PRODUCT DISTRIBUTION FROM THE HYDROGEN DONOR CONVERSION OF EASTERN U.S. SHALE

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INTRODUCTION

Extensive deposits of oil shale have been found[1] in the Eastern U.S. While these deposits are reasonably rich in organic carbon content, the shales yield only about 10 gal/ton of rock by simple retorting, Fischer Assay (FA). This represents only about one-third of the available carbon, so techniques, such as hydrogen donor solvation, are being applied to increase carbon recovery. The objective of this paper is to summarize yield data from the conversion of two Eastern U.S. shales and to provide a characterization of products from two representative runs.

EXPERIMENTAL

Two samples of Eastern U.S. shales were used. The first was taken from the Hilpat site (Fleming Co., KY), and it is classified as a Cleveland member, Ohio shale. The second shale was mined at the Black Shale No. 1 site, Marysville (Clark Co., IN). It is a Clegg Creek member, New Albany (Devonian) shale. The shales had Fischer Assays of 10.1 and 11.8 gal/ton and carbon contents of 12.2 and 12.0, respectively. The solvents were obtained from Fisher Scientific, and they were used as received.

The experiments were made in a "cascade unit" consisting of a series of three reactors arranged such that a feed slurry of shale with solvent, tetralin, was injected from a feed tank into a preheated reactor. After the reaction period of 1 hr, the products were quickly transferred into a cold receiver, from which they were recovered for analysis. The amount of slurry retained in the feed tank was determined by toluene flushing and Soxhlet extraction. The gases were analyzed using a Carle 111A unit. The liquid portion of the raw slurry product was analyzed by GC/MS (Finnigan 9600). The raw slurry was filtered; the filtrate was stripped (N_2 @ 90°C) to recover "reactor residue", and the cake was Soxhlet extracted to recover toluene insolubles and asphaltenes. The reactor and receiver were also flushed with toluene and the slurry was analyzed as shown in the material balances of Figures 1 and 2. In summary, the products consisted of gases, distillate (the

liquids identified by GC/MS boiling between C_4 and about C_{20}, but excluding donor solvent, namely tetralin, naphthalene, 1-methylindan, and butylbenzene), reactor residue (bottoms from filtrate stripping), asphaltenes (toluene solubles from Soxhlet extraction), and toluene insolubles.

A material balance of the Indiana shale run (445°C, 60 min) is given in Figure 1. Of the 148 g of moisture free (MF) shale placed in the feed tank, 104 g was transferred to the reactor. This shale was recovered as 93 g toluene insolubles, 1.3 g asphaltenes (toluene solubles), 3.4 g reactor residue, 2.4 g distillates, and 2.8 g of gases (including H_2S, CO_2, etc. but not including N_2 transfer gas). On a mineral matter basis, recovery was 98%, and on a carbon basis, namely shale carbon fed vs product carbons (excluding solvent) the balance was 96.6%.

A comparable run was made with Hilpat shale (see Figure 2). Of the 146 g MF shale charged, 141 was transferred to the reactor. The shale was recovered as 121 g toluene insolubles, 3.9 g asphaltenes, 2.6 g reactor residue, 4.4 g distillate, and 2.2 g gases (but H_2S was not determined). The material balance of mineral matter was about 98%, and the carbon balance was 99.6%.

Using as a basis 100 units of organic carbon in the feed shale, the overall distribution of product fractions from both the FA and donor solvent runs is given in Table 1. The product fractions are categorized as shale-derived or solvent-derived. All hydrocarbon gases are assumed to be shale related. With the exception of solvent dimers (i.e. ditetralin, etc.), all distillates are assumed to be shale-derived. Adducted tetralin and naphthalene derivatives, as estimated from ^1H and ^{13}C NMR, are reported as such. Toluene insolubles are considered to be unconverted shale. (All of these assumptions will be discussed below.)

Gases

The yields of gases from the FA pyrolyses were essentially the same as those of the donor solvent runs, namely about 12% for Indiana shale and 6% for Hilpat shale. On a carbon basis, the distribution of gases was $C_1 > C_2 > C_3 > C_4+ > CO_2 + CO$.

Distillates

The recoveries of distillate, designated oil, from the FA pyrolysis of Indiana and Hilpat shales were 11.8 and 10.0 gal/ton or 32 and 29% carbon recoveries. The oils had similar levels of hydrogen (10.1 wt%), nitrogen (1.2 wt%), and sulfur (1.6 and 1.8 wt%). The Hilpat-derived oil contained more oxygen, though (3.1 vs 1.7 wt%).

As shown in Figures 3 and 4, the boiling point distributions of the two oils were greatly different. The Hilpat oil was of much higher boiling point, and it also contained a regular pattern of alkyl components above the broad envelope of compounds. The MS signals of about 105 primary components

of both fractions were characterized. The distributions of the compound classes are shown in Table 2. While both oils contained the same level of alkanes (25%), Hilpat oil contained more alkanes (17 vs 10%). The Indiana derived oils had much higher levels of cycloalkanes and cycloalkenes (15 and 11% vs 4 and 0.5%, respectively). While both oils had comparable levels of alkylbenzenes (27-30%), the Hilpat-derived oil contained much higher levels of alkyl naphthalenes and indanes (13 and 10% vs 1 and 2%, respectively). In summary, the Indiana shale oil contained more cycloparaffins while the Hilpat shale oil contained more alkyl naphthalenes and indanes.

The compilation of GC/MS results of the donor solvent runs are also given in Table 2. While the distillate product of the pyrolysis of Indiana shale is about evenly divided between paraffins, cycloparaffins and substituted benzenes (C_1 through C_6), the donor solvent product has these components in addition to naphthalenes and hydronaphthalenes. In the case of Hilpat shale, pyrolysis distillate primarily consists of paraffins, benzenes and naphthalenes, and the donor process results in an increase in the level of naphthalenes and hydronaphthalenes.

Several aspects should be considered in discussing the above yields. First, Eastern shale is somewhat coal-like and aromatic systems would be expected in the product. Second, pyrolysis results in the rupture of bonds, and the abstraction of available hydrogen from sources such as hydronaphthalenes. Third, there is a high level of basic catalytic surface available which would promote alkylation, isomerization, and dimerization. Therefore, tetralin and naphthalene available from the solvent system are likely to become alkylated if free alkyl groups are available from the cracking of shale kerogen.

It appears that all of these aspects are present with major differences between the two shales. In the case of Indiana shale, much less solvent dimerization is observed than with Hilpat shale, namely 0.1 out of 15.7% distillate yield versus 2.3 out of 23.6%. It would appear that the rock matrix of the Indiana shale would have a relatively low activity for alkylation, and therefore, much of the high yield of naphthalenes and hydronaphthalenes may be shale-derived. Fortuitously, an Indiana run (430°, 30 min) was made in which some flush toluene was left in the reactor from a previous clean-up. The ratio of toluene to tetralin (or shale) was about 3:1. A high yield of alkylbenzenes was observed (28% vs 11%). In particular, 15% of the total distillate product was xylene, while the normal yield is 1-2%. The yield of ethylbenzene was 8.8%, while the normal yield is about 3%. Due to an apparent high level basicity of Hilpat shale and because a high yield of dimers is observed in the distillate product (i.e. 10% of the distillate; 2% of the total product), it would appear that even more transalkylation occurred in the processing of Hilpat shale.

As a test of transalkylation, two micro-autoclave experiments were made at 450°C and an hr reaction period using equal charges of Hilpat shale and tetralin. The first run was made with commercial tetralin, and the second with tetralin having a ^{13}C label at the α-position. Experimental techniques

are summarized in reference 2. The distillate liquids from both runs were characterized by GC/MS. Specific chromatographic peaks that appeared to be solvent-derived were studied by examining the most intense ion and the corresponding ^{13}C ion to calculate the amount of that component due to ^{13}C-labeled solvent.

In the case of 1-methylnaphthalene, 78% of this product in the distillate was derived from the donor solvent (^{13}C-tetralin) and 22% from the shale. The following specific components were also identified as being donor solvent-derived: 2-methylnaphthalene-86%, 1-ethylnaphthalene-82%, 2-ethylnaphthalene-88%, 1-methyltetralin-86%, ethyltetralin-88%, and propyltetalin-86%. In summary, about 70% of the naphthalene and tetralin subfractions of the distillate of the Hilpat run was solvent-derived after the alkylcarbons are subtracted off. Therefore, of the 21.3% "shale-derived" distillates listed in Table 1 for Hilpat shale, about 6.0% may actually be solvent-derived with the remaining 15.3% being shale-derived. (While the catalytic activity of the Indiana shale appears to be low, a detailed experiment would be necessary to confirm that less transalkylation would occur than that observed with Hilpat shale.)

Heavy Liquids

The heavy liquid products of the donor solvent runs consisted of asphaltenes and reactor residue; no appreciable toluene extractables were found in the FA solids. The following table summarizes the analyses of the combined heavy fractions from the Hilpat and Indiana runs:

Element	Carbon	Hydrogen	H/C	Nitrogen	Oxygen	Sulfur
Shale						
Indiana	82.4	7.1	1.03	2.4	2.3	5.8
Hilpat	86.3	7.1	0.99	1.9	1.5	3.2

In summary, the H/C ratios of these heavy products were essentially the same and the Indiana shale-derived product was higher in heteroatom content. As a note: the reactor residues were higher in hydrogen, nitrogen and oxygen than the asphaltenes, but lower in sulfur.

The characteristics of the residue and asphaltene fractions were examined by ^{1}H and ^{13}C NMR using experimental techniques outlined in another paper presented at this meeting.[3] Spectra contain a large number of sharp signals in the aromatic region. These sharp signals are due to the presence of trimers and adducted species produced from the solvents. The broad underlying resonance in the aromatic region is due to aromatic material from the shale. The aromaticities of these oils are high, in the range of 75-80% of the total carbon. The aromatic region can be divided into three basic regions; substituted alkyl/aryl/heteroatom (133.5 ppm - end of aromatic); bridge carbon (133.5-129.5 ppm); and non-substituted aromatic carbon. In addition, an estimate of the aromatic carbon from tetralin/naphthalene is made

and given in Table 3. Another structural parameter available from ^{13}C NMR is the chain ratio. The higher the chain ratio the longer the chain. However, an average chain length cannot be computed in this case because the sample is a mixture of aromatic and aliphatic structures. The aliphatic structural parameters given in Table 3 are from 'H NMR which gives a better analysis of this region than ^{13}C NMR.

An examination of the NMR data given in Table 3 shows that the asphaltenes derived from the two shale samples are similar. A comparison of the asphaltenes of the two shales shows slight differences in the aliphatic carbon, α to aromatic carbon content, hydroaromatic content and long chain content. The higher α to aromatic carbon content in the Indiana shale liquid is in agreement with the larger amount of alkyl substituted aromatic carbon. The slightly higher level of hydroaromatic carbon in the Hilpat shale is due to both tetralin and to hydroaromatic structures in the shale. The higher level of long chain material in the Hilpat shale corresponds with the higher chain ratio in this sample.

The Indiana spectra have more sharp lines than the Hilpat spectra in the aromatic region indicating the presence of more adducted tetralin and naphthalene. This is also reflected in the naphthalene content of the Indiana shale heavy product. The Indiana shale heavy product also has more heteroatom/aryl substituted aromatic carbon than does the Hilpat. This is partially due to both adducted naphthalene and to the higher heteroatom content of the Indiana asphaltenes.

Rock Matrix, Minerals

Due to apparent different catalytic properties of the two shales, an x-ray mineral analysis was done using a Philips APD-3100 diffractometer. The results were analyzed using a technique, "X-Ray Powder Diffraction Search System," of G. G. Johnson of Penn State University. While both the Indiana and Hilpat shales have quartz (50-60%) and montmorillonite (6-10%) as major components, the Hilpat shale contains more alkali metal (Na, K) components than does the Indiana shale. As pointed out by K. Tanabe[4], the more basic a catalyst (or clay), the more likely that it is to promote polymerization, isomerization and alkylation. This observation is consistent with the results discussed herein.

CONCLUSIONS

Extensive conversion of two samples of Eastern U.S. Shale has been accomplished using a hydrogen donor solvent system in a DOE sponsored project. In a series of previously reported autoclave runs, the extent of conversion of the organic carbon varied from 20 to 75% depending upon temperature, reaction time, and solvent type. As a comparison, the Fischer Assay (FA) conversions of these shales were about 40%. Selected products from the FA runs and two "cascade unit" (slurry injection) runs made at 450°C and 1 hr using a donor-solvent process were analyzed by elemental, GC/MS, and NMR techniques. The yields of gases from the donor-solvent and FA processes were

about equivalent. More distillates were recovered from the FA runs but heavy fractions were recovered from the donor-solvent process while not present from the FA runs. Compositional trends observed in the FA liquids, such as high levels of alkanes and cycloalkanes, appeared to carry over into the liquids from the donor-solvent systems. Two experiments were made using either unlabeled or ^{13}C-labeled donor solvent, tetralin, to isolate solvent derived products from those generated from the kerogen. It was shown that a high level of transalkylation occurred between the shale-derived species and the solvent; therefore, a portion of the donor solvent can appear in the higher boiling distillate fractions. Similarly, a sizable level of solvent adduction with the shale-derived heavy fractions occurs. These reactions appear to be related to shale basicity.

ACKNOWLEDGMENT

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3. Galya, L. G., Cronauer, D. C., and Solash, J., "Adduction in Donor Solvent Conversion of Eastern Oil Shale," ACS Chicago Meeting, 1985.

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Table 1

Distribution of Products on a Carbon Basis

Shale	Indiana		Hilpat	
Run Conditions (°C/MIN)	F.A. 500/40	Tetralin 445/60	F.A. 500/40	Tetralin 441/60
Yield (on Carbon)				
Gases	12.7	11.1	5.8	6.6
Distillates				
Shale-derived	32.5	15.6	29.3	21.3
Solvent-derived(1)	--	0.1	--	2.3
Total	32.5	15.7	29.3	23.6
Reactor Residue				
Shale-derived	--	18.7	--	12.2
Solvent-derived(2)	--	3.0	--	1.2
Total	0.0	21.7	0.0	13.4
Asphaltenes				
Shale-derived	--	7.0	--	18.0
Solvent-derived(2)	--	1.1	--	1.7
Total	0.0	8.1	0.0	19.7
Toluene Insolubles	60.3	40.0	60.3	36.3
Total Shale-derived	105.5	92.4	95.4	94.4
Total Solvent-derived	0.0	4.2	--	5.2
Total	105.5	96.6	95.4	99.6

Notes: (1) Dimers, only; a part of the shale-derived distillate may be alkylated solvent, though - see text.

(2) Tetramers plus adducted solvent.

Table 2

Compound Classification of Distillates

Run No.	Indiana Shale Fischer Assay	Indiana Shale Donor Run	Hilpat Shale Fischer Assay	Hilpat Shale Donor Run
Distribution (RIC area %)				
Alkanes	26.2	25.7	24.9	18.7
Alkenes	10.0	0.2	16.5	0.0
Cycloalkanes	15.5	13.7	4.2	6.6
Cycloalkenes	10.7	2.0	0.5	1.2
Alkylbenzenes	30.0	11.9	26.6	13.7
Alkylnaphthalenes	1.2	21.9	12.8	22.2
Indanes	2.3	4.5	12.0	16.2
Alkyltetralins and H_x naphthalenes	--	13.4	--	21.4
Heterocompounds	4.1	6.7	2.5	--
	100.0	100.0	100.0	100.0

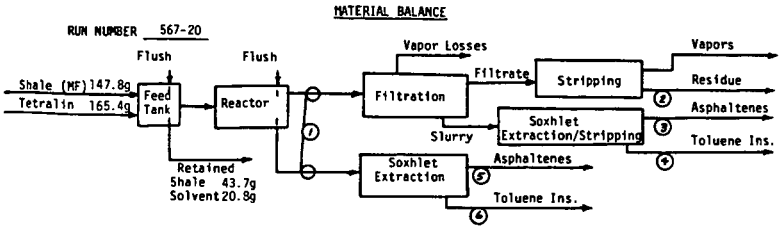
Table 3

Structural Parameters From 'H and ^{13}C NMR of Asphaltenes Derived From the Donor Solvent Conversion of Indiana and Hilpat Shales

Shale		Indiana		Hilpat
% Aromatic Carbon				
% alkyl substituted	8.9		7.0	
% heteroatom/aryl substituted	20.9		15.4	
total alkyl or heteroatom/aryl substituted		29.8		22.4
% bridge carbon		10.1		10.9
% non-substituted carbon		37.6		43.8
Total Aromatic Carbon		77.5		77.1
% Aliphatic Carbon				
% α methyls		4.3		3.7
% α CH_2		4.6		3.3
% hydroaromatic		3.2		4.4
% long chain material		10.4		11.5
Total Aliphatic Carbon		22.5		22.9
Chain Ratio		2.6		3.9
Adducted Solvent				
% tetralin*		0.0		0.7
% naphthalene*		13.1		8.0

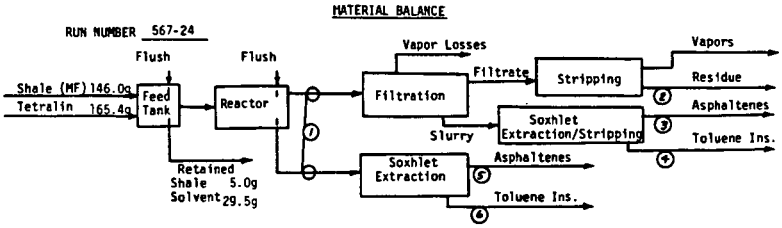
* Present as adducted species or trimers or tetrimers; no monomers or dimers were observed by GC techniques.

FIGURE 1 MATERIAL BALANCE OF THE INDIANA SHALE CASCADE UNIT RUN



Stream:					Reactor		Flush	
Designation	Shale Feed	Gases	Distillate	Residue	Asphaltene	Toluene Ins	Asphaltene	Toluene Ins
Number	-	-	1	2	3	4	5	6
Amount, grams								
Carbon	12.92	1.44	2.03	2.81	0.13	0.39	0.92	4.78
Hydrogen	1.50	0.79	0.29	0.26	0.01	0.05	0.07	0.46
Nitrogen	0.36	--	0.03	0.08	0.00	0.02	0.03	0.19
Oxygen	--	0.38	0.03	0.09	0.01	0.24	0.02	(2.88)
Sulfur	5.02	0.14	0.00	0.12	0.01	0.28	0.14	3.01
Total (incl. minerals)	104.13	2.75	2.39	3.36	0.16	7.02	1.18	85.87

FIGURE 2 MATERIAL BALANCE OF THE HILPAT SHALE CASCADE UNIT RUN



Stream:					Reactor		Flush	
Designation	Shale Feed	Gases	Distillate	Residue	Asphaltene	Toluene Ins	Asphaltene	Toluene Ins
Number	-	-	1	2	3	4	5	6
Amount, grams								
Carbon	16.89	1.12	3.98	2.27	0.75	1.39	2.57	4.75
Hydrogen	1.87	0.22	0.44	0.18	0.06	0.17	0.21	0.54
Nitrogen	0.58	--	--	0.06	0.02	0.08	0.04	0.23
Oxygen	7.34	0.30	--	0.04	0.01	--	0.04	--
Sulfur	3.34	ND	--	0.05	0.04	0.44	0.12	1.34
Total (incl. minerals)	141.00	--	4.42	2.60	0.88	29.38	2.98	91.45

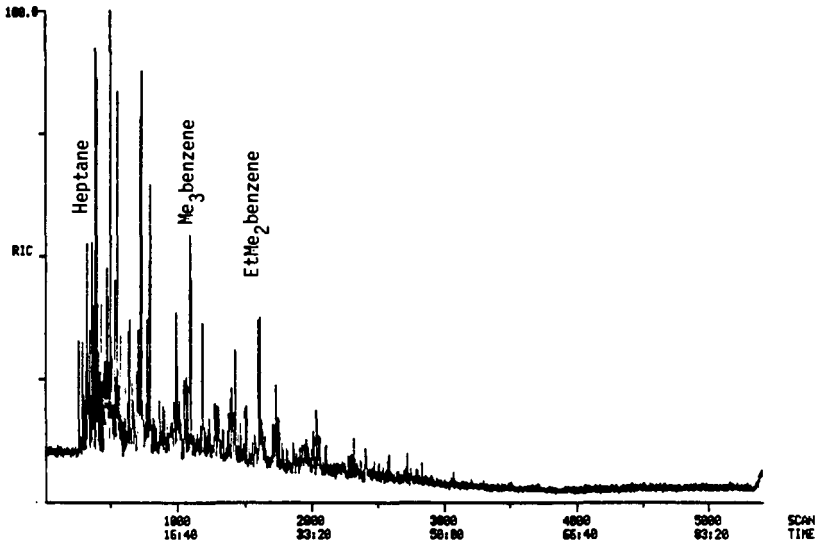


FIGURE 3 GC/MS (RIC) SCAN OF INDIANA SHALE FA OILS

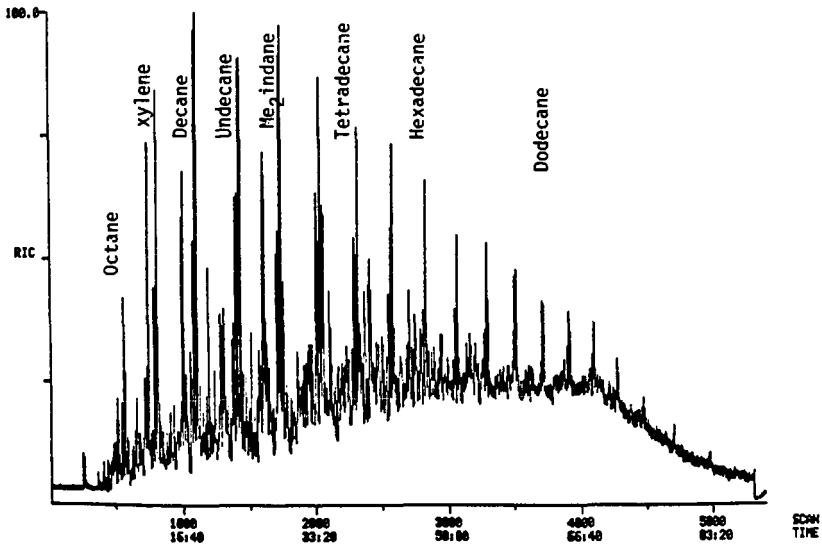


FIGURE 4 GC/MS (RIC) SCAN OF HILPAT SHALE FA OILS