

## NITROGEN TYPES IN SYNCRUDES FROM IN SITU CRUDE SHALE OIL

C. M. Frost and R. E. Poulson

Energy Research and Development Administration,  
Laramie Energy Research Center, Laramie, Wyoming 82070

## INTRODUCTION

Crude shale oils produced by in situ combustion retorting of Green River oil shale contain more than twice as much nitrogen as high-nitrogen petroleum crudes. Because existing refineries would not be able to cope with the high nitrogen content of shale oil if it were a substantial part of the refinery feed, the National Petroleum Council (NPC) has suggested (1) that crude shale oil be upgraded at the retorting site by a process of catalytic hydrogenation to produce a premium feedstock called "syncrude."

We have already shown (2) that a premium refinery feedstock can be produced from in situ crude shale using methods suggested by the NPC. We have also determined (3) the nitrogen-compound types remaining in the finished syncrude since it would be these compounds with which a refiner would have to deal if he used a similar crude in his refinery feed.

In the NPC process, the crude shale oil is distilled to produce naphtha, light oil, heavy oil, and residuum. The residuum is processed in a delayed-coking unit to produce petroleum coke and a vapor stream. The vapor stream from the coking unit flows back to the crude distillation unit for separation into various fractions. The naphtha, light oil, and heavy oil are subsequently hydrogenated to remove nitrogen and sulfur and to reduce the viscosity and pour point of the finished syncrude.

One alternate method of preparing syncrude from crude shale oil would be to hydrogenate the total crude shale oil in a one-step process. This would not only reduce the number of processing units required at the retorting site, but could result in higher yields of liquid and gaseous products since the coking step would be eliminated.

The purpose of the present work was to prepare a syncrude of total nitrogen content comparable to that of an NPC-type syncrude produced earlier (2-3) by catalytically hydrogenating the total in situ crude shale oil in one step, and to determine the amounts and types of nitrogen compounds remaining in the finished syncrude. Yields of products, properties of the finished syncrude, and amounts and types of nitrogen compounds remaining in the one-step syncrude are compared with those of a multistep syncrude prepared by an NPC-type process.

## PROPERTIES OF IN SITU CRUDE SHALE OIL

The crude shale oil used in this work, the same as that used in our previous studies (2-3), was obtained from an in situ combustion retorting experiment near Rock Springs, Wyo., during the last week of the experiment. It is considered to be a representative "steady state" oil. Properties of the in situ crude shale oil are shown in table 1.

## ANALYTICAL METHODS

Standard ASTM procedures were used wherever practicable. Catalyst deposit percentages were calculated from the weights of carbon dioxide collected on ascarite when the deposits were burned with a stream of air passed through the reactor at the end of a run. Hydrogen consumption was calculated from precise measurements of the amount of hydrogen fed to the unit and that collected in the product gas. Total nitrogen values in the oils were determined with a reductive, hydrogen-nickel

TABLE 1. - Properties of in situ crude shale oil

Gravity, ° API	28.4
Nitrogen, weight-percent	1.41
Sulfur, weight-percent	0.72
Pour point, ° F	40
Viscosity, SUS at 100° F	78
Carbon residue, weight-percent	1.7
Ash, weight-percent	0.06

pyrolysis tube and an ammonia microcoulometer. Sulfur values were determined with an oxygen combustion tube and a sulfur dioxide microcoulometer. Samples were water washed. Samples for sulfur analysis were also extracted with mercury and filtered.

Nonaqueous potentiometric titration (4-7) was used to classify the nitrogen types into weak-base (pKa + 2 to + 8), very weak-base (pKa - 2 to + 2), and neutral types (nontitratable). Infrared spectrometry (6-8) was used to determine the concentration of pyrrolic N-H type nitrogen (which includes carbazoles). Colorimetry (with p-dimethylaminobenzaldehyde) (6, 9-10) was used to determine pyrroles and indoles with an unsubstituted  $\alpha$  or  $\beta$  position which are termed here pyrrolic nitrogen (excludes carbazoles).

#### EXPERIMENTAL

The total in situ crude shale oil was hydrogenated over a presulfided, nickel-molybdenum catalyst in a fixed-bed, bench-scale unit. The crude oil was mixed with 5,000 scf of hydrogen per barrel and passed downflow over the catalyst bed at a rate of 0.7 weight of oil per weight of catalyst per hour ( $W_o/W_c/hr$ ). The catalyst was contained in a stainless steel reactor. The temperature of the reactor was maintained at 815° F by means of a four-zone electric furnace, each zone of which was independently controlled. Pressure in the reactor was maintained at 1,500 psig by means of a backpressure regulator, and liquid products were collected in a separator maintained at 200 psig. Tail gas from the separator was metered and sampled. The hydrogenation was accomplished in a continuous 10-day run.

Liquid products were drained from the separator after each 24-hour period of operation and washed with water to remove ammonia and hydrogen sulfide before a sample was taken for analysis. Aliquot portions of the daily liquid products were combined to form the finished syncrude. A portion of the syncrude was then fractionated to obtain a C<sub>5</sub> - 175° F light naphtha, a 175°-350° F heavy naphtha, a 350°-550° F light oil, and a 550° F+ heavy oil. Preparation of the multistep syncrude was described in detail earlier (2) but consists basically of a distillation unit, a delayed coker, and three catalytic units for hydrogenations of heavy oil, light oil, and naphtha separately.

#### RESULTS AND DISCUSSION

In table 2, the yields of products from hydrogenation of the total in situ crude shale oil (one-step) are compared with yields of products from separate hydrogenation of various distillate fractions (multistep) (2). The yield of C<sub>4</sub>+ liquid product was 104.5 volume-percent for the one-step process and 103 volume-percent for the multistep process. The yield of C<sub>5</sub>+ liquid product was only slightly higher for the one-step process, but there was a substantial decrease in the yield of heavy oil with a corresponding increase in the yields of gas, naphtha, and light oil. Hydrogen consumption was somewhat higher for the one-step process (1,475 scf/bbl versus 1,280 scf/bbl) as the result of the increased depth of conversion.

TABLE 2. - Comparison of product yields from multistep and one-step hydrogenation of in situ crude shale oil

Product, percent of crude	Multistep		One-step	
	Weight	Volume	Weight	Volume
C <sub>4</sub> + liquid product	93.81	102.99	95.27	104.54
C <sub>5</sub> + liquid product	92.66	101.24	93.42	101.67
C <sub>5</sub> - 175° F light naphtha	2.34	2.96	2.62	3.33
175°-350° F heavy naphtha	19.60	22.65	21.14	24.20
350°-550° F light oil	45.68	49.45	51.44	55.03
550°-850° F heavy oil	25.04	26.18	18.22	19.11
Coke (catalyst deposit)	<sup>1/</sup> 3.24			0.13
Hydrogen	<sup>2/</sup> -2.19		<sup>3/</sup> -2.53	
Methane	0.69		1.31	
Ethane	0.68		1.37	
Ethylene	0.03		-	
Propane	0.72		1.41	
Propylene	0.09		-	
Isobutane	0.26	0.41	0.46	0.76
Butane	0.79	1.20	1.39	2.11
Butenes	0.10	0.14	-	
Ammonia	1.57		1.69	
Hydrogen sulfide	0.62		0.75	

<sup>1/</sup> Multistep process includes a coking step.

<sup>2/</sup> 1,280 scf/bbl.

<sup>3/</sup> 1,475 scf/bbl.

Table 3 shows the effect of operating time on the nitrogen contents and gravi-

TABLE 3. - Effect of operating time on nitrogen contents, denitrification rate constants and gravities of liquid product

Days on stream	Nitrogen content of liquid product, ppm	Denitrification rate constant $\ln N_0/N_t (.7)$	Gravity, ° API
1	51	5.26	44.2
2	83	4.79	43.8
3	148	4.20	43.8
4	177	4.00	43.3
5	195	3.92	43.2
6	207	3.86	43.2
7	238	3.72	43.2
8	306	3.47	43.1
9	316	3.44	43.1
10	338	3.37	43.0

ties of the liquid products. Under the conditions used in this experiment there was a significant decrease in the activity of the catalyst during the course of the run. This indicates that crude shale oil could not be processed under these severe conditions in a fixed-bed unit without frequent regeneration of the catalyst.

Properties of the syncrudes and their various distillate fractions are shown in table 4. Sulfur contents of both of the syncrudes discussed was near the lower

TABLE 4. - Comparison of syncrudes and distillate fractions from multistep and one-step hydrogenation of in situ crude shale oil

	Multistep	One-step
Syncrude, volume-percent of in situ crude	102.99	104.50
Gravity, ° API	43.9	44.6
Nitrogen, ppm	250	225
Sulfur, ppm	5	6
Butanes and butenes, volume-percent of syncrude	1.7	2.7
C5-350° F naphtha, volume-percent of syncrude	24.8	26.3
Gravity, ° API	54.7	53.4
Nitrogen, ppm	1	83
Sulfur, ppm	8	3
350°-550° F light oil, volume-percent of syncrude	48.1	52.7
Gravity, ° API	41.5	38.5
Nitrogen, ppm	79	200
Sulfur, ppm	1	5
550° F+ heavy oil, volume-percent of syncrude	25.4	18.3
Gravity, ° API	35.6	36.2
Nitrogen, ppm	935	513
Sulfur, ppm	9	5

level of experimental uncertainty. Although sulfur could be detected down to 0.5 ppm, the significance of a few parts per million is doubtful because of difficulty in removing hydrogen sulfide and colloidal sulfur. The total nitrogen contents of the syncrudes were essentially equal; however, there were substantial differences in the distribution of nitrogen in the distillate fractions.

In table 5, the distribution of nitrogen in the two syncrudes and their distillates is shown. Although total nitrogen in the two syncrudes is comparable, it is seen that the nitrogen in the one-step syncrude occurs in significantly higher concentrations in the heavy naphtha and light oil fractions and in lower concentration in the heavy oil fraction in comparison with the multistep syncrude.

In table 6 the nitrogen distributions as percent of total nitrogen in the syncrudes and their distillates is summarized according to basic and neutral types. Almost all (86.5 percent) of the nitrogen in the multistep syncrude appears in the heavy oil, but for the one-step syncrude only about half (49.7 percent) appears in the corresponding distillate. The neutral nitrogen in these heavy oils is about 40 percent of the total nitrogen in the syncrude. This neutral nitrogen appears to be largely carbazole type in either oil. This can be inferred from table 5 by the large values for N-H type nitrogen and small values for ( $\alpha$  or  $\beta$  unsaturated) pyrrolic-type nitrogen. A predominance of carbazole structures was indicated by mass spectrometry in the characterization of the multistep heavy oil (3), but mass spectrometry was not used in characterization of the one-step syncrude. The fate of the neutral nitrogen then appears similar in either multistep or one-step processing; the neutral type concentrating in the heavy oil while other, more readily hydrogenated types react.

As shown in table 6 the amounts of basic nitrogen (weakly basic plus very weakly basic nitrogen) relative to the total nitrogen is similar for the two syncrudes, but differs markedly for the corresponding distillate fractions in the two oils as does the occurrence of primary and secondary amines. In the multistep



TABLE 6. - Basic and neutral nitrogen distribution in syncrudes and their fractions

	Nitrogen, percent of total in syncrude			
	Total	Basic	Neutral	I°, II° amines <sup>1/</sup>
Syncrude <sup>2/</sup>	100	60.0	40.0	0
Syncrude <sup>3/</sup>	100	64.4	35.6	3.5
Light naphtha <sup>2/</sup>	0	0	0	0
Light naphtha <sup>3/</sup>	0	0	0	0
Heavy naphtha <sup>2/</sup>	0	0	0	0
Heavy naphtha <sup>3/</sup>	10.6	10.5	0.1	2.2
Light oil <sup>2/</sup>	13.5	13.5	0	0
Light oil <sup>3/</sup>	39.7	34.9	4.8	2.0
Heavy oil <sup>2/</sup>	86.5	42.9	43.6	0
Heavy oil <sup>3/</sup>	49.7	12.9	36.8	0

<sup>1/</sup> I° and II° amines included in basic nitrogen.

<sup>2/</sup> Multistep.

<sup>3/</sup> One-step.

syncrude, the weakly basic nitrogen compound types were shown to be largely pyridines, and the very weakly basic nitrogen compound types were shown to be largely pyrroles and indoles by a combination of techniques including mass spectrometry. Although mass spectrometry was not used in characterization of the one-step syncrude, the compound types are probably similar.

Presence of large amounts of nitrogen in the light oil and heavy naphtha of the one-step syncrude can be attributed to hydrocracking and thermal cracking reactions in the heavy oil and residual portions of the crude. Buildup of nitrogen compounds in the lighter oil products from heavy oil hydrogenation in the multistep syncrude production was observed in earlier work (3). This lighter oil produced from the heavy oil hydrogenation is then hydrogenated in the various lighter oil reactors in the multistep process (2). The basic types are readily converted to ammonia as found by others (4, 12) and as evidenced by the relatively mild conditions required to reduce the nitrogen content in the fractions boiling below 550° F to the low values in table 6 (2).

The occurrence of small amounts of primary and secondary amines in both the heavy naphtha and light oil fractions from the one-step syncrude is consistent with the work of Brown (11) who found anilines made up nearly one-third of the tar bases from a recycle, hydrocracked shale-oil naphtha. None of these amines were found in the multistep syncrude product although anilines were identified in intermediate fractions (light oil products from the heavy oil hydrogenation unit). In the multistep process these amines are removed readily in the lighter oil reactors as part of the basic types which were discussed in general earlier.

#### SUMMARY

Total crude shale oil produced by underground combustion retorting was hydrogenated in one step over a nickel-molybdenum catalyst at an operation temperature of 815° F, an operating pressure of 1,500 psig, and a space velocity of 0.7  $W_o/W_c/hr.$  A high yield (104.5 volume-percent) of synthetic crude oil, called a one-step syncrude, containing 225 ppm total nitrogen was attained. Hydrogen

consumption was 1,475 scf/bbl. A combination of microcoulometry, nonaqueous potentiometric titration, colorimetry, and infrared spectroscopy was used to determine the amounts and types of nitrogen compounds present in the syncrude and its various distillate fractions.

Light naphtha comprised 3.2 percent of the syncrude and contained no nitrogen. Heavy naphtha comprised 23 percent of the syncrude and contained 83 ppm nitrogen. The light oil comprised 53 percent of the syncrude and contained 200 ppm nitrogen, and the heavy oil comprised 18 percent of the syncrude and contained 513 ppm nitrogen.

The nitrogen compounds in the naphtha were shown to be 95 percent weak base of which 6 percent were primary and secondary amine types, 4 percent very weak base, and 1 percent neutral compounds. Nitrogen compounds in the light oil were shown to be 80 percent weak base of which 5 percent were primary and secondary amine types, 8 percent very weak base, and 12 percent neutral compounds. The nitrogen compounds in the heavy oil were shown to be 14 percent weak base, 12 percent very weak base, and 74 percent neutral compounds. More than 80 percent of the neutral compounds were largely carbazole types.

The one-step syncrude produced in this work was compared with a multistep syncrude of comparable total nitrogen content and basic and neutral nitrogen compound-type content produced earlier by a process suggested by the NPC. These syncrudes contained comparable amounts of neutral nitrogen-type compounds in their heavy oil fractions. Basic nitrogen-type compounds in the one-step syncrude were distributed in much larger amounts in the light oil and heavy naphtha fractions than in the corresponding multistep syncrude fractions. There was no nitrogen in either of the light naphtha fractions. The distribution of basic nitrogen into the lower boiling syncrude fractions is interpreted as a consequence of cracking of the heavy oil and residual portions of the crude oil subjected to the one-step process. The basic cracking products are readily denitrified in the lighter oil reactors in the multistep process.

#### LITERATURE CITED

1. U. S. Energy Outlook, An Interim Report. National Petroleum Council, 2, 1972, p. 80.
2. C. M. Frost, R. E. Poulson, and H. B. Jensen, Preprints, Div. of Fuel Chem., ACS, 19, No. 2, 1974, p. 156.
3. R. E. Poulson, C. M. Frost, and H. B. Jensen, Preprints, Div. of Fuel Chem., ACS, 19, No. 2, 1974, p. 175.
4. R. M. Koros, S. Bank, J. E. Hoffman, and M. I. Kay, Preprints, Div. of Petrol. Chem., Inc., ACS, 12, No. 4, 1967, p. B165.
5. B. E. Buell, Anal. Chem., 39, 1967, p. 756.
6. R. E. Poulson, H. B. Jensen, and G. L. Cook, Preprints, Div. of Petrol. Chem., Inc., ACS, 16, No. 1, 1971, p. A49.
7. H. F. Silver, N. H. Wang, H. B. Jensen, and R. E. Poulson, Preprints, Div. of Petrol. Chem., Inc., ACS, 17, No. 4, 1972, p. G94.
8. A. Pozefsky and Ira Kukin, Anal. Chem., 27, 1955, p. 1466.
9. R. B. Thompson, T. Syman, and C. Wankat, Anal. Chem., 24, 1952, p. 1465.
10. M. A. Muhs and F. T. Weiss, Anal. Chem., 30, 1958, p. 259.
11. Dennis Brown, D. G. Earnshaw, F. R. McDonald, and H. B. Jensen, Anal. Chem., 42, 1970, p. 146.
12. C. M. Frost and H. B. Jensen, Preprints, Div. of Petrol. Chem., Inc., ACS, 18, No. 1, 1973, p. 119.