CHEMISTRY LETTERS, pp. 1461 - 1464, 1984.

REMARKABLE ABILITY OF TETRAHYDROFLUORANTHENE IN THE LIQUEFACTION OF A SUB-BITUMINOUS COAL AT UNUSUALLY HIGH TEMPERATURE UNDER A MODERATE PRESSURE

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An Australian sub-bituminous coal was effectively liquefied under high temperature short contact time conditions at about 30 kg/cm^2 using 1,2,3,3a-tetrahydrofluoranthene (4HFL) as the solvent. The yields of the oil and asphaltene, the target products, were as high as 54 and 16%, respectively, for a reaction at 560 °C with zero contact time. 4HFL was principally converted into fluoranthene together with some undefined four ring aromatic compounds. The efficacy of the present liquefaction procedures is introduced.

The hydrogen transferring liquefaction of coal has been revealed applicable to the first step of two stage coal liquefaction (TSL) process.$^{1-5)}$ In previous papers,$^{6,7)}$ hydrogen transferring liquefaction using hydrogenated aromatics of adequate size such as hydrogenated pyrene as the solvent was found to be very effective in increasing the asphaltene and oil yields at low pressure (around 30 kg/cm^2). The yields were further improved by applying the short contact time conditions at higher temperatures$^{8,9)}$ than those proposed by Murata et al.,$^{10)}$ Neavel$^{11)}$ and Whitehurst.$^{12)}$

The present letter reports an excellent performance of fluoranthene hydrogenated using a Ni-Mo catalyst (principal component: 1,2,3,3a-tetrahydrofluoranthene (4HFL, Fig. 1)) to produce the oil and asphaltene from an Australian sub-bituminous coal (Wandoan) under a short contact time conditions at unusually high temperatures (510-560 °C) and a low pressure (maximum: 30 kg/cm^2 during the liquefaction). Some quantification of the products and the solvents after the liquefaction may provide information for the further evaluation of the present liquefaction.

The ultimate analysis of Wandoan coal is summarized in Table 1. The liquefaction solvent was hydrogenated fluoranthene, whose ultimate analysis is summarized in Table 2. It consisted of 4HFL, fluoranthene (FL) and other hydrogenated fluoranthenes carrying more than four hydrogens (PHFL), the last of which contained hexa- and per-hydrofluoranthenes and their isomers. Some of them were identified by a gas chromatography and NMR. The

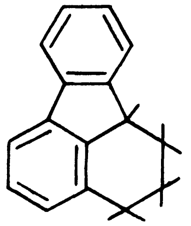

Fig. 1. 1,2,3,3a-Tetrahydrofluoranthere (4HFL).

hydrogenation of fluoranthene (50 g) was carried out in an autoclave (300 cm^3) using a commercial Ni-Mo catalyst (Sphericat) at 250 °C for 8 h under the initial hydrogen pressure of 135 kg/cm^2.

Table 1. Ultimate analyses (wt%) of Wandoan coal

C	H	N	S	O
76.6	6.3	1.1	0.4	15.6

Table 2. Some properties of liquefaction solvent (hydrogenated fluoranthene)

Ultimate analysis (wt%)			Composition (wt%)		
C	H	H/C	4HFL[a)]	PHFL[b)]	FL[c)]
93.3	6.7	0.86	91	6	3

a) 1,2,3,3a-Tetrahydrofluoranthene.

b) Hydrofluoranthenes carrying more than four hydrogens.

c) Fluoranthene.

The liquefaction was carried out in a tube bomb[4,5,12)] (volume: 25 cm^3). The ground 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 pressurized with nitrogen (5 kg/cm^2) at room temperature and immersed into a heated molten tin bath, while agitating axially. The liquefaction temperatures (510-560 °C) were attained within 1.5 min. After the prescribed time, the bomb was removed from the bath and rapidly immersed in cold water to quench the reaction. The gaseous products were volumetically measured by water replacement and analyzed by a gas chromatography. The other products including the solvent and its derivatives remaining in the bomb were scratched and washed out with benzene, and extracted first with benzene and then with hexane for benzene soluble material using a Soxhlet apparatus. The amounts of solvent insoluble materials were calculated on a dry, ash-free coal basis. The benzene insoluble (BI), benzene soluble but hexane insoluble (BS-HI), hexane soluble (HS) and the remaining materials (difference between the initial and recovered sample weights) were defined as preasphaltene, asphaltene, oil and gas, respectively. The solvent and its derivatives after the liquefaction were assumed to be included in the HS yield. Thus, the oil yield was calculated according to the following equation:

$$\text{oil yield} = (\text{HS} - \text{solvent charged})/(\text{initial coal (daf)}) \times 100 \text{ (wt\%)}$$

The composition of solvent after the liquefaction was measured by gas chromatograpy with diphenyl as an internal standard. The gas yield included the loss in the experiment. Gaseous products which were recovered for analysis from the bomb after the liquefaction were carbon monoxide, carbon dioxide, water, hydrogen sulfide and hydrocarbon. Other products were not intended to be analyzed in the present study.

The product distributions of gas, oil, asphaltene, and preasphaltene are illustrated in Fig. 2, where the contact times were variable according to the reaction temperature. 4HFL was a very efficient solvent to liquefy the coal in the temperature range of 510-560 °C. At 510 °C, it produced 38 wt% of oil and 30 wt% of asphaltene with as low as 15 wt% of preasphaltene at the contact time of 1.0 min. No THF insoluble fraction was observed. The gas yield was about 17 wt%. At 540 °C, a contact time of 1.0 min provided a similar product distribution with higher gas yield. A shorter contact time (no soaking time) at 540 °C gave a high oil yield of 48 wt% and a moderate asphaltene yield of 21 wt% with a smaller gas yield of 15 wt% although the yield of preasphaltene was somewhat higher (16 wt%). A further higher temperature of 560 °C, zero contact time provided a more favorable product distribution (oil: 54 wt%, asphaltene: 16 wt%) than the other conditions examined.

The compositions of gases analyzed are summarized in Table 3. The amount of the analyzed gaseous products after the liquefaction at 510 °C for 2.5 min was 13 wt% of the initial coal weight although the gas yield was 22 wt%, indicating that water, hydrogen sulfide, hydrocarbons (C_5+) and the loss were included. The major production of carbon dioxide, methane, ethane, propane and butane was recognized by their weight bases. The formation of the light paraffines was significantly suppressed by the shorter contact time. It should be noted that the formation of carbon dioxide was accelerated at higher temperature, suggesting that the oxygen content in the liquid products would be reduced.

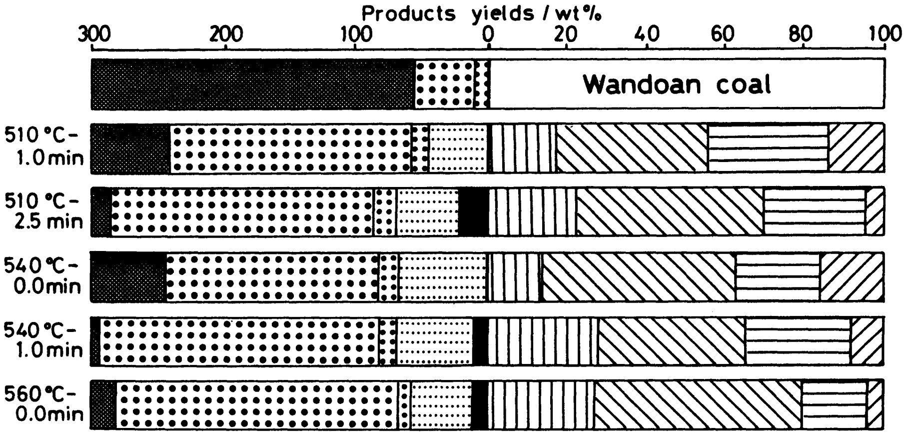

Fig. 2. Influence of liquefaction temperature and time on the reactivity of the solvent and the liquefaction products.

▩: 4HFL, ⁘: FL, ⁙: PHFL, ⬚: FL', ■: unknown, ▥: gas, ▧: oil, ▤: asphaltene, ▨:preasphaltene.

Table 3. The amount of gas[a)] produced in the liquefaction

	Liquefaction condition (°C-min)			
	510-2.5	540-0.0	540-1.0	560-0.0
CO	6	2	6	5
CO_2	9	14	23	16
CH_4	8	2	8	6
C_2H_6	21	5	21	14
C_2H_4	3	1	4	3
C_3H_8	28	5	24	18
C_3 b)	4	1	5	3
C_4H_{10}	15	2	12	8
C_4 b)	7	2	8	4
C_5H_{12}	7	1	8	3
C_5 b)	1	0	7	0
C_6H_{14}	7	1	6	2
C_6 b)	14	0	2	1

a) mg/g-coal.

b) The other hydrocarbons having respective number of carbon.

Gas chromatographic analysis of liquefaction solvent after the liquefaction indicated that 4HFL was converted principally into FL. The amount of remaining 4HFL was very variable according to the liquefaction conditions. At higher temperature, the decrease of 4HFL was more rapid. In contrast, the amount of PHFL did not change. In addition to 4HFL, FL and PHFL, some unidentified peaks were observed in gas chromatogram of oil fraction. These unidentified peaks are assumed to be HFL and FL derivatives. Among them, the peaks of which retention times were longer than that of FL were temporarily identified to be alkylated FL (FL' in Fig. 2). They were produced at rather early stage of liquefaction. Neverthless, it should be remined that four ring aromatic hydrocarbons recovered were almost balanced. The short contact time at unusually high temperature was found very effective to provide high oil and asphaltene yields by using selectively hydrogenated fluoranthene. Since the liquid product was fairly depolymerized and deoxygenated, it is expected to be a suitable feed for the second catalytic stage of the liquefaction.

The high temperature achieved by the rapid heating rate may overwhelmingly accelerate the selective degradation of coals and the hydrogen transfers from the solvent to the coal. The selective degradation breaks limited number of bonds in coal molecules into the desirable size (oil and asphaltene range). Efficient hydrogen transfer is essential for the stabilization of coal radicals to suppress their secondary reactions. Since any secondary consecutive reactions may be also suppressed under the short contact time conditions in spite of the high temperature, the primary reaction of coal degradation leads to rather selective formation of the oil and asphaltene. High dissolving ability of 4HFL or FL against coal derived liquid at the elevated temperature is also favorable to suppress the secondary condensation reaction. Such merits of liquefaction procedure under high temperature SCT conditions can be realized by using the solvent such as FL, of which skeleton is fairly stable at the present temperature range. The large content of hydrogen and suitable reactivity of 4HFL are also favorable for the liquefaction. Detail analyses of liquid products and the kinetic aspects of the liquefaction are now under progress.

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(Received June 7, 1984)