HIGH-PRESSURE CATALYTIC HYDROPROCESSING OF A SIMULATED COAL LIQUID

By

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INTRODUCTION

The catalytic hydroprocessing of coal-derived liquids is poorly understood because of the complexity of the liquids and the large number of competing reactions. The goal of this research was to characterize quantitatively the hydroprocessing of a liquid mixture modelling a coal liquid derived from Powhatan No. 5 coal in the SRC-II process. A specific goal was to determine relstive reactivities of representative reactants and determine the competitive inhibition effects of the various reactants. The experiments were carried out with a mixture of at most nine compounds representing the major functional groups in the coal liquid. The reactants included polynuclear aromatic hydrocarbons, sulfur- and oxygen-containing heterocyclics. 1-naphthol, and basic as well as nonbasic organonitrogen compounds.

There is no one typical coal liquid because the compounds and their relative amounts vary with the source of the coal and with the type and operating severity of the coal liquefaction process. In this study, the choice of model compounds and their relative amounts were based on a detailed analysis of the SRC-II heavy distillate (1,2). The concentrations of compounds containing heteroatoms were chosen to give the same concentrations of functional groups present in the SRC II heavy distillate; the concentrations of aromatic hydrocarbons were chosen to give a molar ratio of 3:2:1 of fused 2-ring, 3-ring, and 4-ring aromatic compounds.

EXPERIMENTAL

Apparatus and Procedure

The experiments were carried out with a fixed-bed flow microreactor (3). The feed was prepared by dissolving the reactant compounds in cyclohexane to give a solution with a total solute mass fraction of 0.0025. Approximately 800 ml of solution was added to either of two 1000-ml high-pressure autoclaves equipped with stirrers. The feed and the vapor space above it were purged with hydrogen for two hours at room temperature with a hydrogen flow rate of 50 ml/min. Carbon disulfide dissolved in another 10 ml of feed was then quickly added to give 0.001 mass fraction of carbon disulfide in the feed. [The carbon disulfide served as a source of hydrogen sulfide via the reaction $CS_2 + 4H_2 \longrightarrow 2H_2S + CH_4$, which occurs rapidly under the reaction conditions (4); the CS_2 maintained the catalyst in the sulfided state.] The autoclave was pressured up to 137.1 atm with hydrogen at room temperature, and the feed was saturated with hydrogen. This resulted in a hydrogen mole fraction of approximately 0.05 in the feed (5) or a 50:1 hydrogen to reactant mole ratio, which prevented the hydrogen mole fraction from varying significantly over the length of the reactor.

The saturation of the feed with hydrogen prior to its introduction into the reactor ensured that only two phases were present in the reactor, which allowed

determination of reaction kinetics in the absence of mixing effects or significant radial gradients in concentration or temperature. Because the reactor was held at a higher temperature and pressure than the autoclave, no degassing of the feed occurred, as confirmed by thermodynamic calculations.

The reactor consisted of a vertical 316 stainless steel tube 25.4 cm long with an internal diameter of 0.95 cm. The bottom 11 cm of the reactor were packed with 90-mesh alundum, the next 3 cm were packed with 0.050 g of catalyst mixed with alundum, and the remainder of the tube was packed with alundum. A detailed description of the reactor is given elsewhere (3).

The catalyst was sulfided by passing a mixture of 10% H_2S in H_2 through the catalyst bed at 30 cm^3/min for two hours at 400°C. The reactor was then cooled to the reaction temperature (usually 350°C) under H_2S/H_2 and then brought to the reaction pressure of 171 atm. The feed was pumped through the reactor by a Waters M-6000A liquid chromatography pump. Liquid samples could be taken from either a sampling valve or a dead volume cylinder, both of which were located downstream of the reactor. For each run, the reactor was operated until steady-state was reached (usually 24-30 h); only data from steady-state samples are reported.

The analyses of the liquid samples were performed with a Tracor 560 gas chromatograph (GC) equipped with a 30-m DB-5 bonded phase capillary column. The GC contained an outlet splitter which permitted the column effluent to be divided into two streams, one going to a flame ionization detector (FID) and the other to a Hall electrolytic conductivity detector. The latter was used to identify nitrogen-containing compounds and the former was used for quantitative product analysis using n-decane as an internal standard. FID response factors relative to n-decane were determined for all the reactants. Some of the samples were also analyzed by gas chromatography-mass spectrometry.

Materials

The catalyst used in this work was American Cyanamid HDS-9A, a $NiO-MoO_3/\gamma-Al_2O_3$ catalyst, the properties of which are listed in Table II. Prior to use, the catalyst was ground from 1/16" extrudates to 80-100 mesh particles. The alundum used to pack the reactor was Alundum RR (Fisher Scientific, Blue Label). All chemicals listed in Table I as well as the cyclohexane solvent were obtained from Aldrich Chemical Company and used as received. n-Decane was obtained from Eastman Chemical Co. High-pressure hydrogen (3500 psig) and the 10% H_2S in H_2 were obtained from Linde and Matheson, respectively.

RESULTS AND DISCUSSION

The first series of experiments was conducted with the simulated coal liquid designated in Table I. These experiments had the following objectives:

a) To determine the reactivities of the various reactants in a mixture at different temperatures and weight hourly space velocities (WHSV).
b) To identify as many reaction products as possible.
c) To establish the limitations of the chromatographic analyses of the products (e.g., determine which peaks could not be resolved). Product chromatograms were expected to be complex, with overlapping peaks.

Experiments were carried out at each of the conditions shown in Table III. In Table IV. the reaction products identified are listed with the methods used to identify them (mass spectrometry and co-injection with a pure compound into the chromatograph). Some problems were encountered in resolving important peaks in the product chromatograms. The major resolution difficulty occurred with dibenzothiophene; a peak of comparable size was merged with it on its down slope, and a small peak from a nitrogen-containing compound appeared on its up slope. The small peak on the up slope was not resolvable from the dibenzothiophene peak on the FID trace (we detected it with the Hall detector); as a result, the calculated dibenzothiophene mass fraction was greater in product samples than in

the feed. Therefore, the only way to determine dibenzothiophene hydrodesulfurization (HDS) was to sum the mass fractions of biphenyl and cyclohexylbenzene in the product and divide by the feed dibenzothiophene mass fraction. A similar difficulty occurred with phenanthrene, as the Hall detector indicated a nitrogen-containing peak at approximately the retention time of phenanthrene, whereas the FID trace showed only one large peak. Since the Hall detector was used only for qualitative analysis. it was not possible to subtract the contributions of the nitrogen-containing compounds. Hence, we expect that the actual phenanthrene conversion was somewhat higher than the calculated results. The additional analytical problem occurred with acridine. Of the approximately six organonitrogen compound peaks expected as acridine products, only one, that for 1,2,3,4,5,6,7,8-octahydroacridine, was identified; no hydrocarbon hydrodenitrogenation (HDN) products were identified.

Table V is a summary of the results for runs at constant temperature (350°C) and varying WHSV with the simulated coal liquid designated in Table I. The conversions of the basic nitrogen compounds, quinoline and acridine, were higher than that of indole, the non-basic nitrogen compound. However, the fraction HDN of quinoline (defined as the moles of the quinoline and nitrogen-containing quinoline derivatives in the product divided by the moles of quinoline in the feed) was considerably less than the quinoline conversion. It was not possible to obtain a reliable value for acridine HDN.

Figure 1 is a pseudo first order kinetics plot for quinoline and indole HDN (i.e., a plot of the fraction of non-dehydronitrogenated compounds vs. inverse space velocity). Quinoline HDN followed pseudo first order kinetics, whereas indole HDN did not.

The conversion of dibenzofuran was too low to be measured reliably; this was the least reactive of the reactants. In contrast, the conversion of 5,6,7,8-tetrahydro-1-naphthol was always greater than 80%. No oxygen-containing products of 5,6,7,8-tetrahydro-1-naphthol were found; it is inferred that the 5,6,7,8-tetrahydro-1-naphthol conversion is identical to is hydrodeoxygenation (HDO).

Dibenzothiophene was converted appreciably only at the lowest space velocity; biphenyl and cyclohexylbenzene were detected as HDS products.

The conversions of phenanthrene, fluoranthene, and pyrene were, in order of decreasing reactivity: fluoranthene > pyrene > phenanthrene. As a consequence of the nitrogen compound peak that was merged with that of phenanthrene, the actual phenanthrene conversion is inferred to have been higher than that shown in Table V. The pseudo first order kinetics plots for these three hydrocarbons suggest that the hydrogenation reactions were reversible, as expected.

Table VI is a summary of runs made at constant space velocity but with the temperature varied from 300 to 400°C with the simulated coal liquid designated in Table I. A sharp increase in quinoline HDN was observed from 300 to 350°C. However, the quinoline HDN hardly changed from 350 to 400°C; the product quinoline mass fraction observed in the run at 400°C was approximately five times that observed at 350°C, which is consistent with earlier observations that quinoline hydrogenations are reversible (6).

The HDN trend with indole was rather different: the large change in HDN occurred from 350 to 400°C, whereas the HDN was practically unchanged from 300 to 350°C; inspection of the indole mass fraction in these runs (Table VI) reveals that the indole conversion paralleled that of the HDN, suggesting that nitrogen-containing intermediates of indole were more reactive than indole itself.

The reactivities of the two oxygen compounds were at extremes: dibenzofuran conversion was low, even at the highest temperature, while the HDO of 5,6,7,8-tetrahydro-naphthol was complete at 350°C. As for dibenzothiophene, the HDS increased with temperature, with the largest change occurring from 350 to 400°C.

Phenanthrene conversion also increased with temperature. However, fluoranthene and pyrene gave a different result: in each case conversion

increased from 300 to 350°C but decreased significantly from 350 to 400°C. The decrease in conversion suggests that pyrene and fluoranthene hydrogenations are rapid but limited strongly by equilibrium at the highest temperature.

From the data presented in Tables V and VI it is evident that the conversions of dibenzothiophene, dibenzofuran, and the aromatic hydrocarbons were all low compared with those of the other compounds. In addition, organonitrogen compounds and water (one of the products of 5,6,7,8-tetrahydro-1-naphthol HDO) are known inhibitors (7, 8). These findings motivated the next set of experiments using another simulated coal liquid, Table VII. This simulated coal liquid contains the same mass fractions of dibenzofuran, dibenzothiophene, and the three aromatics as the one designated in Table I, with the nitrogen compounds and 5,6,7,8-tetrahydro-1-naphthol removed.

Experiments were carried out at 350°C and at WHSV with the simulated coal liquid designated in Table VII, and the results are summarized in Table VIII. The results of Figure 2 suggest that the hydrogenations of fluoranthene and pyrene were reversible; phenanthrene appeared to follow pseudo first order kinetics. Dibenzofuran conversion was again very low, suggesting that its low reactivity — referred to above—was not the result of inhibition by organonitrogen compounds and/or water. On the other hand, dibenzothiophene HDS was markedly greater in this coal liquid compared with the one designated in Table I. It is especially instructive to compare the results from Run 6 (Table VIII) with those from Run 1 (Table VI) as both runs were made with the same catalyst loading, feed flow rate, and the same mass fractions of dibenzofuran, dibenzothiophene, phenanthrene, fluoranthene, and pyrene. The inhibition effect of the organonitrogen inhibitors and/or the 5,6,7,8-tetrahydro-1-naphthol was strong for all the reactants except dibenzofuran.

Additional experiments are planned where 5,6,7,8-tetrahydro-1-naphthol, indole, and quinoline will be subsequently added to the simulated coal liquid specified in Table VII; these should give additional information concerning the cause of the inhibition in the runs with the simulated coal liquid given in Table I.

ACKNOWLEDGMENTS

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REFERENCES

1. Petrakis, L., D. C. Young, R. G. Ruberto, and B. C. Gates, Ind. Eng. Chem. Process Des. Dev. 1983, 22, 298.
2. Gates, B. C., J. H. Olson, G. C. A. Schuit, A. B. Stiles, and L. Petrakis, "Kinetics and Mechanism of Catalytic Hydroprocessing of Components of Coal-derived Liquids," United States Department of Energy Report No. DE-AC22-79ET14880-17, January 17, 1984.
3. Eliezer, K. F. et al., Ind. Eng. Chem. Fundam., 1977, 16, 380.
4. Sapre, A. V., Ph.D. dissertation, University of Delaware, Newark, Delaware, 1981.
5. Berty, T. E., H. H. Reamer, and B. H. Sage, J. Chem. Eng. Data, 1966, 11 (1), 25.
6. Satterfield, C. N. and S. H. Yang, Ind. Eng. Chem. Process Des. Dev., 1984, 23, 11.
7. Bhinde, M. V., Ph.D. dissertation, University of Delaware, Newark, Delaware, 1979.
8. Lipsch, J. M. J. G. and Schuit, G. C. A., J. Catal., 1969, 15, 174.

TABLE I

SIMULATED COAL LIQUID

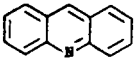
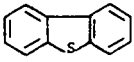
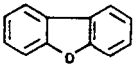
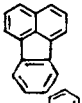
COMPOUND	STRUCTURE	COMPOUND CLASS	RELATIVE MOLE FRACTION
Quinoline		Basic Nitrogen	0.0265
Acridine		Basic Nitrogen	0.0261
Indole		Nonbasic Nitrogen	0.0384
Dibenzothiophene		Sulfur Heterocyclic	0.0347
Dibenzofuren		Oxygen Heterocyclic	0.0639
5,6,7,8-tetra-hydro-1-naphthol		Naphthol	0.1133
Fluoranthene		Fused two-ring Aromatic	0.3489
Phenanthrene		Fused three-ring Aromatic	0.2320
Pyrene		Fused four-ring Aromatic	0.1163

TABLE II

PROPERTIES OF AMERICAN CYANAMID[1] HDS-9A CATALYST

Composition, wt.%	
NiO	3.1
MoO_3	18.3
WO_3	0.04
Na_2O	0.05
Surface Area, m^2/g	149
Pore Volume, cm^3/g	0.51

1. The reported values were determined by the catalyst manufacturer.

TABLE III

CONDITIONS OF FIRST SET OF EXPERIMENTS

PRESSURE = 171 ATMOSPHERES

RUN #	*TEMPERATURE, °C*	WHSV, (g of reactants)/(g of catalyst h)
1	350	0.99
2	350	2.17
3	350	4.14
4	400	1.03
5	300	1.10

TABLE IV PRODUCT IDENTIFICATIONS

REACTANT	PRODUCTS	METHODS OF IDENTIFICATION: Co-Injection in GC	Mass Spectrometry
Quinoline	1,2,3,4-tetrahydroquinoline	x	
	5,6,7,8-tetrahydroquinoline	x	
	Decahydroquinoline	x	
	2-propylaniline	x	
	Propylbenzene	x	
	Propylcyclohexane	x	
Indole	Indoline	x	
	2-ethylaniline	x	
	Ethylbenzene	x	
	Ethylcyclohexane	x	
5,6,7,8-Tetrahydro-1-naphthol	Tetralin	x	x
	cis-Decalin	x	*
	trans-Decalin	x	x
	Naphthalene	x	x

*Identified as octahydromethylindan by mass spectrometry.

Dibenzothiophene	Biphenyl	x	x
	Cyclohexylbenzene	x	x
Phenanthrene	Dihydrophenanthrene		x
	Octahydrophenanthrene		x
Acridine	1,2,3,4,5,6,7,8-Octahydroacridine	x	
Fluoranthene	1,2,3,10b-Tetrahydrofluoranthene		x
Pyrene	Dihydropyrene (isomer unidentified)		x
	Hexahydropyrene (isomer unidentified)		x

TABLE V

SUMMARY OF RESULTS OBTAINED AT T=350C AND VARIABLE WHSV

FEED: SIMULATED COAL LIQUID DESIGNATED IN TABLE I

RUN #	1	2	3
WHSV, (g of reactants)/(g of cat h)	0.99	2.17	4.14
PERCENTAGE CONVERSION			
QUINOLINE	97.9	90.7	88.2
INDOLE	46.4	29.9	22.9
5,6,7,8-TETRAHYDRO-1-NAPHTHOL	100	82.4	82.5
DIBENZOFURAN	4.1	7.5	0.0
DIBENZOTHIOPHENE	15.4	0.0	0.0
PHENANTHRENE	9.9	9.3	7.3
ACRIDINE	72.3	91.9	92.2
FLUORANTHENE	41.7	24.9	23.1
PYRENE	20.3	16.6	18.8
QUINOLINE PERCENTAGE HDN	59.6	33.0	15.7
INDOLE PERCENTAGE HDN	27.8	19.7	13.5

TABLE VI

SUMMARY OF RESULTS OBTAINED AT WHSV=1 AND VARIOUS TEMPERATURES

FEED: SIMULATED COAL LIQUID DESIGNATED IN TABLE I

RUN #	5	1	4
TEMPERATURE, C	300	350	400
WHSV, (g of reactants)/(g of cat h)	1.1	0.99	1.03
PERCENTAGE CONVERSION			
QUINOLINE	98.8	97.9	88.4
INDOLE	41.0	46.4	70.5
5,6,7,8-TETRAHYDRO-1-NAPHTHOL	59.8	100	99.9
DIBENZOFURAN	0.9	4.1	5.1
DIBENZOTHIOPHENE	0.0	15.4	75.9
PHENANTHRENE	3.9	9.9	13.8
ACRIDINE	87.7	72.3	75.9
FLUORANTHENE	30.4	41.7	16.2
PYRENE	12.8	20.3	13.6
QUINOLINE PERCENTAGE HDN	4.2	59.6	54.3
INDOLE PERCENTAGE HDN	27.5	27.8	55.0

TABLE VII

COMPOSITION OF SECOND SIMULATED COAL LIQUID

COMPOUND	RELATIVE MOLE FRACTION
Dibenzofuran	0.0807
Dibenzothiophene	0.0437
Fluoranthene	0.4396
Phenanthrene	0.2921
Pyrene	0.1464

TABLE VIII

SUMMARY OF RESULTS OBTAINED WITH THE SIMULATED COAL LIQUID DESIGNATED IN TABLE VII

RUN #	6	7
TEMPERATURE, C	350	350
PRESSURE, ATM	172	173
WHSV, (g of reactants)/(g of cat h)	0.84	1.73
PERCENTAGE CONVERSION		
DIBENZOFURAN	2.8	2.7
DIBENZOTHIOPHENE	30.7	10.3
PHENANTHRENE	33.1	18.0
FLUORANTHENE	65.6	48.6
PYRENE	37.7	27.6

FIGURE 1
QUINOLINE AND INDOLE PERCENT HDN

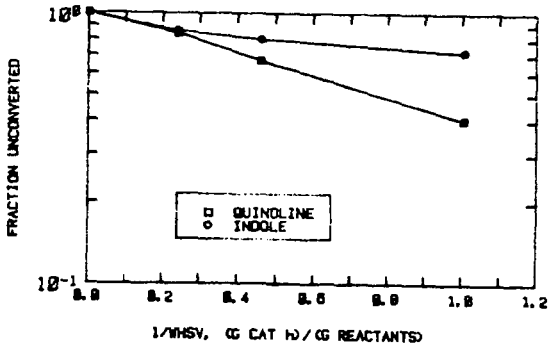
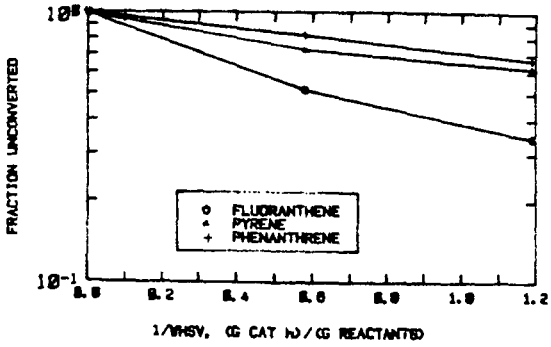



FIGURE 2
REACTIVITIES OF AROMATICS