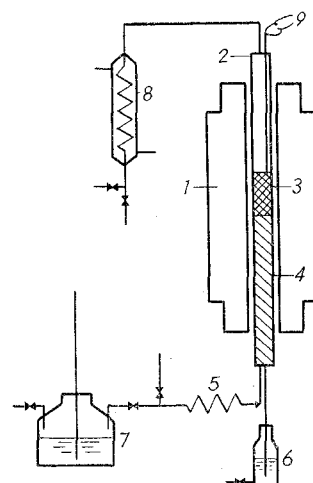

Fig. 1 Secondary activation
apparatus
1: Furnace 2: Reactor 3: Sample
4: Supporting wire 5: Heater
6: Reservoir 7: Steam generator
8: Cooler 9: Thermocouple

Table 1 Properties of the primary activated carbon for comparison

			A	B	C
Ignition loss		%	0.5	0.4	0.4
P H			7.9	8.7	8.0
Specific filterability		%	97.0	26.0	63.0
Decolorizing power	M B	cc	7.0	19.5	12.5
	Caramel	%	73.2	91.2	80.8
	Sugar sol.	%	65.0	83.6	68.3

c. f By testing method of TAKEDA Co. Ltd.

2-3 Benzene adsorption test

Benzene adsorption test is carried out by the quarz spring balance[8] supported within a thermostat at a constant temperature of 20°C. Being exhausted the air for about 4 hours by a vacuum pump, the increase of weight are measured by the cathetometer, while maintaining at the constant concentration of benzene (220 g benzene per Nm^3 air) for 30 min.

2-4 Methylene blue test

Place 0.025 g of the dry carbon being tested in a 100 mℓ beaker. Add 25 mℓ of methylene blue solution of a given concentration $(3 \sim 6 \times 10^{-4} \, mol/ℓ)$, stirring for 25 min at 20°C and filter it by a suction. The light transmitted through the filtrate are measured by the photoelectric colorimeter (filter: 655 mμ).

2-5 Relative true density

It is extremely difficult to measure the true density of activated carbon exactly. Because of this, in this paper, it is necessary to compare the true density of a carbon being examined with the true density of a reference carbon that is kept as a standard for comparison. A mixture of the dry carbon being tested and the distilled water is boiled for an hour and filter through a Whatman paper. Again dry it at 105°C for 48 hours. Place this carbon in a pycnometer and add a distilled water. Allow a mixture to stand for 24 hours after stirring. Thus the relative values of true density are possible to calculate from the observed data.

3 Experimental result and its discussion

3-1 Effects of the activation temperature on the yield, the adsorptive capacity and the true density of the secondary activated carbon

These relations are given in Fig. 2 and 3. In proportion to the rise of temperature, the yield of the secondary activated carbon decreases. The relation between the activation temperature and the yield is approximately the same in the activation by either CO_2 gas or steam and there
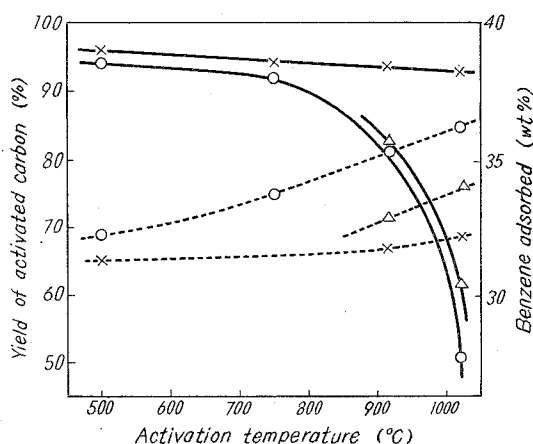

Fig.2 Effects of activation temperature on the yield and adsorbability of activated carbon

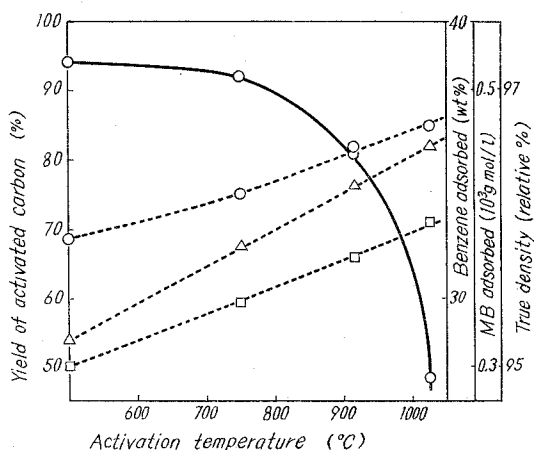| yield	adsorption	activation condition
—×—	·····×·····	N_2 1 hr
—○—	·····○·····	CO_2 1 hr
—△—	·····△·····	H_2O 10 min

Fig. 3 Effects of activation temperature on the yield, adsorbability and true density. Primary activated carbon B
—○—: Yield   ·····○·····: Benzene absorbed
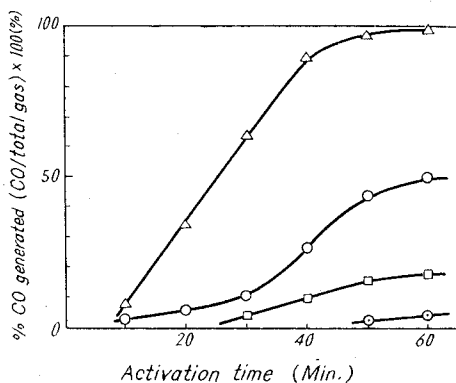·····△·····: M. B. adsorbed   ·····□·····: True density

Fig. 4 Relation between activation
condition and per cent of
CO generated
(CO$_2$ gas activation of the primary
carbon C)
△ : 1030°C, ○ : 915°C, □ : 750°C
⊙ : 500°C

is a break point near the temperature of
850°C. However in a case of N$_2$ gas, no
significant effects are noticed on the activa-
tion. This is probably due to the gasi-
fication reaction.

The relation between activation con-
ditions and CO gas (%) generated in the
CO$_2$ gas activation of the primary activated
carbon (C) is given in Fig 4. With the
rise of temperature the equilibrium of the
reaction, C+CO$_2$⇌2 CO, is advanced to-
ward the right hand. It is thus noticed
that there is a intimate mutual relation
among the per cent of CO gas generated,
the decrease of yield, the increase of ad-
sorbability and true density.

The primary activated carbons have
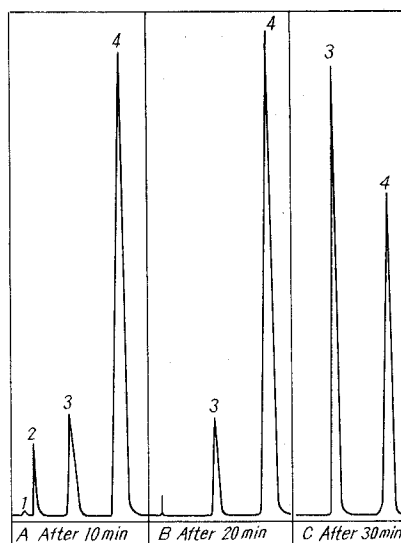been already activated at the temperature
around 1400°C. When these carbons are secondarily activated by CO$_2$ gas at

temperatures above 900°C the existence of
a trace H$_2$ gas is detected at the beginning
of these activation, as shown in Fig. 5. The
amount of H$_2$ gas decreases with the passage
of time and this completely disappears after
30 minutes. In view of this fact, it may be
pointed out that the pores of the primary
activated carbon are blocked up by the higher
hydrocarbons at the end of the formation
and these hydrocarbons are decomposed by
the gaseous reaction. This may be one of
the most reasonable clue to explain the me-
chanism of the increase of adsorptive capa-
city by means of the secondary activation[3].

3-2 Effects of the activation time on the yield, the adsorptive capacity and the true density of the secondary activated carbon

These relations are shown in Fig. 6.
The yield extremely decreases from the be-
ginning till 60 minutes of activation, con-
versely both the adsorptive capacity and the
true density increase. The prolongation of

Fig. 5 H$_2$ gas generated at the course
of CO$_2$ gas activation
Activation temp. 1030°C
Primary carbon C
1 : H$_2$, 2 : N$_2$, 3 : CO, 4 : CO$_2$ gas
Column (6 mm×2 m), Molecular
sieve 5 A, Carrier gas : He 30 mℓ/
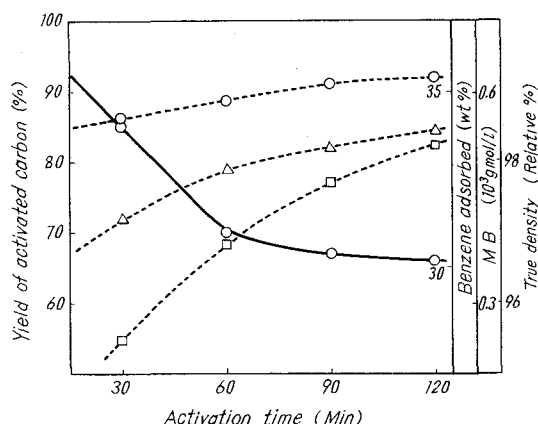min, 40°C

Fig. 6 Effects of activation time on the yield, adsorbability and true density (Relative), CO_2 gas activation 915°C of the primary carbon C

—○—: Yield   ····○····: Benzene adsorbed   ····△····: M B adsorbed   ····□····: True density

the activation time is noticed a little effect on these properties. According to the economic consideration and the purpose of applications it is necessary to determine these activating conditions.

3-3 The primary activated carbon and the efficiency of the secondary activation

Comparing the properties of carbons being examined (A, B and C) before and after the secondary activation with the properties of a reference carbon that is kept as a standard for comparison, the calculated relative values are illustrated in Fig 7 as the efficiency of the secondary activation. The cracked carbons of the Texaco process are superior to the another one in the term of this efficiency.

The properties of the primary activated carbon should be different owing to the structure of furnace and the operating conditions. These are similar to the cases where were gasified such carbonaceous materials as charcoal, lignite and brown coal by the internal heating fluidized furnace[2]~[6]. The carbons of A and C are produced under considerable pressure by the Texaco process. In comparison between A and C, in a case of A it is consequently possible to recognize that the oil is excessively feeded per inner volume of reactor beyond the optimum feed rate. The carbon of B is produced at the ordinary pressure by the Fauser process.

Fig. 7 Effects of the secondary activation on the sources of primary activated carbons
A, C: Texaco process
B: Fauser process

The operating conditions in these cases seem to produce some significant effects on the efficiency of the secondary activation, although these are not possible to
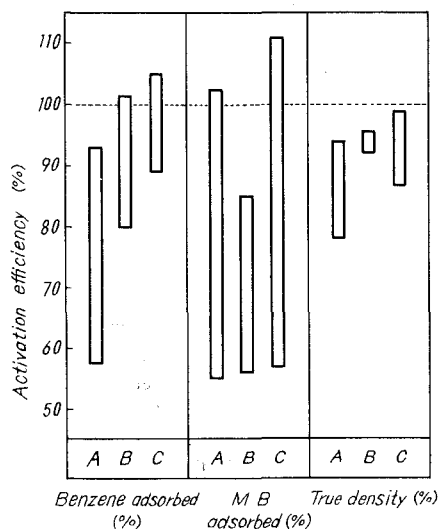
know in datails. One may be expected the intimate relations between the pressure operation and the production of the enclosed pores with higher hydrocarbons. However, further investigations are necessary on this subject.

3-4 X-ray diffraction analyse and electron microscopic photograph

The results of X-ray diffraction regarding the carbons (C) before and after the activation are illustrated in Fig 8. Since the primary activated carbons are produced at temperatures around 1400°C, no change is noticed in the structure of crystallites by the secondary activation of 1000°C or less.
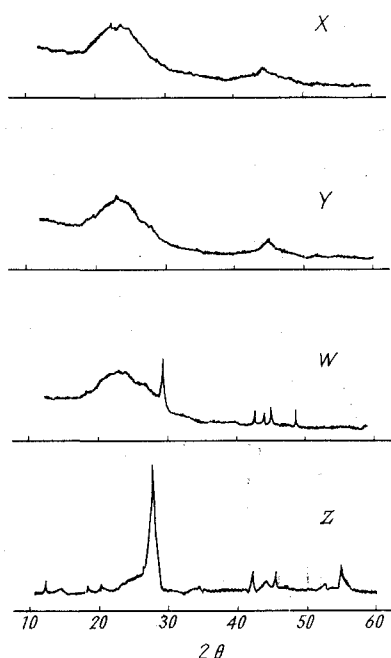

Fig. 8 X-ray diffraction photograph of the primary (X), the secondary (Y), crude activated carbon (C), charcoal (W) and graphite (Z) Time const. 1, Multiplier 1, Ratemeter 16, 30 KV, 15 mA
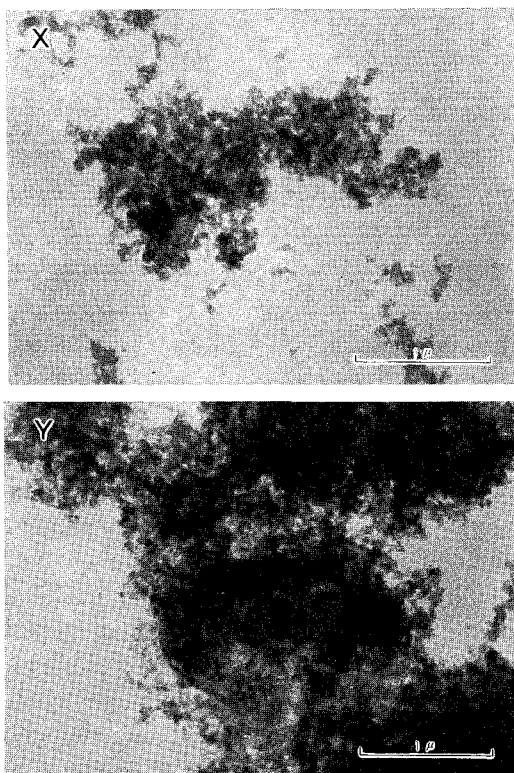
Fig. 9 Electron microscopic photograph of the primary carbon (C) (X) and the secondary activated carbon C (Y)

The electron microscopic photographs for the same sample are shown in Fig 9. According to these photographs, it is confirmed that carbon particles are congregated each other to a considerable degree as the result of a secondary treatment in either carbons of A, B and C. At the end of the period producing so-called amorphous substances having the porous structure the pores of the primary activated carbon are blocked up owing to the higher hydrocarbons deposited on the surface during the cooling stage of exit gases. For this reason, the adsorptive capacity is greatly reduced. However these deposited hydrocarbons

are decomposed and gasified in the course of the secondary activation[3][7]. Consequently the removal of the hydrocarbons is supposed to leave the carbon surface free to attract and adsorb other substances and then these carbons show a tendency to the formation of an assembly, because of the attractive force of carbon particles themselves. Thus the surface area is increased and a tremendus porous structure is developed.

4 Conclusion

The utilization of Texaco and Fauser cracked carbons (now called primary activated carbon) with a fixed bed reactor by the treatment of oxdizing agents-steam, air, carbon dioxide was studied. The mechanisms of this secondary activation were also studied with reference to the results of X-ray diffraction analysis, electron microscope and other physical adsorption techniques. The results are as follows:

It is possible to recognize that to a large degree the activity of primary activated carbons depend upon the gasification condition of crude petroleum, as well as charcoal, lignite and brown coal described in the previous papers and the mechanisms of a secondary activation are covered by a preferential oxidation of hydrocarbons which had been deposited on the surface during the previous stage. Therefore, these effects of a secondary activation on adsorbability and other properties are influenced by the source of primary products, especially the operating pressure of the previous stage. According to electron microscopic photographs, it is confirmed that carbon particles are congregated each other to a considerable degree as the result of a secondary treatment, and thus the surface area is increased and a very porous structure is developed.

Literature cited

1) Iwasaki, T., Yanai, H.: Japan Patent No. 178584 (Apr. 1950).
2) Iwasaki, T., Yanai, H.: Chem. Eng. (Japan), 18, 81 (1954).
3) Yanai, H.: Chem. Eng. (Japan), 26, 518 (1962)
4) Yanai, H.: Chem. Eng. (Japan), 26, 1089 (1962).
5) Yanai, H.: Fuel Soc. (Japan), 41, 976 (1962).
6) Yanai, H.: Wood Ind., 23, 162 (1968).
7) Yanai, H.: J. Chem. Soc. (Japan), 71, 960 (1968).
8) J. W. McBain, A. M. Bakr: J. Am. Chem. Soc., 48, 690 (1926).