A Comparison of Anthracene and Phenanthrene in Coal Liquefaction

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INTRODUCTION

A comparison of anthracene and phenanthrene was made by liquefying either Wyodak coal or Kentucky 9/14 coal in the presence of either hydrogen or nitrogen. 1-methylnaphthalene (1-MN) was employed as a physical solvent. Reaction products are separated into a tetrahydrofuran (THF)-soluble fraction, a preasphaltene fraction, an asphaltene fraction and an oil-plus-gas-plus water fraction.

EXPERIMENTS

A series of reactions were conducted in a 25 cc, 316 stainless steel micro-reactor to liquefy either Wyodak coal or Kentucky 9/14 coal under the various operation conditions. Another series of reactions were performed in a 50 cc flask to dissolve either Wyodak coal or Kentucky 9/14 coal with either neat aromatic compounds such as anthracene and phenanthrene, or mixtures of neat aromatics and their dihydroaromatics under the atmospheric pressure. The reaction product is separated by using a pressure filtration procedure. Conversions of aromatics into hydroaromatics are analyzed by using a gas chromatograph. Coal conversions are calculated on a moisture-and-ash-free-coal basis.

DISCUSSION

Both anthracene and phenanthrene are converted more into their hydroderivatives in the presence of Kentucky 9/14 coal than in the presence of Wyodak coal. This fact may suggest that minerals in Kentucky 9/14 coal act as more active catalysts than minerals in Wyodak coal in hydrogenating aromatics such as anthracene and phenanthrene in the presence of molecular hydrogen (Table 1).

Wyodak coal is converted more into an oil-water-gas fraction in the presence of anthracene than in the presence of phenanthrene, while producing the same amount of preasphaltene plus asphaltene in the presence of either anthracene or phenanthrene. Therefore, anthracene and its derivatives are to some degree better solvents than phenanthrene and its derivatives in liquefying Wyodak coal (Table 1).

The conversion of Kentucky 9/14 coal is influenced more by hydrogen pressure than the conversion of Wyodak coal in the presence of either anthracene or phenanthrene (Table 1). This fact suggests that molecular hydrogen may play a more dominant role than hydroaromatics in liquefying Kentucky 9/14 coal or that the minerals in Kentucky 9/14 coal are actively hydrogenating the aromatic solvent. The analysis of the oil fraction suggests the latter.

The conversion of both anthracene and phenanthrene to dihydroderatives increases as the initial hydrogen pressure increases. The conversion of Wyodak coal increases from 44 % to 58 % and the hydrogenation of anthracene increases from 6 % to 17 % in the presence of anthracene, whereas the conversion of Wyodak coal increases from 40 % to 48 % and the hydrogenation of phenanthrene does not increase by increasing the initial hydrogen pressure from 500 psig to 1100 psig (Table 1). These facts show that anthracene is readily hydrogenated and its derivatives are better hydrogen donors or shuttlers than phenanthrene and its derivatives in liquefying Wyodak coal.

The conversion of Ky 9/14 coal is 42.4 % and the hydrogenation of anthracene is 4.4 % in the presence of nitrogen (Table 1). The conversion of Ky 9/14 coal is 38 % and no hydrogenation of phenanthrene is observed in the presence of nitrogen. This fact demonstrates that anthracene is more active than phenanthrene

in liquefying Ky 9/14 coal in the absence of hydrogen, by extracting hydrogen from coal to be converted into dihydroanthracene and then breaking down coal structure.

Conversions of Ky 9/14 coal and anthracene to hydroanthracenes are 72.4 % and 17.6 % respectively in the presence of 500 psig hydrogen, while conversions of Ky 9/14 coal and phenanthrene are 75.3 % and 0 % respectively in the presence of 500 psig hydrogen, in spite of the fact that more hydrogen donor is available in the former case (Table 1). Preasphaltene-plus-asphaltene fraction is 53 % in the presence of anthracene and 500 psig hydrogen, whereas preasphaltene-plus-asphaltene fraction is 46 % in the presence of phenanthrene and 500 psig hydrogen. This fact may indicate that either solubility of Ky 9/14 coal in phenanthrene and its derivatives is inherently better than in anthracene and its derivatives, or that dihydroanthracene may be undergoing extensive retrogressive reaction with coal or itself, producing more preasphaltene-plus-asphaltene fraction. This evidence may also suggest that the transfer rate of labile hydrogen from coal to anthracene is much faster than that of molecular hydrogen from the gaseous phase to liquid anthracene during the very early reaction stage due to low hydrogen pressure.

A series of runs were carried out to understand solvent quality on conversion of Wyodak coal in the presence of hydrogen, as shown in Run 3, Run 4 and Run 44 in Table 2. Conversions of coal in the presence of anthracene and its derivative is considerably higher than in the presence of either phenanthrene or 1-MN, where conversion of anthracene is 22.2 % as shown in Run 3. This indicates that a good hydrogen donor solvent may play a more dominant role than molecular hydrogen in liquefying Wyodak coal and that the solvent power of 1-MN is better than that of phenanthrene in the presence of hydrogen for the liquefaction of Wyodak coal.

Another series of runs were conducted to determine solvent quality on the liquefaction of Wyodak coal in the presence of nitrogen as shown in Run 45, Run 48 and Run 49 in Table 2. Conversion of Wyodak coal is higher in the presence of phenanthrene than in the presence of anthracene in the absence of hydrogen. This fact may demonstrate that phenanthrene is a better physical solvent than anthracene in the absence of hydrogen in the liquefaction of Wyodak coal, suggesting that it is the ease of hydrogenation of anthracene and the excellent H-donor behavior of its hydroderivatives that makes anthracene a good solvent in the presence of hydrogen.

Conversion of coal in the presence of anthracene is higher than that of phenanthrene at the reaction temperature of both 350 °C and 425 °C. Phenanthrene is not hydrogenated at 350 °C or 425 °C, but hydrogenations of anthracene are 2.6 % at 350 °C and 4.4 % at 425 °C (Table 2). The difference in coal conversion between anthracene and phenanthrene is less significant at lower reaction temperature. This fact suggests that less labile hydrogen from coal to anthracene is transferred at the lower temperature and the inherent solvent power of the vehicle used is important.

A series of experiments were carried out by liquefying coal with neat aromatic compounds or mixtures of neat aromatic compounds and their hydroderivatives at their boiling temperature under the atmospheric environment (Table 3). Conversion of Wyodak coal in the presence of phenanthrene is higher than in the presence of anthracene, where no hydrogenation of both anthracene and phenanthrene was observed. This fact shows that the solubility of Wyodak coal in phenanthrene is higher than in anthracene under the atmospheric environment and in the absence of other solvents.

Conversion of Ky 9/14 in the presence of phenanthrene is higher than in the presence of anthracene, where hydrogenation of both phenanthrene and anthracene was not observed as shown in Run 19 and Run 22 in Table 3. On the other hand, the conversion of Ky 9/14 coal in the presence of phenanthrene is lower than in the presence of anthrance at 350 °C under 2000 psig nitrogen pressure, as shown in Run 40 and Run 41 in Table 2. This fact suggests that either labile hydrogen does not react with anthracene or escapes into the atmosphere before reacting with anthracene due to the low pressure, whereas labile hydrogen reacts with

anthracene at high pressure. The conversion of Ky 9/14 coal in the presence of a mixture of phenanthrene and dihydrophenanthrene is higher than in the presence of a mixture of anthracene and dihydroanthracene, and the conversion of dihydrophenanthrene is higher than that of dihydroanthracene, as shown in Run 23 and Run 24 in Table 3. On the other hand, the effect of dihydroanthracene on the increment of coal conversion, as shown in Run 19 and Run 23 in Table 3 is higher than the effect of dihydrophenanthrene on the increment of coal conversion, as shown in Run 22 and Run 24 in Table 3. This fact again suggests that dihydroanthracene is a better hydrogen donor solvent than dihydrophenanthrene. Neat anthracene is a poorer solvent than neat phenanthrene (about 1/3) for both Wyodak coal and Ky 9/14 coal at 330 °C. But when 20 % of the dihydrocompound is present, the anthracene compound mixture is a better solvent than the phenanthrene mixture. With Ky 9/14 coal, the phenanthrene is the best solvent, neat and in the presence of the dihydrocompound.

The disappearance of the dihydrocompounds is in agreement with the liquefaction of coal. In the presence of Ky 9/14 coal, dihydrophenanthrene is lost most rapidly, whereas in the presence of Wyodak coal, dihydroanthracene is lost most rapidly (Table 3).

A series of reactions were performed in the presence of neat aromatic compounds and 1100 psig nitrogen (initial) as shown in Table 4. The conversions of Ky 9/14 coal are 32 % in the presence of anthracene and 51 % in the presence of phenanthrene whereas the conversions of Wyodak coal are 33 % in the presence of anthracene and 43 % in the presence of phenanthrene. These data also show that neat phenanthrene is a better physical solvent than neat anthracene in liquefying both Wyodak coal and Ky 9/14 coal in the absence of hydrogen.

Another series of runs with Ky 9/14 coal were compared in the absence of hydrogen in terms of initial nitrogen pressure, as shown in Table 1. The conversions of Ky 9/14 coal are 42 % in terms of the THF soluble fraction and 29 % in terms of the preasphaltene-plus-asphaltene fraction at the 1100 psig initial nitrogen pressure, whereas the conversions of Ky 9/14 coal are 39 % and 24 % respectively at the zero psig initial nitrogen. The closeness of the values for dihydroanthracene formed suggests that the conversion and product distribution would also be similar. The only firm conclusion is that pressure helps total liquefaction and seems to hint oil-water-gas formation. Anthracene is a better solvent than phenanthrene under these conditions.

CONCLUSIONS

The relative behavior of phenanthrene and anthracene depends on whether the solvents are compared neat or in the presence of other solvents, upon the gaseous environment, and upon the coal. When anthracene is the better solvent, conditions appear to favor the formation of dihydroanthracene which is an excellent hydrogen donor. When phenanthrene is the better solvent, the inherently better solvent power of phenanthrene itself for that coal appears to be the dominant factor. The minerals in the coal, and possibly the coal itself, are also important in determining the preferred solvent.

REFERENCES

1. Appell, H. R. "The Effect of Solvent Composition on Product Distribution." Unpublished, Pittsburgh Energy Technology Center.

2. Curtis, C. W., J. A. Guin, and K. C. Kwon. "Coal and Solvolysis in a Series of Model Compound System." Presented to the AICHE Annual Meeting, November, 1982, Los Angeles.

3. Curtis, C. W., J. A. Givin, K. C. Kwon, and N. L. Smith. "Selectivity of Coal Minerals Using Cyclohexane as a Probe Reactant." Fuel (In Press), London, England.

4. Derhyshire, F. J. and D. D. Whitehurst. "The Influence of Polyaromatic Solvent Components on Coal Liquefaction." Proceedings on the Fifth Annual EPRI Contractor's Conference on Coal Liquefaction", p. 9-1, 1980.

5. Gangwar, T. E. and H. Prasad. "HYdrogen-Trasfer Catalytic Activity of Minerals Common to Coal." Fuel, 58, p. 577, London, England, 1979.

6. Garg, D. and E. N. Givens. "Pyrite Catalysis in Coal Liquefaction." Ind. Eng. Chem. Process Design and Development, 21, p. 113, 1982.

7. Guin, J. A., C. W. Curtis, and K. C. Kwon. "Pyrite Catalyzed Coal Liquefaction Using Quinoline/Tetrahydroquinoline as a H-Donor System." Fuel, In Press, London, England, 1983.

8. Jackson, W. R., F. P. Larkins, M. Marshall, D. Rash, and N. White. "Hydrogenation of Brown Coal. 1. The Effects of Additional Quantities of the Inorganic Constituents." Fuel, 58, p. 281, London, England, 1979.

9. Lytle, J. M., R. E. Wood, and W. H. Wiser. "Kinetics of Coal Liquefaction: Effect of Catalyst, H_2 Concentration and Coal Type." Fuel, 59, p. 471, London, England, 1980.

10. Mochida, I., A. TaKarabe, and K. Takeshita. "Solvolytic Liquefaction of Coals with a Series of Solvents." Fuel, 58, p. 17, London, England, 1979.

11. Neavel, R. C. "Exxon Donor Solvent Liquefaction Process." Phil. Trans. Royal Society, London, A 300, p. 141, London, England, 1981.

12. Padrick, T. D., A. W. Lynch and H. P. Stephens. "Effect of Solvent on the Dissolution of Wyodak Coal." Proceedings of the Department of Energy Integrated Two-Stage Liquefaction Meetings, p. 6-2, Alberque, New Mexico, October, 1982.

13. Rottendorf, H. and M. A. Wilson. "Effects of In-Situ Mineral Matter and a Nicket-Molybdenum Catalyst on Hydrogenation of Lidell Coal." Fuel, 59, p. 175, London, England, 1980.

14. Utz, B. R., H. R. Appell and B. D. Blaustein. "Vehicle Studies in Short Contact Time Liquefaction." Proceedings of the Department of Energy Integrated Two-Stage Liquefaction Meetings. p. 7-1, Alberquerque, New Mexico, October, 1982.

15. Utz, B. R., Narain, N. K., Appell, H. R. and Blaustein, B. D. "Solvent Analysis of Coal Derived Products, Using Pressure Filtration," Am. Chem. Soc. Symp. Ser., edited by Fuller, American Chemical Society, Washington, D. C., 1982.

Table 1 - Effects of Hydrogen Pressure on Coal Conversions for 15 min. at 425 °C

RUN NO.	45	1	3	2	4	37*	9	6	38*	10	7	47**
Hydrogen Charge at the Room Temperature (psig)	0	500	1100	500	1100	0	500	1100	0	500	1100	0
1 gm Aromatics plus 4 g 1-MN												
Anthracene	-	+	+	-	-	+	+	+	-	-	-	+
Phenanthrene	-	-	-	+	+	-	-	-	+	+	+	-
Type of Coal												
Wyodak	+	+	+	+	+	-	-	-	-	-	-	-
Ky 9/14	-	-	-	-	-	+	+	+	+	+	+	+
Coal Conversion (wt %)												
THF Soluble	36.1	44.3	57.7	40.3	47.9	42.4	72.4	83.8	37.7	75.3	84.7	39.5
Preasphaltene	-	-	-	-	-	11.0	26.3	26.9	13.4	21.0	27.6	10.0
Asphaltene	-	-	-	-	-	18.1	26.5	33.6	14.9	25.1	30.0	13.9
Preasphaltene plus Asphaltene	8.0	14.0	12.6	11.6	10.6	29.1	52.7	60.5	28.3	46.2	57.6	23.9
Oil, Water and Gas	28.2	30.3	45.1	28.7	37.3	13.2	19.7	23.2	9.5	29.1	27.0	15.6
Conversion of Aromatics (wt %)												
Conversion to Dihydroaromatics	NA	6.4	16.9	0	0	4.4	17.6	28.4	0	0	3.8	4.5
Unconverted Aromatic	NA	93.6	77.2	100	100	95.6	71.7	50.7	100	100	95.3	95.5

*1100 psig initial nitrogen pressure at the room temperature

**14.7 psig initial nitrogen pressure at the room temperature

Table 2 - Conversions of Coals under the Various Reaction Conditions and for 15 min. at 425 °C

RUN NO.	3	4	6	7	37	38	40**	41**	42*	44*	45*	46*	48	49
Type of Coal (1 g)														
Wyodak	+	+	-	-	-	-	-	-	-	+	+	-	+	+
Ky 9/14	-	-	+	+	+	+	+	+	+	-	-	+	-	-
1 g Aromatic Plus 4 g 1-MN														
Anthracene	-	+	+	-	+	-	+	-	-	-	-	-	+	-
Phenanthrene	+	-	-	+	-	+	-	+	-	-	-	-	-	+
Gas Charge at the Room Temperature (1100 psig)														
Hydrogen	+	+	+	+	-	-	-	-	+	+	-	-	-	-
Nitrogen	-	-	-	-	+	+	+	+	-	-	+	+	+	+
Coal Conversion (wt %)														
THF Soluble	57.7	47.9	83.8	84.7	42.4	37.7	30.1	27.9	84.5	51.2	36.1	39.8	37.1	39.5
Preasphaltene	-	-	26.9	27.6	11.0	13.4	11.6	15.7	21.3	-	-	7.6	-	-
Asphaltene	-	-	33.6	30.0	18.1	14.9	13.7	12.6	31.2	-	-	16.4	-	-
Preasphaltene plus Asphaltene	12.6	10.6	60.5	57.6	29.1	28.3	25.3	27.9	52.4	14.1	8.0	23.9	8.6	9.1
Oil, Water and Gas	45.1	37.3	23.2	27.0	13.2	9.5	4.9	0	32.1	37.1	28.2	15.9	28.5	30.4
Conversion of Aromatics (wt %)														
Conversion to Dihdro-aromatics	16.9	0	28.4	3.8	4.4	0	2.6	0	NA	NA	NA	NA	3.3	0
Unconverted aromatic	77.8	100	50.7	95.3	95.7	100	97.4	100	NA	NA	NA	NA	96.8	100

*5 g 1-Methylnaphthalene introduced in the absence of aromatics

**350 °C of reaction temperature

Table 3 - Effects of Aromatic Compounds and Dihydroaromatic Compounds on Coal Conversion at the Atmospheric Pressure and in the Absence of 1-Methylnapthalene

RUN NO.	5	8	11	12	19	22	23	24
Type of Coal								
Wyodak	+	+	+	+	-	-	-	-
Ky 9/14	-	-	-	-	+	+	+	+
Aromatics								
10 g Anthracene	+	-	-	-	+	-	-	-
10 g Phenanthrene	-	+	-	-	-	+	-	-
8 g Anthracene plus 2 g Dihydroanthracene	-	-	+	-	-	-	+	-
8 g Phenanthrene plus 2 g Dihydrophenanthrene	-	-	-	+	-	-	-	+
Temperature (°C)	339	335	340	330	336	334	333	329
Coal Conversion (wt %)								
THF Soluble	6.5	18.3	51.8	21.6	9.8	32.6	37.3	45.8
Preasphaltene	2.2	1.0	2.3	1.4	6.2	7.2	19.4	15.8
Oil, Water, Gas and Asphaltene	4.3	17.3	49.5	20.2	3.6	25.4	17.9	30.0
Conversion of Dihydro-aromatic (wt %)	0	0	36.3	18.9	0	0	14.8	26.0

Table 4 - Effects of Neat Aromatic Compounds at 425 °C and 15 min. on Coal Conversion in the Presence of 1100 psig Nitrogen at the Room Temperature and in the Absence of 1-Methylnaphthalene

RUN NO.	50	51	52	53
Type of Coal (1 g)				
Wyodak	-	-	+	+
Ky 9/14	+	+	-	-
5 g Aromatics				
Anthracene	+	-	+	-
Phenanthrene	-	+	-	+
Coal Conversion (wt %)				
THF Soluble	32.4	51.3	33.1	42.6
Preasphaltene	10.8	11.1	10.8	0.5
Asphaltene	8.8	14.0	6.7	14.1
Preasphaltene plus asphaltene	19.6	25.1	17.5	14.5
Oil, Water and Gas	12.8	26.1	15.7	28.1
Conversion of Aromatic (wt %)				
Conversion to Dihydroaromatic	0	0	2.7	0
Unconverted Aromatic	100	100	97.3	100