Effect of Butylation on Hydropyrolysis of Coal

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Effect of introduction of butyl group into Yubari coal on hydropyrolysis was investigated. The strong promoting effect of butyl group on gasification of coal was observed at considerably low temperature, 500 °C: The yield of gas increased from 29 wt% of Yubari coal to 82 wt% of butylated Yubari coal.

A solvent-soluble product from coal butylated with zinc and butyl iodide is an appropriate sample for analyzing coal structure because of its mild reaction conditions (at 130 °C, under atmospheric pressure); however, the soluble products are too heavy to investigate the more detailed structure of coal.[1] Therefore, we hydrogenated the soluble products of Yubari coal under mild conditions to investigate them in detail. When the heavy products were hydrogenated at 400 °C, none of organic products were formed in a reactor.[2] These very interesting results led us to the present study where hydropyrolysis of the coal butylated with zinc and butyl iodide are investigated.

Yubari coal[3] butylated with zinc and butyl iodide at 130 °C for 5 h was used as a sample. For comparison, original Yubari coal was also used. Details of the reaction conditions of the butylation were described previously.[1,4] Yields of butylation of Yubari coal, hexane soluble (HS), and hexane insoluble-benzene soluble products (HIS-BS) were 169, 45.6 and 43.6 wt%, respectively.[5] Hydropyrolysis was carried out in a 500ml autoclave with a glass tube (30 mmϕ × 165 mm) in it at 400, 450 and 500 °C (the rate of heating: 3 °C/min) for 0 min[6] under an initial hydrogen pressure of 10.1 MPa. Three grams of Yubari coal or butylated Yubari coal (Bu-Yubari) was hydropyrolyzed without catalysts. After the reaction, gaseous products were trapped in the cold finger cooled at -198 °C by passing the exit gas through it. Uncondensable hydrogen was kept in the gas bag, then condensable gases like CO, CO_2 and C_1 -C_4 hydrocarbons are reserved in the gas bag additionally by warming the cold finger to the room temperature. Gas chromatographic analysis of the products revealed the formation of CH_4, CO_2, ethane, propane, and butane. Discussion of gaseous products and their distribution will appear in the detailed paper. The products remained in the autoclave were then separated into HS, HI-BS, and benzene insoluble products (BIS). Gas yields (in Figure 1) were calculated by difference (100 - HS - HIS-BS - BIS). IR spectra were obtained by diffuse reflectance method.[1,4] Structural parameters[7] were estimated according to the equations proposed by Brown and Ladner[8] and modified by Yokoyama et al.[9]

Figure 1 shows the results of hydropyrolysis of Yubari coal and Bu-Yubari. For Yubari coal, the yields of HS, HIS-BS and gas are low, as hydrogenation of coal without catalyst at three temperatures is not effective for conversion of coal. However for Bu-Yubari, the yields of HS, HIS-BS, and gas after hydropyrolysis are higher than original yields of Bu-Yubari before hydropyrolysis, and at 500 °C the yield of gas increases up to 82 wt%. The strong promoting effect on gasification is observed at 500 °C: The butyl groups introduced into coal lead to

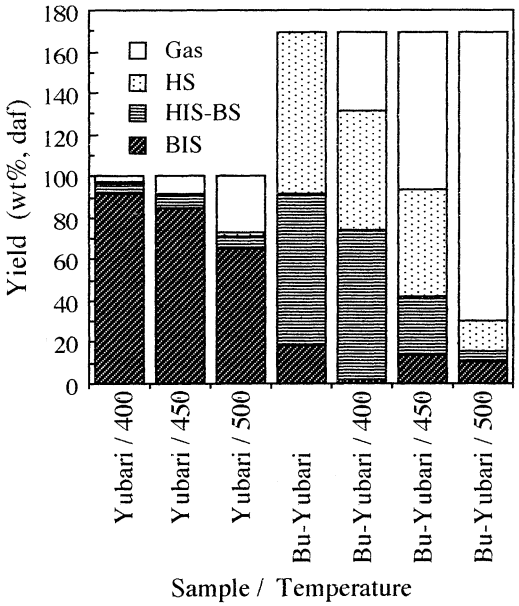

Figure 1. Effect of butyl group on hydrogasification of Yubari coal. H_2 10.1 MPa, 0 min, 3 °C/min, no catalyst. HS, hexane soluble; HIS-BS, hexane insoluble-benzene soluble; and BIS, benzene insoluble product.

increase from 29 wt% to 82 wt% in yield of gasification. In addition, the aromatic moieties of coal are converted to hydroaromatic ones in the butylation of coal, because reductive butylation also occurs.[10] These hydroaromatic moieties are expected to be susceptible to hydropyrolysis. Because most of the butyl groups introduced into coal come from Bu-Yubari up to 450 °C, both butyl group and coal itself are hydropyrolyzed between 450 and 500 °C.

Structural analysis of HS and HIS-BS from the hydropyrolysis of Bu-Yubari was carried out to analyze structural features of solvent-soluble products, and the structural parameters are given in Table 1. For HS from 400 °C to 500 °C, an increase

Table 1. Structural parameters of HS and HIS-BS from hydropyrolysis of Bu-Yubari

Sample	Temp (°C)	Structural Parameter[a] fa	Hau/Ca	σ al	L
HS	400	0.45	0.73	0.51	3.2
	450	0.52	0.78	0.46	2.6
	500	0.72	0.74	0.31	1.7
HIS-BS	400	0.55	0.74	0.42	2.6
	450	0.62	0.69	0.36	2.5
	500	0.76	0.69	0.23	2.0

[a]Notations are described in the References and Note.

in fa from 0.45 to 0.72 as well as a decrease in σ al from 0.51 to 0.31 and in L from 3.2 to 1.7 are observed, and the similar tendency of changes in fa, σ al and L is also shown for HIS-BS. Thus these results reveal that aliphatic moieties of the solvent-soluble products decrease with increasing temperature. A size of aromatic rings is considered to be similar among all the HS and HIS-BS, because the values of Hau/Ca do not change so much. The results of structural analysis also indicate that aliphatic moieties of Bu-Yubari converted into gas.

For coal pyrolysis, O-alkylation of coal has significant effect on the increasing yield of volatile matter, since elimination of hydroxyl groups in coal prevents the formation of new cross linkages.[11, 12] Because no bands attributed to hydroxyl and carbonyl groups are observed in the IR spectrum of the Bu-Yubari, the butylation using zinc and butyl iodide is believed to eliminate both hydroxyl and carbonyl groups in coal. In addition, most of butyl groups are released up to 450 °C, and then coal itself is hydropyrolyzed up to 500 °C. Therefore the significant increase in gas yield probably occurs by the prevention of new cross linkages in coal and by the destruction of coal structure caused by the elimination of butyl groups. The related works to the present study are in progress.

References and Note

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3 Elemental analysis: Yubari coal, C, 84.9 wt%; H, 6.0 wt%; O, 9.1 wt% by difference.
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5 The yields (daf) of butylation of Yubari coal and the solvent-soluble products are based on Yubari coal and butylated Yubari coal, respectively.
6 When temperature was attained at 400, 450, and 500 °C, the reactions were terminated.
7 The structural parameters concerned are as follows: The ratio of the number of the aromatic carbons for the total number of carbons, fa; the ratio of the number of peripheral aromatic carbons to total number of aromatic carbons (degree of aromatic ring condensation), Hau/Ca; the degree of aromatic ring substitution of the aliphatic chain, σ al; and the length of the aliphatic chain, L.
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