Hydrogen-Transferring Liquefaction of Two Different Rank Coals Employing Hydrogenated Anthracene Oil as a Donor Solvent

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The liquefaction of two coals, a low-volatile bituminous coal and a lignite, was studied using a hydrogenated anthracene oil as donor solvent. An inert atmosphere was employed to ensure that all the hydrogen incorporated by coal was supplied by hydrogenated compounds from the anthracene oil. Reaction products were separated according to their solubility and the following fractions were obtained: oils, asphaltenes, preasphaltenes, and an unreacted coal organic matter. The amount of hydrogenated compounds in the oil was related to the kinetics of coal solubilization. It compares favorably with the calculated profile of hydroaromatics assuming that only the first hydrogenation derivatives participate in hydrogen donation. An activation energy of about 13 000 K (E/R) was obtained for both coals. For the bituminous coal, 41% of the organic matter was not reactive, whereas for the lignite, the amount of unreactive organic matter was only 26%.

Introduction

At a temperature of above 650 K, coal produces a wide range of pyrolytically generated molecular fragments which, in the absence of a source of hydrogen, undergo reactions leading to a preponderance of gas and char. The stabilization of these coal fragments takes place with hydrogen obtained from three main sources: directly from the gas phase, by chemical rearomatization of hydroaromatic parts of the coal (hydrogen shuttling), or from hydrogenated solvents (hydrogen donation). In this conventional view of a direct liquefaction process, the solvent merely stabilizes the thermally generated radicals without playing any role in promoting bond cleavage. Several researchers have shown that the kinetics of coal conversion is influenced by the amount of hydrogen donor compounds contained in the solvent and have suggested the participation of hydrogenated light molecules in bond scission (Honda and Yamada, 1974; Allen and Gavallas, 1984; McMillen et al., 1987a). A molecular model involving this mechanism has been proposed by McMillen et al. (1987b).

In a donor solvent liquefaction process the concentration of hydrogen donor compounds must be carefully controlled. These molecules must provide enough hydrogen to avoid recondensation of thermally produced radicals and retrogressive reactions leading back to insoluble material. However, an excess has a detrimental effect, increasing gas production and decreasing oil yield. Moreover it has been shown that when hydrogenated substances are in excess, they can react, to give back the aromatic molecule and a naphthenic compound (Mochida and Takeshita, 1980). Both naphthenic and perhydroaromatic compounds exhibit a low donor ability, and therefore, their formation must be avoided.

Extensive work has been performed on coal liquefaction with anthracene oil (Gürüz et al., 1992; Berkowitz et al., 1988; Fabregat et al., 1987) and hydrogenated anthracene oil (Cronauer et al., 1987; Davies et al., 1977; Chiba et al., 1987). The results show that the extraction efficiency of hydrogenated anthracene oil is much greater than that of the fraction prior to treatment for any cut throughout the boiling range. This is clearly due to the presence of a fairly high concentration of polynuclear hydroaromatics. The aim of this work is to determine the effect of the degree of hydrogenation of an anthracene oil on the liquefaction behavior of two different rank coals. The evolution of the solvent composition was related to the kinetics of solubilization. Special attention has been paid to the differences in depletion of hydroaromatic compounds as a function of liquefaction conditions.

Experimental Section

Materials. A light fraction of the anthracene oil was supplied by Industrial Química del Nalón (NalonChem, Spain). The raw material (90% recovered between 215 and 400 °C) was hydrogenated over a sulfided nickel–molybdenum catalyst (BASF, M8-24) to obtain two fractions with a different hydroaromatic compound content. Hydrogenation conditions were temperature 340 °C, hydrogen pressure 100 kg/cm², and reaction time 1 h for oil no. 1 and 5 h for oil no. 2. Major components of the hydrogenated solvents are listed in Table I. Details on the analysis are given elsewhere (Rosal et al., 1992). Fraction

Table I. Composition of the Hydrogenated Fractions of Anthracene Oil

component	oil no. 1 (wt %)	oil no. 2 (wt %)
2a,3,4,5-tetrahydroacenaphthene	0.19	1.30
acenaphthene	5.60	4.62
dibenzofuran	3.06	3.02
fluorene	4.57	4.75
9,10-dihydroanthracene	4.25	2.56
9,10-dihydrophenanthrene	0.87	3.32
1,2,3,4-tetrahydroanthracene	1.01	2.76
1,2,3,4-tetrahydrophenanthrene	0.70	1.16
phenanthrene	17.1	14.6
anthracene	0.85	0.66
carbazole	2.79	3.22
1,2,3,10b-tetrahydrofluoranthene	1.68	4.74
4,5-dihydropyrene	0.81	1.50
fluoranthene	8.40	5.12
pyrene	4.99	4.40

Table II. Properties of the Coals Used

	Meirama	True Energy, Olga
moisture (as received)	57.4	7.8
ash[a]	8.3	6.0
volatile matter[a]	51.1	19.6
fixed carbon[a]	40.6	74.4
sulfur content[a]	1.3	0.6

[a] Weight percent of dry coal.

no. 2 shows a higher hydrogen content in all hydroaromatic and naphthenic compounds except 9,10-dihydroanthracene because it hydrogenates to 1,2,3,4-tetrahydroanthracene.

Two different coals were used: a low-volatile bituminous coal (True Energy, Olga) and a lignite (Meirama, La Coruña). Some properties of these coals are listed in Table II. Prior to use, the coal was crushed and screened up to three different particle sizes (0.030–0.100, 0.100–0.400, and 0.400–1.500 mm) and dried at 110 °C during the time necessary to get constant weight. Particle fractionation was performed so that mean diameters and interval widths follow a logarithmic sequence.

Apparatus and Experimental Procedure. All liquefaction experiments were conducted in a 15-cm³ batch tubing bomb reactor consisting of a 316 stainless steel Swagelok Tee ($^1/_4$ in.). The reactor was shaken vertically at 600 cycles/min and with an oscillation amplitude of 25 mm. The shaking device was held over a heated fluidized sand bath, allowing the reactor to be introduced once the desired temperature was reached. At the end of the reaction, the reactor was separated from the shaking device and cooled with water. Reaction conditions were measured by means of a pressure transducer and a thermocouple. A similar device have been described elsewhere (Neavel, 1976).

In all runs, 3 g of coal and 9 g of anthracene oil or hydrogenated anthracene oil were accurately weighed. Reactions were carried out under inert (N_2) atmosphere to ensure that all the hydrogen incorporated by coal was transferred from a given amount of hydrogenated compounds. The temperature varied from 375 to 425 °C, and reaction time was 20, 40, or 60 min combined with temperature according to a factorial design with duplicate runs. A total of 114 experiments were performed.

Analytical. After the reaction, gas was vented and analyzed. The rest of the products were separated by sequential extraction with toluene, tetrahydrofuran (THF), and n-hexane following the PERC method (Mima et al., 1976). Four fractions were obtained: oils (defined as n-hexane soluble material), asphaltenes (toluene soluble and n-hexane insoluble), preasphaltenes (THF soluble and toluene insoluble), and a THF insoluble material consisting of ash and insoluble organic matter. The insoluble organic matter content of these residues was calculated assuming the weight of ash to be invariable during liquefaction. The weight of all insoluble fractions was recorded after drying at 120 °C for 2 h.

Both anthracene oil and n-hexane soluble fractions were analyzed by gas chromatography in a Hewlett-Packard 5987A apparatus, equipped with a flame ionization detector and a capillary column (50 m, 0.25-mm i.d.) with OV-101 as stationary phase. Peak assignment was performed by GC–MS, and calibration factors were determined with pure compounds, whenever possible. In the case of substances for which no pure standards were available, the calibration factors were assumed to be the unity. The error introduced was low as all reactive components in hydrogenated anthracene oil are hydrocarbons whose response factors are close to 1.

Results and Discussion

The amount of organic matter (OM) and the yields of preasphaltenes (P), asphaltenes (A), and oils (O) were calculated on the basis of the initial weight of moisture- and ash-free (maf) coal as follows:

$$y_{OM} = (\text{THF ash-free insoluble})/(\text{initial maf coal}) \quad (1)$$

$$y_P = [(\text{toluene insoluble}) - (\text{THF ash-free insoluble})]/(\text{initial maf coal}) \quad (2)$$

$$y_A = [(n\text{-hexane insoluble}) - (\text{toluene insoluble})]/(\text{initial maf coal}) \quad (3)$$

$$y_O = (n\text{-hexane soluble})/(\text{initial maf coal}) \quad (4)$$

The oil fraction, which is essentially a spent anthracene oil, contains a substantial amount of volatile compounds such as indane, tetralin, or naphthalene, a part of which is inevitably lost during the processes of solvent evaporation. The yield of oil was calculated by difference, including thus the weight of gases formed during reaction, whose accurate determination was not possible (y_{O+G}). For the same reason, tetralin was not taken into account in determining the weight of hydroaromatic compounds in the oils from the extraction process. This did not lead to serious errors because the amount of tetralin in hydrogenated oil was low enough to justify ignoring its contribution.

In all liquefaction runs performed, coal conversion increased rapidly with time at the initial stage of the reaction, but after a period that depended upon the severity of the treatment, the rate of coal dissolution stabilized, though there was still unconverted coal organic matter. There are two main possible explanations for this behavior. It could be the consequence of the disappearance of reactive components in the coal, the rest being inert organic matter, or the result of reversible reactions that lead to insoluble material from the preasphaltene or asphaltene fractions. Accordingly, the initial solubilization reaction defines two sets of rival models for the liquefaction process:

$$OM \rightleftharpoons P \rightarrow \text{other compounds} \quad (5)$$

$$OM \rightarrow P \rightarrow \text{other compounds} \quad (6)$$

Nagaishi et al. (1988) suggested that a combination of both mechanisms might explain the rate of formation of a pyridine soluble fraction during the liquefaction of several different coals. Their model assumes that a part of the organic matter reacts to yield oil and gases as the final step of a sequence that involves consecutive degradation to preasphaltenes and asphaltenes. Another part of the organic matter is converted directly to oils and gases whereas

a certain residual amount of organic matter is not reactive. This combination is necessary to explain the production of oils during the early stages of the reaction, a fact recognized by a number of authors (Cronauer et al., 1987; Shalabi et al., 1979; Mohan and Silla, 1981; Shah et al., 1981).

In this work, a reaction scheme according to pathway 5 was tested and rejected because the reaction yielding insoluble organic matter from preasphaltenes did not seem to be affected by the temperature. As a consequence, the activation energy and the specific velocity for this reaction showed a high degree of uncertainty when fitted to an Arrhenius expression. It is clear that, by increasing the complexity of the series-parallel reaction network, the visual fitting of the data would be better, due to the larger number of parameters. Liebenberg and Potgieter (1973) pointed out that in such pathways some reactions are not consistent, as they exhibit no exponential dependence with temperature.

The classical (Weller et al., 1951) and simplest mechanism of progressive degradation to lighter compounds was used to relate the depletion of hydrogenated compounds of the oil to the evolution of the coal organic matter, preasphaltenes, and asphaltenes:

$$OM \rightarrow P \rightarrow A \rightarrow O \qquad (7)$$

Under the reaction conditions at which most runs were performed (absence of hydrogen in the gas phase), little oil is formed, the main products being the relatively heavier preasphaltenes and asphaltenes. The reactions leading to oils other than the one included in (7) could be ignored, especially considering that the yield of oil was obtained by difference and should not be taken into account in the regression analysis.

It has been stated (Whitehurst et al., 1980) that, in certain cases, the rate of coal conversion is not dependent on the initial particle size. Results are quite fragmentary, but a widely accepted explanation is that, at early stages of the reaction, coal undergoes rapid disintegration so that after a short period of time liquefaction behavior is similar for materials with a different granulometry. For higher rank coals and under low severity conditions, a certain increase in conversion was detected by decreasing the particle diameter (Gray and Shah, 1981). If no disintegration at all occurred, the rate of coal dissolution would be proportional to the external surface available and therefore, for a given mass, to the inverse of the mean diameter.

It has been found in this work that the rate of liquefaction of Olga coal depended on the initial particle size, whereas for Meirama lignite, the effect was not detected. This is in good agreement with the fact that lignite conversion was considerably higher than that of the bituminous coal for the same conditions and above 40% even in disadvantageous cases.

To state the mathematical model for reaction pathway 7, it was assumed that the rate of all the reactions was proportional to the amount of hydrogenated compounds relative to the initial weight of maf coal, namely y_H. It was also assumed that all the hydrogen from donor compounds is employed in solubilization reactions. This implies that hydrogen transfer reactions in the solvent are negligible under extraction conditions. The first column of Table III shows the result of thermal treatment in nitrogen of oil no. 2. A comparison with the values reported in Table I indicates that the loss of hydrogen due to rearrangements in the solvent was not significant. The rate of coal dissolution and preasphaltene and asphaltene degradation was reasonably well-fitted by first-order reaction laws with

Table III. Composition (wt %) of the Oils Obtained in Several Reactions

component	treatment			
	a	b	c	d
2a,3,4,5-tetrahydroacenaphthene	1.25	0.09	0.59	0.12
acenaphthene	4.65	5.50	5.28	5.72
dibenzofuran	3.14	3.13	3.08	3.19
fluorene	4.81	4.46	4.98	4.63
9,10-dihydroanthracene	2.12	0.13	0.54	0.20
9,10-dihydrophenanthrene	3.23	0.11	0.33	0.18
1,2,3,4-tetrahydroanthracene	2.83	0.18	0.84	0.16
1,2,3,4-tetrahydrophenanthrene	1.12	0.27	0.82	0.25
phenanthrene	15.2	17.4	17.5	17.6
anthracene	0.82	5.77	4.64	5.59
carbazole	3.15	2.84	3.19	3.36
1,2,3,10b-tetrahydrofluoranthene	4.35	0.20	1.24	0.31
4,5-dihydropyrene	1.43	0.08	0.50	0.12
fluoranthene	5.56	9.83	8.62	9.46
pyrene	4.52	5.79	5.46	5.81

[a] 40-min heating in the absence of coal at 400 °C. [b] From Meirama lignite treated at 425 °C with oil no. 1. [c] From Meirama lignite treated at 425 °C with oil no. 2. [d] From Olga low-volatile bituminous coal treated at 425 °C with oil no. 2.

regard to y_H. This explains the reactions from both Olga and Meirama coal. All combinations involving zero-order kinetics with regard to y_H resulted in a poorer fitting. This behavior reflected an active role of the hydrogenated molecules of the solvent in the liquefaction process as stated before.

All considerations mentioned above led to the following expressions for the kinetic model:

$$-r_{OM} = -dy_{OM}/dt = k_1[(y_{OM} - \zeta)^a/D_0^b]y_H \qquad (8)$$

$$r_P = dy_P/dt = k_1[(y_{OM} - \zeta)^a/D_0^b]y_H - k_2 y_P y_H \qquad (9)$$

$$r_A = dy_A/dt = k_2 y_P y_H - k_3 y_A y_H \qquad (10)$$

$$-r_H = -dy_H/dt =$$
$$c\{k_2 y_P y_H + k_3 y_A y_H + k_1[(y_{OM} - \zeta)^a/D_0^b]y_H\} \qquad (11)$$

In the case of lignite liquefaction $b = 0$.

The amount of hydroaromatic compounds necessary for the conversion of 1 g of coal, preasphaltenes, or asphaltenes was assumed to be the same for the three reactions. Its value, c, was considered a parameter for the model. As it is not clear which hydrogenated compounds participate in bond scission and radical stabilization reactions, the values of hydroaromatic concentration were not used in the fitting. Instead of that, the profile for y_H required for the model was compared with actual measurements of the mass of hydrogenated substances in the oil. The integration of eqs 8–11 was performed considering only experimental values for the initial concentration of hydroaromatics. It was found that better fittings were obtained when the initial concentration of hydroaromatics was the sum of the first hydrogenation derivatives: 2a,3,4,5-tetrahydroacenaphthene, 9,10-dihydroanthracene, 9,10-dihydrophenanthrene, 1,2,3,10b-tetrahydrofluoranthene, and 4,5-dihydropyrene.

Kinetic constants were considered to vary with temperature following an Arrhenius type expression. For a better convergence in the minimization procedure, the following reparameterization was adopted, where T_m is the average temperature of the experiments (673 K):

$$k_i = k_i' \exp\{(-E_i/R)[(1/T) - (1/T_m)]\} \qquad (12)$$

Parameter estimation was based on the minimization of the determinant (Hunter, 1967):

$$\mathbf{B} = \det(b_{ij}) = \det[\sum_{}^{n} (y_{ik} - \beta_{ik})(y_{ij} - \beta_{ij})] \qquad (13)$$

Table IV. Parameter Estimates for Coal Conversion Reactions

parameter (eqs 8–11)	confidence intervals ($\alpha = 0.90$)	
	lower limit	upper limit
Olga Low-Volatile Bituminous Coal		
$k_1'{}^a$ (min^{-1}) 3.15 × 10^{-2}	2.89 × 10^{-2}	3.51 × 10^{-2}
$k_2'{}^a$ (min^{-1}) 5.41 × 10^{-2}	3.85 × 10^{-2}	9.63 × 10^{-2}
$k_3'{}^a$ (min^{-1}) 1.44 × 10^{-1}	1.12 × 10^{-1}	1.69 × 10^{-1}
E_1/R (K) 1.31 × 10^{4}	1.12 × 10^{4}	1.50 × 10^{4}
E_2/R (K) 2.41 × 10^{4}	1.80 × 10^{4}	3.18 × 10^{4}
E_3/R (K) 2.07 × 10^{4}	1.62 × 10^{4}	2.45 × 10^{4}
a^b 3.55 × 10^{-1}	2.42 × 10^{-1}	4.54 × 10^{-1}
b^b 3.42 × 10^{-1}	3.10 × 10^{-1}	3.86 × 10^{-1}
c^b 5.29 × 10^{-1}	4.91 × 10^{-1}	5.71 × 10^{-1}
ξ^b 4.09 × 10^{-1}	2.79 × 10^{-1}	4.92 × 10^{-1}
Meirama Lignite		
$k_1'{}^a$ (min^{-1}) 1.32 × 10^{-1}	1.17 × 10^{-1}	1.53 × 10^{-1}
$k_2'{}^a$ (min^{-1}) 6.82 × 10^{-1}	4.35 × 10^{-1}	8.32 × 10^{-1}
$k_3'{}^a$ (min^{-1}) 4.25 × 10^{-3}	2.34 × 10^{-3}	7.66 × 10^{-3}
E_1/R (K) 1.40 × 10^{4}	1.10 × 10^{4}	1.56 × 10^{4}
E_2/R (K) 1.49 × 10^{4}	1.26 × 10^{4}	1.68 × 10^{4}
E_3/R (K) 1.51 × 10^{4}	1.10 × 10^{4}	1.87 × 10^{4}
a^b 8.69 × 10^{-1}	6.43 × 10^{-1}	9.95 × 10^{-1}
c^b 1.94 × 10^{-1}	1.76 × 10^{-1}	2.10 × 10^{-1}
ξ^b 2.61 × 10^{-1}	2.32 × 10^{-1}	2.98 × 10^{-1}

^{a} From eq 8. ^{b} Dimensionless parameters.

where n is the number of experiments, y_{ik} is the kth response for the ith experiment, and β_{ik} is the kth response for the ith calculated value. Differential equations were integrated via a fourth-order Runge–Kutta algorithm, and minimization of the objective determinant, **B**, was performed by Powell's method. Confidence intervals were derived from the α-probability level confidence surface given by

$$\det(b_{ij}) = \det(b_{ij})_{\min}[\exp\chi^2(s-1,\alpha)/n] \qquad (14)$$

s being the number of observed responses, in this case three (y_{OM}, y_P, and y_A). In Table IV all parameter estimates are listed with the limits of their 90% confidence interval calculated from eq 14.

The apparent order of reaction of the organic matter was 0.38 in the case of Olga coal and 0.87 for the lignite, indicating greater reactivity in the latter. Moreover, the amount of hydroaromatic substances required for the solubilization of 1 g of coal (or coal-derived products) was 2 times more for the bituminous coal, as could be expected considering its more aromatic structure.

Figure 1 shows the evolution of the yield of each fraction at a temperature of 375 °C (Figure 1a) and 425 °C (Figure 1b) for the liquefaction of Olga coal. In Figure 2 the corresponding values for the lignite reaction are presented. The curves have been obtained from eqs 8–11. Particle diameter was in the interval 0.030–0.100 mm and the hydrogenated anthracene oil no. 2 was used. The dotted line indicates the profile of hydrogenated substances required by the model, assuming that 1,2,3,4-tetrahydroanthracene and 1,2,3,4-tetrahydrophenanthrene do not participate in the reaction. The experimental data are not shown in these figures as they were not employed in the fitting.

The activation energies obtained for the solubilization of the bituminous coal are in the range of those found by other groups. Leonard and Silla (1983) indicated an activation energy of about 10 000 K for all the steps in the liquefaction pathway of Kentucky No. 6 and Illinois No. 6 coals, the reaction conditions being similar to those of this work. Mohan and Silla (1981) reported activation energies from 8000 to 15 000 for the donor solvent liquefaction of an Illinois No. 6 coal. Cronauer, Shah, and Ruberto (1987) indicated lower values. For the reaction of coal organic matter to yield preasphaltenes they reported 7000 K, for preasphaltenes to yield asphaltenes 6500
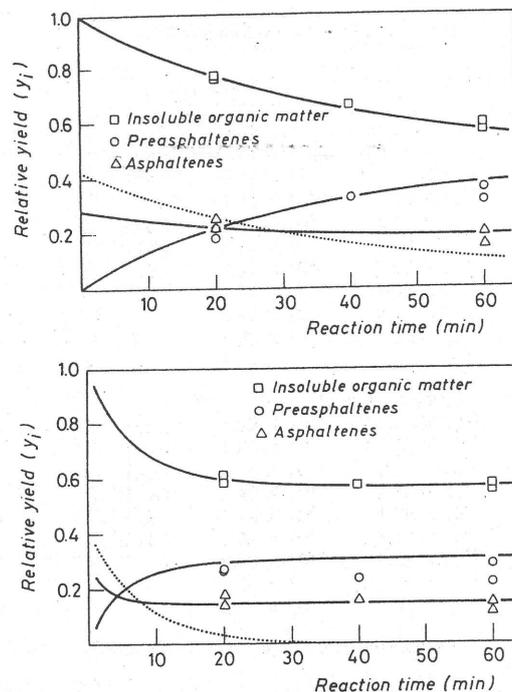
Figure 1. Conversion of Olga coal and evolution of the relative amount (y_i) of its reaction products. (a, top) 375 °C; (b, bottom) 425 °C.
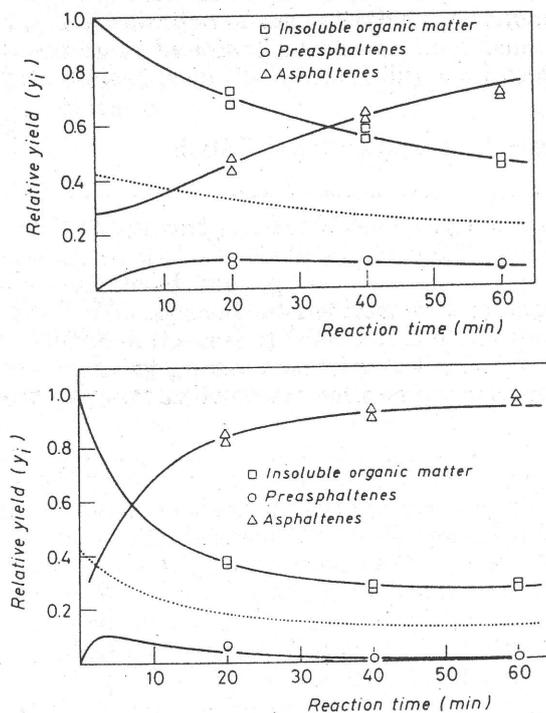
Figure 2. Conversion of Meirama coal and evolution of the relative amount (y_i) of its reaction products. (a, top) 375 °C; (b, bottom) 425 °C.

K, and for the reaction of asphaltenes to product oils 8100 K. The activation energies for the subsequent reaction steps are higher than those reported before. A possible explanation could be a certain contribution of reverse reaction yielding back heavier material once the hydrogen was consumed. In the case of lignite, all three activation energies are similar, nearly 15 000 K, but comparison with data from other authors is difficult because not much work has been performed on kinetics of lignite liquefaction in donor solvents. For the first step of the reaction, although the activation energy was almost the same in both cases, there was 41% of organic matter in Olga coal that could
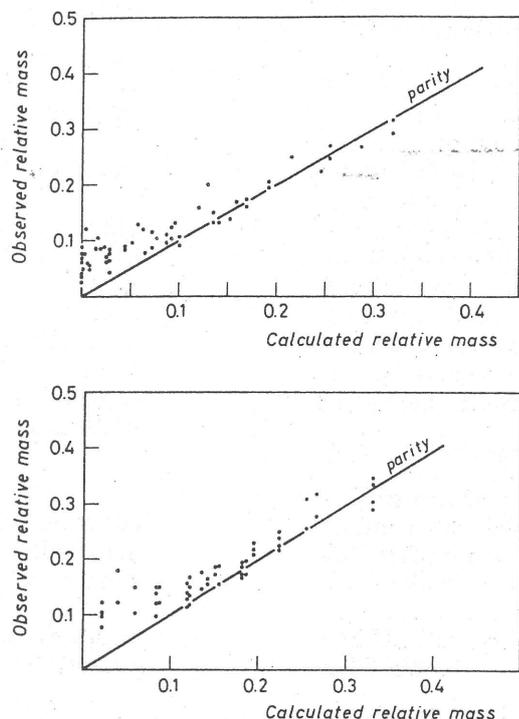
Figure 3. Amount of hydroaromatics (y_H) required by the liquefaction model for Olga low-volatile bituminous coal compared with the actual relative mass of hydrogenation products excluding tetrahydroanthracene and tetrahydrophenanthrene. (a, top) Olga bituminous coal; (b, bottom) Meirama lignite.

not be dissolved, whereas in the case of lignite, this amount was only 26%.

Table III shows some representative analyses of the oils, which are essentially a depleted anthracene oil. The data are consistent with the evolution expected from eq 11. In the case of Meirama coal liquefaction at 425 °C with oil no. 2, a significant amount of hydrogenated compounds still undergo no reaction, whereas for Olga bituminous coal the oils contain only a very small amount of hydroaromatics. This is in good agreement with the results presented in Figures 1b and 2b. Figure 3 compares the profile for hydroaromatics required by the model with actual measurements of the concentration of hydrogenated substances. Only the first hydrogenation derivatives were considered for these figures, as mentioned before. Good agreement was observed except in the area of low concentration of hydroaromatics. The difference reflects a concentration of hydrogenated compounds higher than expected. This can be attributed to the reaction of tetrahydro derivatives of anthracene and phenanthrene yielding back dihydroanthracene and dihydrophenanthrene.

Conclusions

The yields of unreacted organic matter, preasphaltenes, and asphaltenes from the liquefaction of the two coals fitted satisfactorily to a simple kinetic expression of progressive degradation. Good agreement was obtained, assuming that a part of the coal was inert under the reaction conditions at which extraction was performed. This amount was 41% for the bituminous coal (Olga) and 26% for the lignite (Meirama).

Given that the reaction rate of all liquefaction reactions is proportional to the mass of hydrogenated substances in the solvent, the calculated profile of hydroaromatics is in good agreement with their actual concentration measurements, when only the first hydrogenation derivatives are taken into account.

The activation energy (E/R) for the process of coal dissolution was similar in both coals (13 000 K). However, for the degradation of preasphaltenes and asphaltenes the values are greater for the bituminous coal (about 20 000 K) than for the lignite (15 000 K). A certain contribution of retrograde reactions might explain the difference. The data reported in this work do not rule out this possibility.

In the case of Meirama lignite, the specific reaction rate for the degradation of asphaltenes was 2 orders of magnitude lower than those of the other steps of the reaction pathway. This resulted in a relative accumulation of asphaltenes during the first stage of the reaction. In the case of Olga coal, the rate of reaction of asphaltenes was larger than that of formation so that they did not accumulate.

Acknowledgment

Nomenclature

$\mathbf{B}$ = determinant defined in eq 13
a, b = fitting parameters, dimensionless
b_{ij} = element of $\mathbf{B}$, dimensionless
C = fitting parameter, dimensionless
D_0 = initial mean diameter of coal particles, mm
E_i = activation energy, J/mol
k_i = reaction rate coefficient, dimensionless
k_i' = reaction rate coefficient defined by eq 12, dimensionless
n = number of experiments
$-r_i$ = rate of disappearance of substance i, s^{-1}
r_i = rate of formation of substance i, s^{-1}
R = gas constant, J/(mol K)
T = absolute temperature, K
T_m = mean temperature of all experiments, K
y_i = yield relative to a maf coal basis as defined in eqs 8–11, dimensionless
y_{ij} = jth response for the ith experiment

Greek Symbols

α = probability level
β_{ik} = kth response for the ith calculated value
ξ = unit percent of inert organic matter in the coal, dimensionless
χ^2 = chi-squared distribution

Subscripts

A = asphaltenes
O = oils
OM = coal organic matter
P = preasphaltenes

Literature Cited

Allen, D. T.; Gavalas, G. R. Reactions of methylene and ether bridges. *Fuel* **1984**, *63*, 586–592.

Berkowitz, N.; Calderon, J.; Liron, A. Some observations respecting reactions paths in coal liquefaction 2. Reactions of a coal/anthracene oil slurry. *Fuel* **1988**, *67*, 1017–1019.

Chiba, K.; Tagaya, H.; Kobayashi, T.; Shibuya, Y. Solvent extract liquefaction of coal with fractionated anthracene oil and recycle solvent. *Ind. Eng. Chem. Res.* **1987**, *26*, 1329–1335.

Cronauer, D. C.; Shah, Y. T.; Ruberto, R. G. Kinetics of thermal liquefaction of Belle Ayr subbituminous coal. *Ind. Eng. Chem. Process Des. Dev.* **1987**, *17*, 281–287.

Davies, G. O.; Derbyshire, F. J.; Price, R. An investigation on coal solubility in anthracene oils. *J. Inst. Fuel* **1977**, *56*, 121–126.

Fabregat, A.; Giralt, J.; Giralt, F. Solvolysis of a catalan lignite with solvents of low hydrogen donor capacity. *Fuel* 1987, *66*, 835–839.

Gray, J. A.; Shah, Y. T. Structure and Properties of Coal and the Mechanism of Coal Liquefaction. In *Reaction Engineering in Direct Coal Liquefaction*; Shah, Y. T., Ed.; Addison-Wesley: London, 1981; Chapter 2.

Gürüz, K.; Kranich, W. L.; Weiss, A. H.; Dyke, C.; Rambelli, P.; Foutsitzis, A. Catalytic hydroliquefaction of North Dakota lignite. Part I: effects of process variables on product distribution. *Fuel Process. Technol.* 1982, *6*, 183–201.

Honda, H.; Yamada, Y. Ashfree liquid fuels. *J. Jpn. Pet. Inst.* 1974, *17*, 853–864.

Hunter, W. G. Estimation of unknown constants from multiresponse data. *Ind. Eng. Chem. Fundam.* 1967, *6*, 461–463.

Leonard, E.; Silla, H. Kinetics of donor solvent liquefaction of Kentucky No. 6 coal. *Ind. Eng. Chem. Process Des. Dev.* 1983, *22*, 445–452.

Liebenberg, B. J.; Potgieter, H. G. Uncatalyzed hydrogenation of coal. *Fuel* 1973, *52*, 130–133.

McMillen, D. F.; Malhotra, R.; Chang, S. J.; Hum, G. P. Hydrogen-transfer-promoted bond scission initiated by coal fragments. *Energy Fuels* 1987a, *1*, 193–198.

McMillen, D. F.; Malhotra, R.; Chang, S. J.; Nigenda, S. E.; Ogier, W. C.; Fleming, R. H. Mechanisms of hydrogen transfer and bond scission of strongly bonded coal structures in donor-solvent systems. *Fuel* 1987b, *66*, 1611–1620.

Mima, M. J.; Schulz, H.; McKinstry, W. E. "Method for the determination of benzene insolubles, asphaltenes and oils in coal derived oil liquids"; U.S. ERDA PERC/RI 76/6, 1976.

Mochida, I.; Takeshita, K. *Coal Liquefaction under Atmospheric Pressure*; Whitehurst, D. D., Ed.; Advances in Chemistry 139; American Chemical Society: Washington, DC, 1980; pp 259–271.

Mohan, G.; Silla, H. Kinetics of donor-solvent liquefaction of bitu-minous coals in nonisothermal conditions. *Ind. Eng. Chem. Process Des. Dev.* 1981, *20*, 349–358.

Nagaishi, H.; Moritomi, H.; Samada, Y.; Chiba, T. Evaluation of coal reactivity for liquefaction based on kinetic characteristics. *Energy Fuels* 1982, *2*, 522–528.

Neavel, R. C. Liquefaction of coal in hydrogen-donor and non-donor vehicles. *Fuel* 1976, *55*, 237–242.

Rosal, R.; Díez, F. V.; Sastre, H. Estimation of the concentration of hydroaromatic compounds in a hydrogenated anthracene oil. *Fuel* 1992, *71*, 761–765.

Shah, Y. T.; Krishnamurthy, S.; Ruberto, R. G. Kinetic models for donor solvent coal liquefaction. In *Reaction Engineering in Direct Coal Liquefaction*; Shah, Y. T., Ed.; Addison-Wesley: London, 1981; Chapter 4.

Shalabi, M. A.; Baldwin, R. M.; Bain, R. L.; Gary, J. H.; Golden, J. O. Noncatalytic coal liquefaction in a donor solvent. Rate of formation of oil, asphaltenes and preasphaltenes. *Ind. Eng. Chem. Process Des. Dev.* 1979, *18*, 474–479.

Weller, S.; Pelipetz, M. G.; Friedman, S. Kinetics of coal hydrogenation. Conversion of asphalt. *Ind. Eng. Chem.* 1951, *43*, 1572–1575.

Whitehurst, D. D.; Mitchell, T. O.; Farcasiu, M. *Coal Liquefaction: the Chemistry and Technology of Thermal Processes*; Academic Press: New York, 1980; pp 108–112.