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HIGH EFFICACY OF SHORT CONTACT TIME PROCEDURE AT HIGH TEMPERATURE IN THE HYDROGEN TRANSFERRING LIQUEFACTION OF BROWN COAL

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Hydrogen transferring liquefaction of an Australian brown coal using pyrene hydrogenated with Li-ethylenediamine or a Ni-Mo catalyst is found very efficient to convert the coal hexane-soluble as well as benzene-soluble at yields as high as 70% and 90%, respectively, under the conditions of short contact time(1.5 min) at high temperatures (490-510°C). The structural differences of hydropyrenes are briefly discussed in relation with their performance in the liquefaction process of the present kind.

Recent development of catalysts tolerant against the ash minerals in the coal further evaluates the two stage coal liquefaction (TSL) process,1) where the solid-liquid separation step between the first (thermal) and the second (catalytic) steps can be eliminated.2) The heavy oil and/or light asphaltene which can be defined by the solubility in hexane and benzene, respectively, may be the most desirable products of the first step in a TSL process. Neavel3) found rapid dissolution of coal in a hydrogen donating solvent and proposed a short contact time (SCT) process.

The hydrogen transferring liquefaction has been revealed applicable to the first step with various coals.3,4) In previous papers5-7) hydrogen transferring liquefaction of an Australian brown coal, when hydrogenated aromatics of adequate size such as hydrogenated pyrenes were used, was found very effective to increase the asphaltene yield at low pressures.

The present letter reports an excellent performance of pyrenes hydrogenated with Li-ethylenediamine or a Ni-Mo catalyst to produce hexane soluble as well as benzene soluble products from the brown coal by a shorter contact time (1.5 min) at further high temperatures (450-510°C) and a low pressure (25 kg/cm^2). The high boiling point, hydrogen donating and dissolving abilities, and the thermal stability after the dehydrogenation of the solvent are expected to be key factors for the excellent performance in the hydrogen transferring liquefaction under high tempereture SCT conditions, which may enhance the reactivity of the coal and abilities of the solvent. Roles of hydrogen reactivity of the solvent are briefly discussed in such a liquefaction process.

Table 1. Ultimate analyses of the coal and solvents

	C	H	N	S	O
Yallourn (daf)	67.3	4.8	1.0	0.3	26.6
BHP[a)]	91.5	7.0	1.5	--	--
CHP[b)]	92.8	7.2	--	--	--

a),b) See text.

The ultimate analyses of the Yallourn brown coal are summarized in Table 1. The liquefaction (hydrogen donating) solvents were hydrogenated pyrenes designated as BHP and CHP, respectively. BHP was prepared by the hydrogenation using Li and ethylenediamine.[6,8)] CHP was prepared by the catalytic hydrogenation with a commercial Ni-Mo catalyst at 330°C under 100 kg/cm^2 of hydrogen pressure. Their ultimate analyses are also summarized in Table 1.

Liquefaction was carried out in a tube bomb (vol. 25 ml). The ground brown coal (2 g) dried at room temperature under vacuum and the solvent (6 g) after well-mixing were transferred, together with a small iron bar to assist stirring, to the bomb. The bomb was then pressurized with nitrogen at room temperature (5 kg/cm^2) and immersed into a heated molten tin bath, while agitating axially. The reaction temperatures were attained within 1.5 min. After the prescribe time of liquefaction, the bomb was removed from the bath and rapidly immersed in cold water to quench the reaction. The volume of gaseous products was measured by water displacement. The products remaining in the bomb were extracted by benzene (Bz) and hexane (Hx). The liquefaction yields (LY(Bz) and LY(Hx)) defined with respective solvents were calculated from the amount of the insoluble material.

$$LY = (1 - \text{solvent insoluble(daf)}/\text{initial coal(daf)}) \times 100\ (\%)$$

Thus, the LY includes yields for gaseous products and lighter oils, although no definite analysis was intended in the present letter.

Figure 1 shows the LY(Bz) at variable liquefaction temperatures and times using BHP and CHP as the hydrogen donating solvents. The values of LY(Bz) with

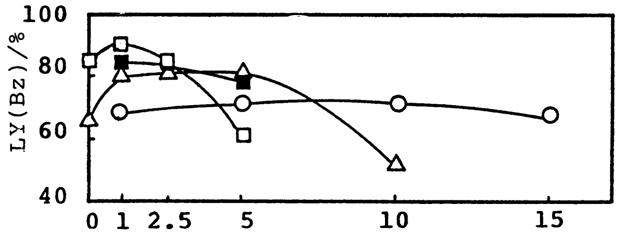


Fig. 1. Influence of reaction temp. and time on liquefaction yield(Bz).
Solvent: BHP □ 510°C, △ 490°C,
○ 450°C
CHP ■ 510°C

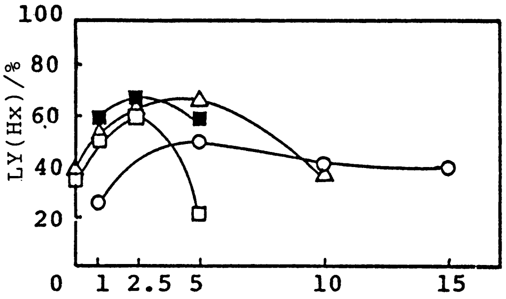


Fig. 2. Influence of reaction temp. and time on liquefaction yield(Hx).
Solvent: BHP □ 510°C, △ 490°C,
○ 450°C
CHP ■ 510°C

BHP increased with the increased temperature, achieving as high as 90% at 510°C. The LY(Bz) varied markedly with the time at 510°C, where it was 85% at zero reaction time, reaching the maximum of 90% at 1 min and then decreased sharply to 60% at 5 min. It varied more moderately at lower temperature. It almost unchanged at the level of 70% for 15 min at 450°C.

Figure 2 shows the LY(Hx) under the same conditions. It should be remarked that the value achieved with BHP as high as 65%. The yield was also very variable with the liquefaction temperature and time. It showed the maximum yield at 490°C, where it increased from 40% at zero reaction time to the maximum (65%) within 5 min and decreased in the similar rate. At higher temperature of 510°C it increased similarly to that at 490°C, but decreased more rapidly, giving the less maximum value of 60% at a shorter reaction time of 2.5 min.

The liquefaction activity of CHP is comparable or slightly better to that of BHP as for the values of LY(Bz) and LY(Hx) at 510°C of the reaction temperature, the latter achieving as high as 70% as shown in Figures 1 and 2. It should be noted that the variation of the yield values due to the reaction time was much more moderate with CHP at this temperature, exhibiting the maximum for both yields at 2.5 min.

Thus, both pyrenes hydrogenated with Li-ethylenediamine or a Ni-Mo catalyst were found to provide very high liquefaction yields of hexane soluble as well as benzene soluble products in the hydrogen donating liquefaction of Yallourn brown coal by the short contact time at relatively high temperatures, which are allowed by the rapid heating rate. Under such conditions thermal degradation of brown coal takes place vigorously9) to produce depolymerized rather small fragments (the unit structure of the brown coal is believed rather small.10)), which are effectively stabilized by hydrogens transferred from hydropyrenes. The dehydrogenation of hydropyrenes, some of which hydrogens are very reactive, is further accelerated under the present conditions to meet the rapid degradation of the coal. Pyrene produced through the dehydrogenation

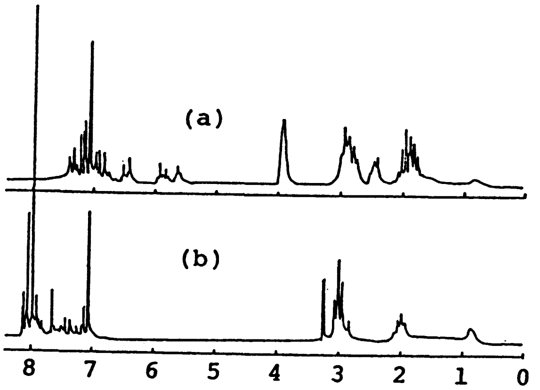
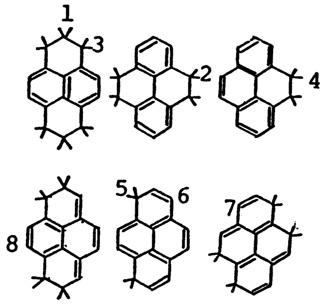


Fig.3. ^{1}H-NMR of BHP(a) and CHP(b).

Proton identification for partially hydrogenated pyrene



1: 1.8-2.2 ppm, 2: 2.3-2.6 ppm,
3: 2.6-3.2 ppm, 4: 3.2 ppm,
5: 3.8-4.0 ppm, 6: 5.5-5.8 ppm,
7: 6.8-7.5 ppm

from hydropyrenes as well as remaining hydropyrenes may form an excellent solvent to dissolve the depolymerized coal liquid, preventing its recondensation reaction under the SCT conditions. Such a best combination of coal, solvent and liquefaction conditions may lead to an excellent yield of the suitable feed to the second step. It is also very favorable that the process can be operated at a low pressure of 25 kg/cm^2 because of high boiling of the solvent.

The hydrogen donating reactivity, which is thus concluded to be one of the most influential factors for the liquefaction, is intimately related to the structure of hydrogens concerned. Figure 3 shows the NMR spectra of BHP and CHP with tentative assignment of their hydrogens.$^{11)}$ BHP carries hydrogens of seven regions except for aromatic ones: 6.3-6.7, 5.8-6.0, 5.5-5.8, 3.4-4.0, 2.6-3.2, 2.3-2.6, and 1.8-2.2 ppm, whereas CHP does ones of only three regions: 3.2, 2.6-3.2, and 1.8-2.2 ppm. Such different constituents of hydrogens in the solvents may bring about the distinct differences in the features of liquefaction above described, because they reportedly exhibit very different reactivities.$^{12)}$ Detailed information on the reactivity of the transferring hydrogens of the solvent is required to design a better non-catalytic liquefaction procedure under the short contact time conditions at unusually high temperatures.

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