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COMPOUND-TYPE DISTRIBUTION IN SHALE OILS PRODUCED BY
FLASH HYDROPYROLYSIS OF EASTERN U. S. OIL SHALE

By

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INTRODUCTION

Rockwell International has been developing technology for the flash hydrolysis (FHP) of carbonaceous feedstocks under U. S. Department of Energy (DOE) sponsorship since 1975. FHP is based on the high-temperature (1100 to 1900°F) reaction of pulverized solid carbonaceous feedstocks with hydrogen in a single-stage, short-residence-time, entrained-flow reactor. Gases and liquids are produced in the reactor and unreacted material forms a dry, free-flowing char. Following product gas quench, liquid products are separated and gases are processed for recycle and product recovery. By varying the reactor operating conditions, the makeup of the product slate can be controlled over a broad range - from predominately a syncrude oil with SNG byproduct, to SNG with a relatively pure benzene byproduct, to SNG alone as the sole hydrocarbon product.

A key element of FHP is the injector/reactor technology pioneered and developed by Rockwell. This technology, first used in liquid-fueled rocket engines, has several distinctive features that make it superior to alternative means of achieving hydrolysis of carbonaceous feedstocks. These include extremely rapid mixing and heating of reactants (10 to 20 ms), precise and uniform control of temperature and reaction time, rapid startup and shutdown, unrestricted choice of feedstock and simple scaleup. In addition, because FHP operates in a short-residence-time (20 ms to 5 s), high-pressure (500 to 1500 psig), entrained-flow mode, the reactor is inherently compact.

The major oil shale development within the United States has focused on western oil shale and on recovery by pyrolytic methods. Eastern shales are hydrogen deficient compared with western shales and the corresponding oil yields produced by pyrolytic methods are much lower. The Rockwell FHP reactor seems particularly well suited for processing eastern shales, since oil yields are substantially increased by operating under a high hydrogen partial pressure.

In September, 1982, Rockwell International was awarded a DOE contract entitled "Investigation into the Application of Hydrolysis to the Hydroconversion of Eastern Oil Shale". The project had two major objectives: (a) testing, data reduction and chemical analysis to determine the performance of eastern oil shale in an FHP reactor and (b) selection of an operating point suited to high yields of shale oil and performance of a preliminary process analysis and economic assessment of the process.

A series of six tests was performed between January and March, 1983. Testing was conducted in Rockwell's existing 1-ton/h process development unit (PDU). A simplified schematic of this unit is shown in Figure 1. Three liquid products were obtained from each test: a heavy oil, a light oil and a BTX fraction.

The eastern oil shale used during the reactor testing was a blend of nine stockpiles taken from various depths in the Cleveland Member of the Ohio shale. The shale was obtained from the University of Kentucky's Institute for Mining and Minerals Research (IMMR) and pulverized to 70% through 200 mesh in an inert (nitrogen) atmosphere by Kennedy Van Saun Company, Danville, Pennsylvania. The tested shale had an average carbon content of 12.7 wt % and a Fischer Assay of ~13 gal/ton.

Key results and findings on the program were presented at the 1983 Eastern Oil Shale Symposium (1), while full details on the six tests are covered in the final report submitted to the Department of Energy, Laramie Project Office (2). Test results showed total carbon conversions as high as 70.0% and carbon conversions to liquid as high as 55.5%. Production of raw shale oil ranged from ~13.5 to 19.0 gal/ton of shale fed.

The composition of shale oil is dependent on the geographic origin of the oil shale and the pyrolysis method of extracting the liquid product (3, 4). This paper reports on the effect of process conditions in the Rockwell hydrolypyrolysis PDU on the composition of the resulting shale oil. Elemental carbon, hydrogen, nitrogen and sulfur values in each of the three liquid products were determined and H/C ratios were related to process conditions. Liquid products from three tests were further characterized by nuclear magnetic resonance (NMR) to report carbon and hydrogen aromaticities and the approximate level of aromatics, olefins and aliphatics. Nitrogen basicity was determined on the same liquid products. Finally, light-oil products from two tests representing moderate and severe process conditions were fractionated by chromatography to compare the effect of process conditions on the nitrogen compound distribution in the oil.

EXPERIMENTAL

Testing

To fulfill program objectives, two reactors were tested over a 1100 to 1400°F reactor temperature range. All tests were conducted at a nominal reactor pressure of 1000 psig and a nominal oil shale flow rate of 3/4 ton/h. The first reactor, used in tests 1 through 3, produced a nominal residence time of 200 ms; the second, used in tests 4 through 6, produced a nominal residence time of 75 ms. An average total of 1688 lb of oil shale (~212 lb of carbon) was fed per test for an average test duration of 68 min. Test conditions are summarized in Table I. At the conclusion of each test, the heavy oil product was removed from the flash drum while it was fluid and duplicate samples were taken for chemical analysis. The light-oil/water mixture was drained from the decanter after each test into 55-gal drums and duplicate representative samples were taken from each drum for analysis. The activated carbon-bed adsorber recovery system provided for recovery of vapor phase BTX and other light hydrocarbon oils in the product gas stream leaving the light-oil condenser. After each test, the bed was steamstripped to desorb the "BTX fraction". The BTX and condensed water were separated by decantation and duplicate samples were taken for chemical analysis. One set of samples was sent to the Rockwell Analytical Labs, the other to the Western Research Institute (WRI).

TABLE I
SUMMARY OF 1-TON/H PDU TEST CONDITIONS

Test	Pressure (psig)	Reactor Outlet Temp. (°F)	Residence Time (ms)	Test Duration (min)	Total Oil Shale Flowed (lbm)
OS-83-1	998	1198	198	75.1	1742
OS-83-2	1001	1329	185	68.4	1500
OS-83-3	999	1098	211	66.1	1753
OS-83-4	999	1203	74	70.2	1811
OS-83-5	1000	1422	67	60.3	1398
OS-83-6	998	1115	78	71.1	1925

Analytical Methods

The heavy-oil and BTX samples were analyzed as received, while the light-oil samples were centrifuged at 15,000 rpm at 12°C in a Sorvall Superspeed Centrifuge to separate the oil from the water. Heavy oils were analyzed for moisture content by the ASTM method for moisture in coal, while the light oils and BTX were analyzed by a Karl Fischer titration. The ash content was determined by evaporation in stages, followed by combustion at 750°C. The carbon, hydrogen and nitrogen contents of all three fractions were determined using a Perkin-Elmer 240B semimicrocombustion apparatus. Sulfur was determined by a Parr bomb combustion followed by gravimetric precipitation as barium sulfate.

The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained on a JEOL FX-270 spectrometer under short-pulse delay times (2.5 s and 10 s, respectively). Shale oil samples were prepared in 5-mm tubes for the ¹H and ¹³C experiments. Deuteriochloroform (CDCl₃) was used as solvent for all samples and tetramethylsilane (TMS) was used as reference. 1% TMS in CDCl₃ provided the lock signal for ¹H and the solvent CDCl₃ provided the lock signal for ¹³C NMR spectra. Average molecular structure parameters for the shale oil samples were calculated from the normalized ¹H and ¹³C spectral areas according to equations used by Netzel and Miknis (3).

Solvent-compensated infrared spectra were recorded in the absorbance mode on a Perkin-Elmer Model 621 grating infrared spectrophotometer. High-resolution mass spectra were obtained

with a VG-ZAB mass spectrometer (accelerating voltage 8 kV, ionizing voltage 70 V and resolution at 20,000). A Finnigan-Incos data system was used to acquire and analyze the data. Samples were introduced under reduced pressure at 200°C via an oven.

At WRI, elemental nitrogen was determined by chemiluminescence using an Antek Model 771 pyroreactor with an Antek Model 720 digital nitrogen detector. A Mettler potentiometric titrator was used to titrate basic nitrogen. Titrations were done in acetic anhydride:toluene (2:1) and in acetonitrile:toluene (2:1) with perchloric acid in dioxane as titrant.

Fractionation by Adsorption Chromatography

Light-oil samples were fractionated into eight compound-type fractions using basic alumina and silica adsorption chromatography according to the procedures by Holmes (5). Linear solvent gradients of 0 to 100% methyl *tert*-butyl ether in cyclohexane and 0 to 100% methylene chloride in hexane were pumped via a Waters Model 600 solvent programmer onto basic alumina and silica gel, respectively. A variable wavelength UV/visible detector was used to indicate fraction collection end points. The chromatographic scheme is presented in Figure 2. The eight fractions were named for characteristic compound types identified by spectroscopic and titration analyses and corroborated by model compounds. Alkylpyridine-type compounds have a wide range of adsorptivity values on alumina and silica. Hindered alkylpyridine-type compounds elute early from alumina (pyridine I), whereas nonhindered alkylpyridine-type compounds elute late (pyridine III).

RESULTS AND DISCUSSION

Carbon Conversions

Experimental values of overall carbon conversion, carbon conversions to gases (total and methane only) and liquids and the distribution among the collected liquid products (heavy oil, light oil and stripped BTX oil) are summarized in Table II. Based on Rockwell's FHP experience in related fossil fuels programs, a convenient dependent variable that correlates much of the carbon conversion data is carbon conversion to methane. As temperature and residence time are increased in FHP reactors (i. e., higher reactor severity), more carbon in the feedstock is converted to methane. When the conversion and methane data in Table II are plotted in Figure 3, all data points fall along a single curve, providing an excellent correlation. Hereafter, all references to reactor severity are based on the relative conversion of carbon in shale to methane. Tests 3 and 6 had the lowest severity; tests 2 and 5 had the highest.

TABLE II
SUMMARY OF CARBON CONVERSION RESULTS

Test	Overall	To Char	To Gases		To Liquids By Difference	Liquids Distribution		
			Total	Methane Only		Stripped BTX Oil	Light Oil	Heavy Oil
OS-83-1	67.74	32.26	17.08	3.45	50.66	1.62	24.43	24.61
OS-83-2	69.99	30.01	26.11	7.39	43.88	2.43	26.61	14.84
OS-83-3	62.56	37.44	7.11	1.30	55.46	2.97	28.26	24.23
OS-83-4	67.27	32.73	14.35	2.72	52.92	4.93	24.76	23.23
OS-83-5	69.79	30.21	28.62	8.51	41.17	2.74	26.47	11.96
OS-83-6	61.43	38.57	7.15	1.19	54.28	1.02	24.52	28.74

Elemental Characterization of Oils

The chemical composition (carbon, hydrogen, nitrogen, sulfur and ash content) of the heavy oils, light oils and BTX oils are reported on a dry basis in Tables III, IV and V, respectively. A significant amount of spent shale (char) was carried into the heavy-oil collection system, as evidenced by the high ash contents (4.75 to 17.5 wt %) listed in Table III. The elemental composition of the heavy oils on a spent shale-free basis is, therefore, also presented in Table III. Nitrogen values increase from low-severity tests (tests 3 and 6) to high-severity tests (tests 2 and 5). The light oils (Table IV) show the same moderate effect of reactor severity on nitrogen content. The BTX oils (Table V) were all too low in nitrogen content to demonstrate an effect.

Compound-Type Distribution Produced Under Different Process Conditions

Liquid products produced by Rockwell oil shale FHP tests 3, 4 and 5 representing low, moderate and high processing severities (see Figure 3) were analyzed by ¹H and ¹³C NMR spectroscopy and potentiometric titration. Light oils from tests 4 and 5 were fractionated and compound types were determined by data from infrared spectroscopy, potentiometric titration and mass

spectrometry. The following discussion will focus on hydrocarbon and nitrogen compound-type distributions; ketones, ethers, sulfoxides and phenols were observed but are not reported here.

TABLE III
COMPOSITION OF HEAVY OILS

Test	OS-83-1	OS-83-2	OS-83-3	OS-83-4	OS-83-5	OS-83-6
<u>Wt % (dry)</u>						
Carbon	75.1	70.2	80.3	76.8	72.9	80.9
Hydrogen	5.76	4.76	6.89	6.53	5.02	7.56
Nitrogen	2.96	2.87	2.53	2.85	3.20	2.55
Sulfur	1.53	1.34	1.52	1.64	1.45	1.45
Ash	6.58	17.5	6.34	10.7	14.9	4.75
Atom H/C	0.91	0.81	1.02	1.01	0.82	1.11
Heavy Oils (Char-free)						
Carbon	80.5	85.4	85.8	86.2	85.7	85.0
Hydrogen	6.17	5.76	7.37	7.33	5.88	7.94
Nitrogen	3.17	3.48	2.70	3.19	3.75	2.67
Sulfur	1.56	1.35	1.54	1.70	1.50	1.46
Atom H/C	0.91	0.80	1.02	1.01	0.82	1.11

TABLE IV
COMPOSITION OF LIGHT OILS

Test	OS-83-1	OS-83-2	OS-83-3	OS-83-4	OS-83-5	OS-83-6
<u>Wt % (dry)</u>						
Carbon	85.2	86.1	85.2	85.3	86.4	85.3
Hydrogen	9.23	8.00	10.36	9.82	7.79	10.58
Nitrogen	1.61	2.16	1.43	1.43	2.14	1.06
Sulfur	1.82	2.11	1.73	1.72	2.42	1.92
Ash	0.05	0.07	0.08	0.04	0.27	0.13
Atom H/C	1.29	1.11	1.45	1.37	1.07	1.48

TABLE V
COMPOSITION OF BTX OILS

Test	OS-83-1	OS-83-2	OS-83-3	OS-83-4	OS-83-5	OS-83-6
<u>Wt % (dry)</u>						
Carbon	87.1	87.4	86.8	86.4	87.2	87.0
Hydrogen	11.83	10.35	11.89	12.54	10.81	10.84
Nitrogen	0.05	0.16	0.12	0.00	0.00	0.01
Sulfur	1.17	2.01	1.33	1.08	2.41	2.22
Ash	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Atom H/C	1.62	1.41	1.63	1.73	1.48	1.48

^1H and ^{13}C NMR Spectrometric Analyses - Average molecular structure parameters calculated from the normalized proton and carbon-13 spectral areas are presented for the BTX and light oils in Table VI. As the severity of test conditions increased, hydrogen and carbon aromaticity values increased in the light oils produced from tests 3, 4 and 5. Amounts of aromatics were 54, 70 and 91 mol % in the oils from tests 3, 4 and 5, respectively. Significantly greater amounts of monoaromatics than diaromatics were present. The amount of olefins did not follow that pattern. Olefinic content was greater in the light oil produced under conditions of intermediate reactor temperature and short residence time (test 4). The aromaticities of the BTX products did not increase with reactor severity; the hydrogen and carbon aromaticities of test 4 BTX were lower than either test 3 or 5 products, while the corresponding olefinic and aliphatic contents of test 4 BTX were higher. Because of paramagnetic material resulting from the inclusion of spent shale in the heavy

oils, uncertainty in the calculations preclude determining average molecular structure parameters for the heavy-oil products. However, Table VII presents the ^1H and ^{13}C NMR data for these oils. Again, process conditions of increasing severity produced heavy oils with increased aromatic content and decreased olefinic content. To reduce the effect of the paramagnetic material, the heavy oils were benzene-extracted; NMR data on these oils are also presented in Table VII. The benzene-soluble fraction represents 87, 93 and 75%, respectively, of the char-free heavy oils for tests 3, 4 and 5.

TABLE VI
COMPOSITION OF BTX AND LIGHT OILS DETERMINED FROM NMR ANALYSIS

Test	BTX			Light Oil		
	3	4	5	3	4	5
Hydrogen aromaticity	0.22	0.13	0.29	0.16	0.18	0.43
Olefinic hydrogen	0.06	0.08	0.06	0.03	0.04	0.01
Carbon aromaticity ^a	0.48	0.38	0.56	0.34	0.45	0.73
Mol % aromatics	49	34	64	54	70	91
% mono-	48	33	63	40	62	69
% di-	1	1	1	14	8	22
Mol % olefins	11	15	10	6	10	2
Mol % alkanes	41	51	26	39	20	6
Total atomic H/C	1.63	1.73	1.48	1.45	1.37	1.07
Aromatic H/C	0.74	0.61	0.76	0.67	0.55	0.63
Aliphatic H/C	2.44	2.42	2.39	1.84	2.05	2.29

a. Uncertainty is ± 0.05 . Includes olefinic carbons.

TABLE VII
NMR ANALYSIS OF HEAVY OILS PRODUCED BY FHP

Test	Heavy Oil		
	3	4	5
Total Heavy Oil			
Hydrogen aromaticity	0.23	0.28	0.37
Olefinic hydrogen	0.03	0.01	0.00
Carbon aromaticity ^a	0.59	0.56	0.88
Benzene-Extracted Heavy Oil			
Hydrogen aromaticity	0.28	0.31	0.47
Olefinic hydrogen	0.04	trace	0.00
Carbon aromaticity ^a	0.53	0.56	0.76

a. Includes olefinic carbons.

Potentiometric Titration Analysis - Potentiometric titration measures basicities in oils. Different classes of nitrogen compounds often display different basicities, which then provide general information regarding the distribution of nitrogen compound types. An alkylamine is more basic than an arylamine, which is much more basic than alkylindole.

Measurements of wt % nitrogen were obtained by chemiluminescence detection for the BTX, light oil and heavy oils produced from tests 3, 4 and 5 and these values are presented in Table VIII. The heavy oil values are the nitrogen content of the benzene-soluble material. These results demonstrate that nitrogen is concentrated in the heavier oil fractions. In general, the amount of nitrogen increases in the corresponding oils from tests 3, 4 and 5 as reactor severity increases.

Results of the potentiometric titration analyses are also shown in Table VIII. Except for the BTX liquids, as the severity of processing conditions increased, the amount of basic nitrogen in corresponding oils also increased. The percent of total nitrogen which is weak base I (pKa of the conjugate acid 7 to 9), primarily pyridine-type compounds, generally increased from heavy oil to light oil to BTX. The percent of total nitrogen which is weak base II (pKa of the conjugate acid 2 to 7), primarily alkylarylamines, was very low. These compound types were probably reaction intermediates resulting from hydrogenation of reactive nitrogen-containing compounds during processing.

For heavy and light oils, the percent of total nitrogen that was nonbasic nitrogen was equal to or greater than the amounts of basic nitrogen and represents compound types such as alkylindoles and alkylamides.

TABLE VIII
POTENTIOMETRIC TITRATION RESULTS OF SHALE OILS
PRODUCED BY FLASH HYDROPYROLYSIS

Test	Wt % Nitrogen	% of Total Nitrogen			
		Basic			Nonbasic (pka >2)
		Weak Base I (pka 7 to 9)	Weak Base II (pka 2 to 7)		
BTX					
3	0.065	45	0	55	
4	0.018	87	0	13	
5	0.036	69	0	31	
Light Oil					
3	1.22	36	2	62	
4	1.36	40	<1	59	
5	1.87	48	4	48	
Heavy Oil					
3	2.42	26	2	72	
4	2.78	31	2	67	
5	3.04	49	3	48	

Compound-Type Fractionation Analysis - Chromatographic techniques were used to fractionate the complex matrix of two light oils into simpler compound-type fractions. Although overlap of similar compound types occurred in successive fractions, characterization of these fractions by spectroscopic and titration analyses helped to determine the compound-type distribution in each oil. In the following discussion, emphasis is on the nitrogen compound-type distributions determined in the light oils from tests 4 and 5.

As shown earlier in Figure 2, adsorption chromatography generated eight compound-type fractions displaying distinct infrared absorbances characteristic of major compound types: hydrocarbon, pyridine I, pyridine III/phenol, pyridine III/amide, pyrrole, ketone/pyrrole, diazaaromatic and pyridine II. Each light oil was comprised of significant amounts of neutral hydrocarbons with 46 and 54 wt % of the oil from tests 4 and 5, respectively, composed of nonhydrocarbon fractions (nitrogen-containing). The nonhydrocarbon fractions from test 5 oil were considerably more aromatic, as indicated from infrared and mass spectrometric analyses, than those from the test 4 oil. For example, quinolines and their homologs composed 17 wt % of the pyridine I fractions from the light oils of tests 5 and only 9 wt % in the same fraction from test 4. Quinolines were not found in the pyridine III/phenol fraction from the test 4 oil, but they amounted to 4 wt % in a similar fraction from the test 5 oil.

Each fraction was further characterized by methods previously reported by Holmes and Thompson (4) that allowed determining the nitrogen compound distribution in the light oils from tests 4 and 5. Table IX presents these results. About 94 and 92% of the nitrogen in oils from tests 4 and 5, respectively, was characterized; the remaining nitrogen was either lost by fraction drying or irreversible adsorption onto the chromatographic adsorbents. Strong bases such as alkylamines/piperidines were found only in the test 4 oil and in very small amounts. Lesser amounts of alkylpyridines/quinolines were found in the test 4 oil than in the test 5 oil. Significantly greater amounts of alkylhydroxypyridines and alkylazaindoles/diazaaromatics were found in the test 4 oil, but greater amounts of alkylpyrroles/indoles/carbazoles/nitriles and N-alkylcarbazoles were found in the test 5 oil.

The more severe processing conditions employed in test 5 produced a light oil containing a greater amount of total nitrogen, the most being in the form of weak base I nitrogen compounds (37%). Generally, greater amounts of the reaction intermediates weak base II such as N-alkarylamines and alkarylamines were present in the test 5 oil. The significantly greater amounts of N-alkylcarbazoles and alkylpyrroles/indoles/carbazoles/nitriles present in the test 5 oil may have resulted from more organic material having been converted from the kerogen under severe processing conditions. These latter compound types are relatively more stable, especially compared with amide-type compounds, as hydrogenation accompanies processing. The differences in the distribution of nitrogen compound types in these two light oils may affect hydrotreating conditions necessary to reduce nitrogen content to produce a viable transportation fuel or chemical feedstock.

TABLE IX

NITROGEN COMPOUND-TYPE DISTRIBUTION IN LIGHT OILS FROM TESTS 4 AND 5

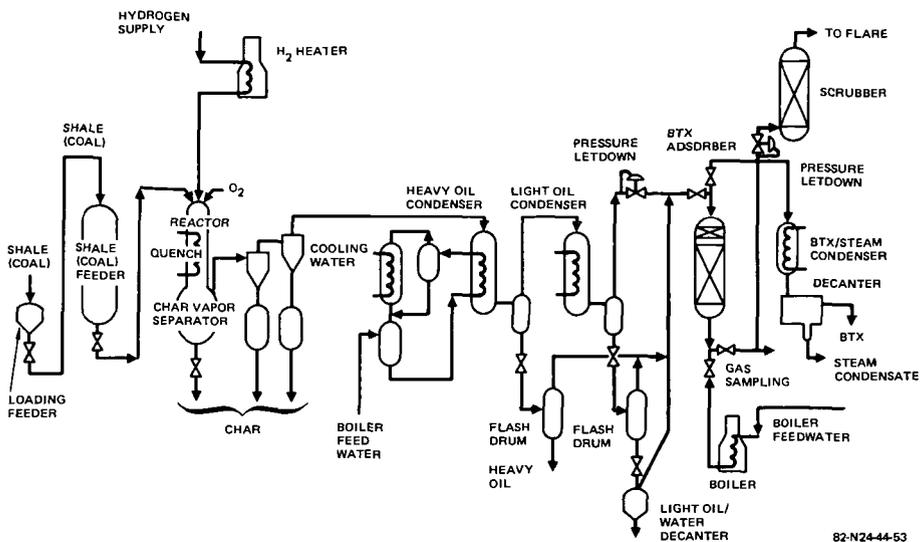
Compound Type	Wt % Nitrogen		% of Total Nitrogen	
	Test		Test	
	4	5	4	5
Strong Base				
Alkylamines/piperidines	0.005	-	0.4	-
Weak Base I				
Hindered alkylpyridines/quinolines	0.167	0.228	12.3	12.2
Less hindered alkylpyridines/quinolines	0.161	0.254	11.9	13.6
Nonhindered alkylpyridines/quinolines	0.134	0.214	9.9	11.4
Weak Base II				
Unknown	0.030	0.044	2.2	2.4
N-alkylarylamines	0.002	0.036	0.2	1.9
Alkylarylamines	0.046	0.056	3.4	3.0
Very Weak Base				
N-alkylindoles	0.032	0.027	2.4	1.4
Alkylpyrroles/indoles	0.178	0.283	13.2	15.1
Alkylloxazoles	0.008	0.007	0.6	0.4
Alkylhydroxypyridines	0.148	0.069	10.9	3.7
Alkylazaindoles/diazaaromatics	0.031	0.023	2.2	1.2
Nonbasic				
N-alkylcarbazoles	0.012	0.047	0.8	2.5
Alkylpyrroles/indoles/carbazoles/nitriles	0.171	0.312	12.6	16.7
Alkylanilides/N-acetylindoles	0.006	-	0.5	-
Alkylbenzamides	0.100	0.114	7.3	6.1
Alkylazaindoles/diazaaromatics	0.044	-	3.3	-
Total	1.28	1.71	94	92

Effect of Catalytic Hydrotreatment on Nitrogen Compound Types - In earlier work (3), different nitrogen compound types were shown to have different reactivities toward catalytic hydro-treatment. The ease of hydrogenation of nitrogen types from least to most difficult are: amides, pyridines, pyrroles and hindered alkylpyridines. Amounts of these compound types in the light oils from tests 4 and 5, respectively, are determined from Table IX: amides (19 and 10%), pyridines (22 and 25%), pyrroles (29 and 36%), hindered pyridines (12 and 12%). Earlier compositional studies (4) of crude and hydrotreated western (Green River) and eastern (Sunbury and New Albany) shale oils produced by IGT in the Hytort Process Development Unit were used to establish the amount of nitrogen removal by catalytic hydrotreatment as a function of the nitrogen compound-type distribution in the crude shale oil (HDN factor). The hydrotreating conditions used in establishing the relationship were: 2000 psia (13.8 MPa) hydrogen pressure, 800°F (428°C) catalyst temperature, LHSV of 0.4 and nickel/molybdenum catalyst. Details of deriving the relationship are summarized elsewhere (7). Allowing for differences in the total nitrogen content of the light oils, the HDN factors for these oils from tests 4 and 5 were calculated to be 1.02 and 0.69, respectively. Projections of the amount of nitrogen removal based on Figure 4 and the calculated HDN factors show that at the quoted hydrotreatment conditions about 95% of the nitrogen in the light oil from test 4 and 84% of the nitrogen in the light oil from test 5 may be removed. Presumably, the greater severity of processing conditions employed in test 5 produces a light oil containing more nitrogen in more nonreactive nitrogen compounds than that in the oil from test 4. This may result in decreased nitrogen removal during catalytic hydrotreatment of test 5 light oil.

SUMMARY AND CONCLUSIONS

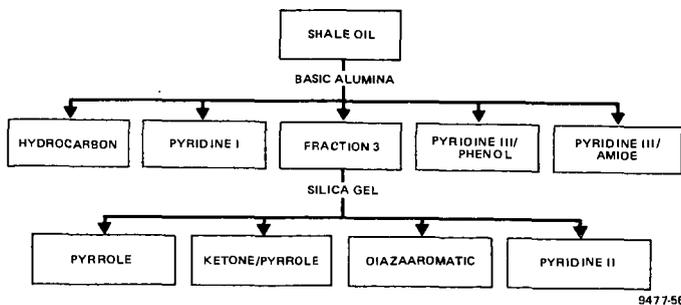
The chemical composition of shale oils produced by flash hydrolysis is dependent on process conditions. The atomic H/C ratios of light and heavy oils decrease with increasing process severity, while the nitrogen content increases. In contrast, process severity seems to have little effect on either H/C or nitrogen content with the BTX oils, which comprise less than 10% of the liquid products. For light, heavy and BTX oils, olefinic content decreases, aromatic content increases, aliphatic content decreases and basic nitrogen increases with increasing severity.

Increasing process severity converts more refractory compounds of the kerogen in shale to liquids and simultaneously converts labile liquids to gases by cleaving alkyl groups from aromatic



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Figure 1. Simplified schematic of Rockwell 1-ton/h liquefaction PDU



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Figure 2. Scheme for the fractionation of shale oils from Rockwell FHP Tests 4 and 5 into compound-type fractions.

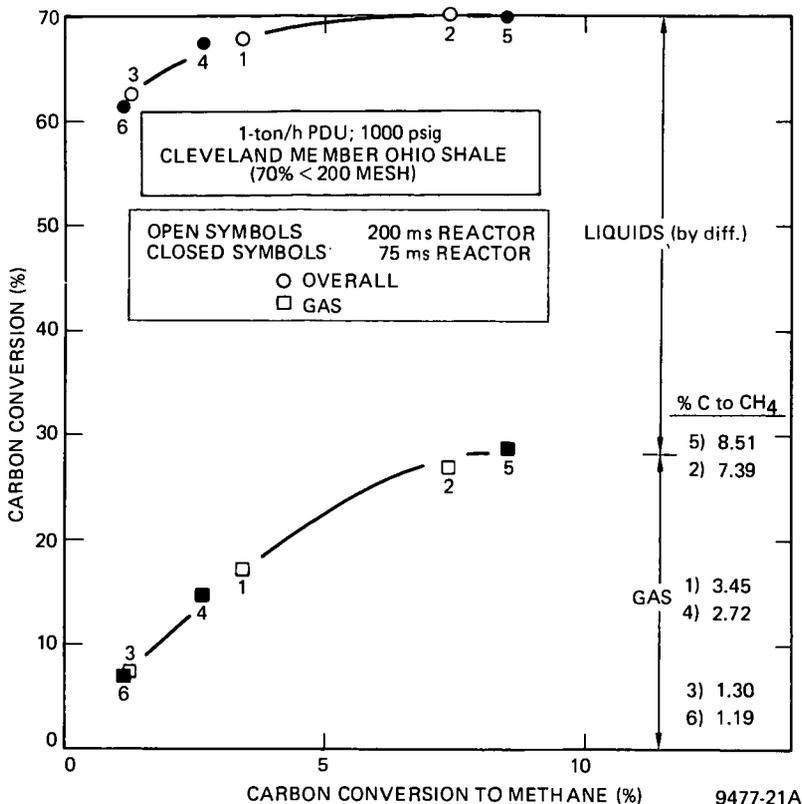


Figure 3. The effect of reactor severity on carbon conversion.

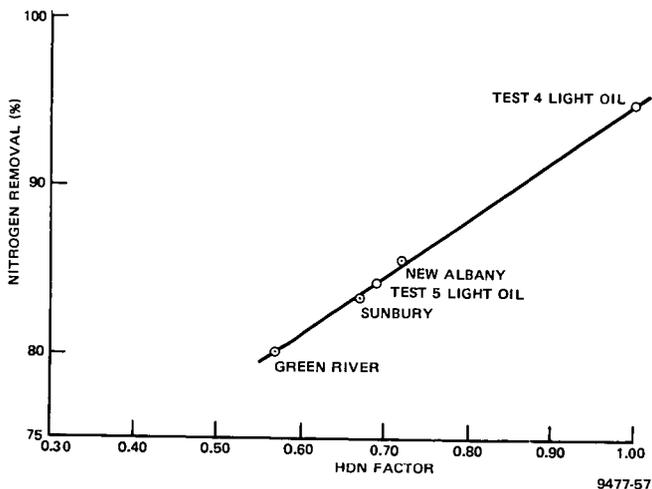


Figure 4. Relative ease of nitrogen removal from light oils from Tests 4 and 5 by catalytic hydrotreatment.

rings. This results in liquids of high-aromatic, low-olefinic and low-aliphatic content. In general, increasing process severity produces oils containing greater amounts of nitrogen in compounds less susceptible to hydrogenitrogenation. It suggests that increasing the severity of hydrotreating will be required to reduce their nitrogen content.

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