

SYMPOSIUM ON CHARACTERIZATION AND CHEMISTRY OF OIL SHALES
PRESENTED BEFORE THE DIVISIONS OF FUEL CHEMISTRY AND
PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
ST. LOUIS MEETING, APRIL 8 - 13, 1984

SHALE OIL UPGRADING: EFFECT OF CATALYTIC HYDROTREATMENT
ON NITROGEN COMPOUND TYPES

By

S. A. Holmes and L. F. Thompson

Western Research Institute, P. O. Box 3395, University Station, Laramie, Wyoming 82071

INTRODUCTION

Inspection of the chemical composition of different shale oil feedstocks has become of increasing importance to the refiner by providing an indication of the oil's utilization potential as a fuel and/or petrochemical feedstock. Different retort processes applied to oil shale from different sources produce feedstocks requiring different upgrading conditions. Knowledge of the chemical composition of the retorted shale oil provides insight for selecting upgrading conditions. A summary of work recently presented (1) emphasizes the importance of determining chemical composition:

- i) the method of retorting has a minor effect on the hydrocarbon composition of syncrude from the same shale source;
- ii) retorting has a marked effect on the shale oil boiling range and on elemental nitrogen distribution;
- iii) boiling range end-point is a key control to catalyst activity; and
- iv) hydrogen consumption and catalyst performance are predictable from feed inspections.

Because nitrogen content is high (1.5 to 2.2 wt %) in retorted shale oil, it must be significantly reduced (<50 ppm) for use as a transportation fuel to meet environmental standards and to minimize storage instability problems. Catalytic hydrotreatment may be better optimized for nitrogen removal if nitrogen-containing compounds are known. Hydroprocessing Australian and Colorado shale oil showed that the nitrogen compound types in material boiling greater than 496°C were more difficult to remove than those in material boiling below 496°C, although hydrogen consumption increased (1). The rate of removal of three-ring hetero compounds was less than that for two-ring hetero compounds. Highly alkyl-substituted nitrogen-containing species were more difficult to remove than less alkyl-substituted species (2).

Differences in severity of hydrotreating conditions have been found to affect relative hydrodenitrogenation reactivities of nitrogen-containing compounds. For example, hydrotreating Green River shale oil over a wide range of temperature and hydrogen pressure over a cobalt-molybdena catalyst, investigators (3) found that hydrodenitrogenation of pyridine types was faster than pyrrole types at lower temperature and pressure but that the converse occurred at more severe temperatures >440°C and pressures >13.8 MPa.

In the present studies, nitrogen compound-type distributions in shale oils produced by direct retorting (direct-heat mode) and hydrotreating of eastern and western U. S. oil shales were determined by characterization techniques. Differences in the distribution of nitrogen types in catalytic hydrotreated oils and in the retorted oils provided information as to relative hydrodenitrogenation reactivities of different nitrogen types under hydrotreating conditions. A method for predicting the extent of catalytic hydrotreatment as a function of the nitrogen-type composition in the retorted shale oil is presented.

SHALE OIL PROCESSING

The retorted shale oils studied in this work had been produced by direct retorting or hydrotreating. Shale oils from Green River Formation oil shale of western Tertiary (Eocene) age produced by direct retorting (4) using Paraho, Geokinetics, or Occidental technologies and by hydrotreating using the Institute of Gas Technology (IGT) Hytort technology (5) were studied. Shale oils from the Kentucky New Albany and Sunbury oil shale of eastern Devonian and Mississippian age produced by hydrotreating using IGT Hytort technology were also studied.

The upgraded shale oils studied had been processed from the retorted oils by catalytic hydrotreatment. The hydrotreating conditions employed in upgrading Occidental, Paraho, Geokinetics and the IGT Hytort oils are shown in Table I. Shale oils from direct retorting were hydrotreated

over nickel-molybdena catalysts at similar hydrogen pressures (10.4 MPa). Space velocities (LHSV) were about 1.0 except for Sohio hydrotreatment in which the LHSV < 0.6. In the hydrotreatment of Occidental oil, the catalyst temperature was increased resulting in greater hydrogen consumption and nitrogen reduction. The hydrotreating conditions used in the LETC-2 process removed 68% of the nitrogen content in the Occidental oil, but a relatively lower temperature in the LETC-3 process removed 80% of the nitrogen content in the Paraho oil. Because Sohio hydrotreatment recycled the residuum, unreactive nitrogen compound types in the higher-boiling residuum were concentrated in the hydrotreated oil (6). A higher temperature and lower space velocity than that employed in the LETC-3 process were necessary to achieve 80% nitrogen reduction in the Paraho oil.

TABLE I
HYDROTREATING CONDITIONS USED IN UPGRADING SHALE OILS
USING NICKEL-MOLYBDENA CATALYSTS

Source	Process		LHSV	Temperature, °C	H ₂ Pressure, MPa	H ₂ Con- sumption ³ K mole/m ³	Nitrogen Removal, %
	Retort	Hydro- treating					
Green River	Occidental	LETC-1 ^a	1.0	350	10.4	7.5	51.7
Green River	Occidental	LETC-2	1.0	399	10.4	9.0	67.5
Green River	Paraho	Sohio ^b	<0.6	406	10.4	12.0	79.7
Green River	Paraho	LETC-3	1.0	385	10.4	8.3	80.3
Green River	Occidental	LETC-4	1.0	413	10.4	9.4	83.4
Green River	Geokinetics	LETC-5	1.1	413	10.4	9.8	80.6
Green River	Hytort-1	HTC-6 ^c	0.4	428	13.8	36.2	80.1
Sunbury	Hytort-2	HTS-8	0.4	437	13.8	36.7	83.4
New Albany	Hytort-3	HTNA-3	0.6	426	13.9	25.0	85.6

a. LETC processing utilized bench-scale equipment without residuum recycle at the Laramie Energy Technology Center.

b. Standard Oil of Ohio commercially hydrotreated 11622 m³ of oil and recycled about 1:3 residuum to fresh feed.

c. IGT processed the Hytort oils using a bench-scale catalytic hydrotreating unit without residuum recycle.

Shale oils retorted by IGT Hytort were also hydrotreated over nickel-molybdena catalysts. Significantly higher catalyst temperatures and hydrogen pressures and lower space velocities were used to achieve 80 to 86% nitrogen reduction in these oils. As expected of retorted oils having high aromatic content, hydrogen consumption significantly increased during the production of the hydrotreated oil.

CHARACTERIZATION TECHNIQUES

The results of the nitrogen compound-type distributions presented were determined by the following characterization techniques and discussed in detail in earlier work (7-9). The determination of nitrogen compound types in retorted and hydrotreated shale oils involved chromatographic and spectrometric techniques. The chromatographic procedure resulted in little compound alteration with good material recovery. It was also flexible--having applicability to samples of different aliphatic and aromatic content. The chromatographic procedures incorporated basic alumina adsorption chromatography of the whole shale oil followed by silica gel chromatography of one or more complex fractions generated by the alumina chromatography. Different adsorbent activities, sample loadings and solvent gradients were employed depending upon aromatic content of the shale oil. Several fractions generated from an oil often contained similar compound types which were differentiated by using spectrometric techniques. Each fraction was analyzed by infrared spectroscopy and mass spectrometry. ¹H and ¹³C NMR spectrometry were also utilized in the later stages of the work. Total nitrogen was measured by chemiluminescence detection and basic nitrogen was determined by differential potentiometric titration analysis.

NITROGEN COMPOUND-TYPE DISTRIBUTIONS

Approximately 90% of the nitrogen content in retorted whole shale oil was classified as

one of four nitrogen types: amides, pyridines, pyrroles and hindered pyridines. Amides include compound types such as alkyl-substituted hydroxypyridines, benzamides, oxazoles, anilides and acetylpyrroles. Pyridines include alkyl-substituted pyridines, quinolines and acridines. Pyrroles include alkyl-substituted indoles, carbazoles, diazaromatics and benzocarbazoles. Hindered pyridines are represented by pyridine-type compounds that have alkyl substitution sterically hindering the nitrogen atom. The above nitrogen types also include the respective alicyclic analogs. The remaining 10% of the nitrogen content was distributed in arylamines, nitriles and piperidines and also included losses associated with irreversible adsorption and sample drying during chromatography. Because these latter compound types are also formed as reaction intermediates during hydrotreatment, they are not discussed.

The amounts of major nitrogen types in six retorted and five hydrotreated shale oils are listed in Table II. The distribution of types is somewhat different in oils produced from Green River shale by the first four listed retorting processes. Amide-type nitrogen ranges from 0.97 wt % in the Paraho oil to 0.31 wt % in the Hytort-1 oil. Pyridine-type nitrogen ranges from 0.85 wt % in the Geokinetics oil to 0.32 wt % in the Hytort-1 oil. However, considerably larger amounts of nitrogen in pyrroles and hindered pyridines are found in the Hytort-1 oil than in any of the oils produced by direct retorting. The oils produced from the Sunbury and New Albany shales by Hytort-2 and Hytort-3 contain greater amounts of pyrrolic nitrogen than do the oils from the Green River shale.

TABLE II
DISTRIBUTION OF NITROGEN COMPOUND TYPES IN RETORTED AND
HYDROTREATED SHALE OILS

Process	Total in Sample	Wt % Nitrogen Compound Types			
		Amides	Pyridines	Pyrroles	Hindered Pyridines
<u>Retorted Oils</u>					
Paraho	2.19	0.97	0.77	0.23	0.15
Geokinetics	1.70	0.32	0.85	0.24	0.15
Occidental	1.51	0.38	0.63	0.22	0.13
Hytort-1	2.20	0.31	0.32	0.69	0.66
Hytort-2	1.95	0.25	0.33	0.83	0.31
Hytort-3	1.93	0.33	0.28	0.83	0.24
<u>Hydrotreated Oils</u>					
LETC-1	0.73	0.082	0.245	0.089	0.175
LETC-2	0.49	0.026	0.172	0.086	0.132
Sohio	0.44	0.032	0.157	0.143	0.098
LETC-3	0.42	0.009	0.128	0.123	0.113
LETC-4	0.25	0.025	0.063	0.049	0.076

The nitrogen-type distributions among the hydrotreated shale oils presented in the lower portion of Table II are also significantly different. With the exception of the oil from the LETC-3 process, total nitrogen contents in the oils decrease with increasing severity of hydrotreating conditions (Table I), but the distribution of amides, pyridines, pyrroles and hindered pyridines do not proportionally decrease. For example, the pyrrolic nitrogen in the Sohio and LETC-3 oils range from 0.143 to 0.123 wt % compared with 0.086 and 0.089 wt % for the LETC-2 and LETC-1 oils, respectively. However, total nitrogen removal was 80% during Sohio and LETC-3 hydrotreating compared with 68 and 52% nitrogen removal during LETC-2 and LETC-1 hydrotreatment. The nitrogen-type composition in the LETC-5 hydrotreated oil was not determined.

HYDRODENITROGENATION REACTIVITIES OF NITROGEN COMPOUND TYPES

As previously stated, amounts of different nitrogen types are not removed proportionally to the total nitrogen removal. On the basis of nitrogen removal in percent, Figure 1 shows the amounts of nitrogen removal for different compound types. For example, Sohio hydrotreatment removed about 80% of the nitrogen from the Paraho retorted oil, but it removed 97% of the amide-type, 80% of the pyridine-type, 50% of the pyrrole-type and only 36% of hindered pyridine-type

nitrogen. The nitrogen-type distribution assumes negligible interconversion of nitrogen compound types. This may not have been the case with LETC-1 or LETC-2 hydrotreatment. Actual increased amounts of hindered pyridine-type nitrogen was found in the LETC-1 and LETC-2 oils relative to that in the feedstock (Occidental retorted oil), probably from the buildup of reaction intermediates formed from partial hydrogenation of acridine or quinoline ring systems under mild hydrotreating conditions.

Differences in the amount of nitrogen removal for different nitrogen compound types resulting from hydrotreatment suggest that different compound types have different hydrodenitrogenation reactivities. Relative reactivities of the different nitrogen types expressed as percent nitrogen removal divided by 100 were determined from data used in Figure 1. These results for compound types in the Sohio, LETC-3 and LETC-4 oils are listed in the top portion of Table III. Only the results for these oils are listed because of similar total nitrogen removal (80 to 83%). Because oils were retorted and hydrotreated by different processes, each nitrogen type displays a range of reactivities. For data comparison, the average reactivity value was determined for each nitrogen type and normalized to that of the amide-type nitrogen (a relative value of 1.00 meaning the easiest nitrogen type to remove). Normalized values of reactivity are presented in the bottom portion of Table III. Results suggest amide- and pyridine-type nitrogens are relatively easy to remove, 1.00 and 0.876, respectively. Pyrrole-type nitrogen (0.637) is relatively more difficult to remove and hindered pyridine-type nitrogen (0.352) is the most difficult to remove. However, in the calculation of reactivity, one must not overlook possible contributions from nitrogen-type interconversions caused by hydrogenation. The hydrotreating conditions necessary for 80% nitrogen removal are suggested to minimize the amount of buildup of reaction intermediates.

TABLE III

RELATIVE HYDRODENITROGENATION REACTIVITIES OF NITROGEN COMPOUND TYPES IN OILS UNDER HYDROTREATING CONDITIONS FOR 80% NITROGEN REMOVAL

Hydrotreating Process	Compound Types			
	Amides	Pyridines	Pyrroles	Hindered Pyridines
Sohio	0.967	0.797	0.493	0.355
LETC-3	0.991	0.834	0.564	0.257
LETC-4	0.934	0.899	0.778	0.402
Average	0.964	0.843	0.612	0.338
Normalized Values ^a				
Sohio	1.00	0.824	0.510	0.367
LETC-3	1.00	0.842	0.569	0.259
LETC-4	1.00	0.963	0.833	0.430
Average	1.00	0.876	0.637	0.352

a. Reactivities relative to amide nitrogen which is the easiest nitrogen compound type to hydrodenitrogenate.

HDN FACTOR CALCULATIONS

The amount of nitrogen removal by catalytic hydrotreatment may be estimated from the nitrogen-type composition of the shale oil feedstock and hydrodenitrogenation reactivities. A hydrodenitrogenation (HDN) factor is determined for each nitrogen compound type by multiplying the normalized reactivity by the percent of total nitrogen for each compound type (i) as shown below:

$$\text{HDN Factor}_{(i)} = \frac{\text{Normalized Reactivity}_{(i)} \times \text{Percent of Total Nitrogen}_{(i)}}{100}$$

The summed HDN factor, which is the sum of individual HDN factors for the four different nitrogen compound types, suggests the degree of difficulty of nitrogen removal from a given feedstock during catalytic hydrotreatment.

The nitrogen compound-type distributions in six retorted shale oils are presented on the basis of percent of total nitrogen in the top portion of Table IV. Calculations of the HDN factors are presented in the bottom portion of Table IV. Summed HDN factors range from 0.747 to 0.830 for oils produced from Green River shale by direct retorting. However, these values are significantly different from that for the Hytort-1 oil (0.574) produced from Green River shale. The oils

produced from the Sunbury and New Albany shales by the Hytort-2 and -3 process have similar values (0.602 and 0.632) compared with that for the Hytort-1 oil.

TABLE IV
HDN FACTOR CALCULATIONS

Retorted Oils	% of Total Nitrogen					Total
	Amides	Pyridines	Pyrroles	Hindered Pyridines		
Paraho	44.3	35.2	12.8	6.8		99
Geokinetics	18.8	50.0	14.1	8.8		92
Occidental	25.2	41.7	14.6	8.6		90
Hytort-1	14.1	14.5	31.4	30.0		90
Hytort-2	12.8	16.9	42.6	15.6		88
Hytort-3	17.1	14.5	45.6	12.4		90

Retorted Oils	HDN Factors					Normalized ^a Nitrogen Content
	Amides	Pyridines	Pyrroles	Hindered Pyridines	Summed	
Paraho ^b						
Sohio	0.443	0.290	0.065	0.025	0.823	1.00
LETC-3	0.443	0.296	0.073	0.018	0.830	1.00
Geokinetics	0.188	0.438	0.090	0.031	0.747	1.29
Occidental	0.252	0.402	0.122	0.037	0.813	1.45
Hytort-1	0.141	0.127	0.200	0.106	0.574	1.00
Hytort-2	0.128	0.148	0.271	0.055	0.602	1.12
Hytort-3	0.171	0.127	0.290	0.044	0.632	1.14

- Nitrogen content for each retorted oil is normalized to the nitrogen content in the Paraho oil (2.19 wt % nitrogen).
- Normalized reactivity values from Table III used in the HDN factor calculations for the Paraho oil.

HDN FACTOR ANALYSIS

Relationships of the HDN factors generated from the nitrogen-type composition in a feedstock and the percent nitrogen removal under hydrotreating conditions were established. Because total nitrogen content affects percent nitrogen removal, the nitrogen contents in the retorted oils were normalized to that in the Paraho-retorted shale oil. These values are also presented in the bottom portion of Table IV. Summed HDN factors are adjusted for nitrogen content by multiplying by the normalized nitrogen content. The adjusted HDN factor for each oil feedstock is determined using the equation below.

$$\text{Adjusted HDN Factor} = \text{Summed HDN Factor} \times \text{Normalized Nitrogen Content}$$

Adjusted HDN factors for the oils were plotted versus nitrogen removal for different hydrotreating conditions. The resulting relationships are shown in Figure 2. Oils produced from Green River shale by direct retorting gave a nearly linear relationship ($r^2 = 0.934$) under moderate hydrotreating conditions. Oils produced by hydroretorting from either Green River or Sunbury and New Albany shales establish a different linear relationship ($r^2 = 0.988$) under severe hydrotreating conditions. In each case, about 80 to 86% nitrogen was removed.

Larger values of adjusted HDN factors indicate nitrogen compound-type compositions relatively more susceptible to hydrodenitrogenation. Smaller adjusted HDN factors for the hydroretorted oils suggest a nitrogen-type composition of more unreactive compound types compared with that in the oils produced by direct retorting. Greater amounts of more aromatic and sterically-hindered alkyl-substituted nitrogen compounds are present in oils produced by the Hytort process, particularly, greater amounts of pyrrole- and hindered pyridine-type nitrogen. During hydroretorting, a hydrogen atmosphere allows partial hydrogenation of unsaturated hetero compounds resulting in greater percentages of nitrogen in unreactive nitrogen compounds.

Using severe conditions, hydrotreatment of a Paraho oil removes an amount of nitrogen not defined by either relationship previously discussed. These data are shown in Figure 2.

Hydrotreatment of Paraho oil by LETC-3 or Sohio processes removes 80% of the nitrogen content under moderate conditions, but hydrotreatment under severe conditions, such as those used on the Hytort oils, removes 99% of Paraho oil's nitrogen content. The extent of nitrogen removal is very much dependent upon the conditions of catalytic hydrotreatment. Theoretically, a set of curves similar to those in Figure 2 could be generated for differently retorted oils subjected to different hydrotreating severity.

The relationships in Figure 2 may be used to estimate relative amounts of nitrogen removal from an oil feedstock under moderate or severe hydrotreating conditions. For example, Rockwell International recently produced six light oils from Ohio oil shale using different conditions of flash hydroxyprolysis temperatures and shale residence times (10). These hydroretorted oils differed in their nitrogen-type compositions. Adjusted HDN factors were calculated: 1.022 for an oil produced at a lower temperature (650°C) and 0.694 for an oil produced at a higher temperature (772°C). From the relationship generated by the Hytort data in Figure 2, the amounts of nitrogen removal estimated under severe hydrotreating conditions for upgrading the low and high temperature produced oils are 95 and 84%, respectively. ¹H and ¹³C NMR data indicated that the higher-temperature-produced oil contained about three times the amount of di- and polyaromatic compounds (22 mol %). A relatively greater aromaticity was also found in the nitrogen-containing compounds; the amount of quinolines was significantly greater than that of pyridines. It is expected that the more aromatic nitrogen compounds would be more difficult to hydrodenitrogenate.

SUMMARY

The ease of removing nitrogen from shale oil by catalytic hydrotreatment is dependent upon feedstock characteristics. Several characteristics related to nitrogen distribution which affect hydrodenitrogenation include the amount of nitrogen, nitrogen compound-type composition and distribution of nitrogen according to boiling point. Nitrogen compound-type distributions were significantly different in oils from eastern and western U. S. oil shales produced by direct retorting or hydroretorting.

This work has shown that the types of nitrogen compounds (functional group basis) display different hydrodenitrogenation reactivities. Upgraded oils studied had been hydrotreated over nickel-molybdena catalysts at moderate to severe temperatures <440°C and pressure <13.8 MPa. Reactivities of nitrogen compound types calculated at these conditions indicated that least to most difficult compound types to remove are, respectively: amides, pyridines, pyrroles and hindered pyridines.

The development of HDN factor analysis may allow estimation of the relative amount of nitrogen removal by catalytic hydrotreatment. HDN factors are calculated from nitrogen-type compositions of oil feedstocks and hydrodenitrogenation reactivity values. Adjusted HDN factors are dependent upon the source of the oil shale, retorting method of the oil shale and hydrotreating conditions. Nearly linear relationships result by plotting adjusted HDN factors versus nitrogen removal. Feedstocks hydrotreated by different conditions than described in this work may show different hydrodenitrogenation reactivities and the relationships of HDN factors and nitrogen removal may be different from those presented. Refinement of characterization techniques will better define nitrogen compound types resulting in improved HDN factor calculations. Compositional analyses of differently retorted and hydrotreated shale oils will provide additional data useful in the development of HDN factor analysis.

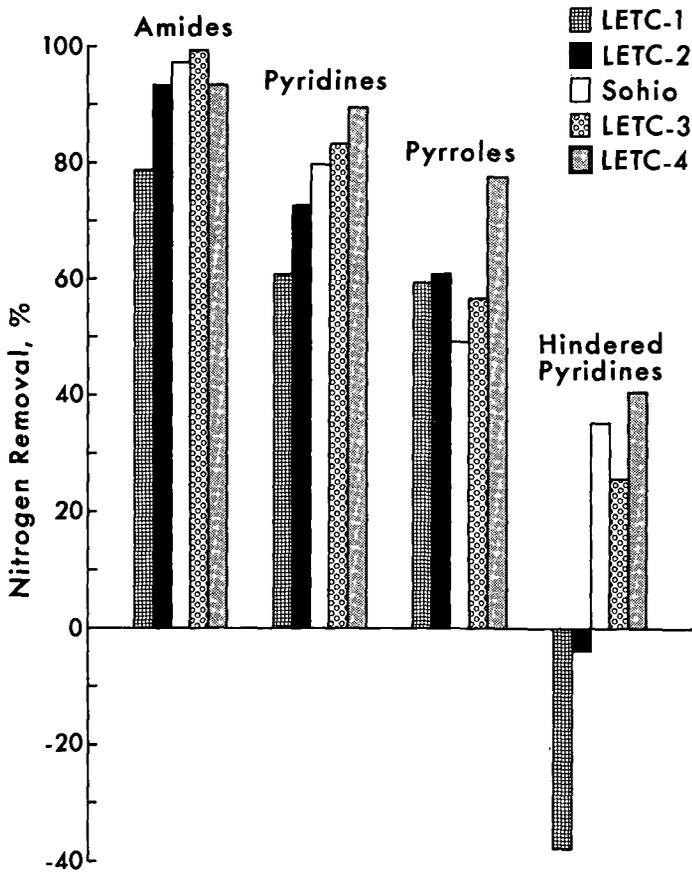


Figure 1. Nitrogen compound type removal by different hydrotreating processes.

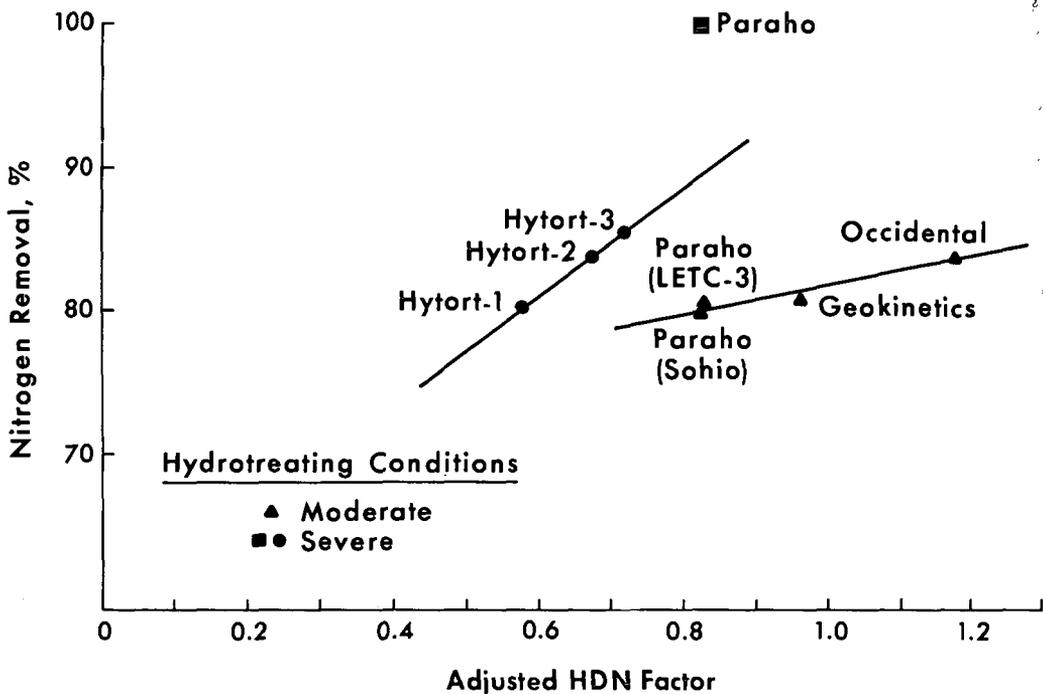


Figure 2. Relative ease of nitrogen removal from shale oils by catalytic hydrotreatment.

LITERATURE CITED

- (1) Hamner, G., Exxon Research, Baton Rouge, LA, private communication.
- (2) Drushel, H. V., Preprints, Div. of Analytical Chem., ACS, Anaheim, CA (1978).
- (3) Frost, C. M. and Jensen, H. B., PREPRINTS, Div. of Petrol. Chem., ACS, 18 (1), 119 (1973).
- (4) Smith, E. B., Laramie Energy Technology Center, private communication.
- (5) Weil, S. A., Proceedings of IGT Synthetic Fuels from Oil Shale Symp., 353, Atlanta, GA (1980).
- (6) Holmes, S. A. and Thompson, L. F., Fuel, 62 (6), 709 (1983).
- (7) Holmes, S. A. and Thompson, L. F., Proceedings, 1982 Eastern Oil Shale Symp., Lexington, KY (1983).
- (8) Holmes, S. A. and Thompson, L. F., Proceedings 14th Oil Shale Symp., Golden, CO, 235 (1981).
- (9) Holmes, S. A., Thompson, L. F. and Heppner, R. A., Proceedings 15th Oil Shale Symp., 424, Golden, CO (1982).
- (10) Falk, A. Y., Garey, M. P. and Rosemary, J. K., Report ESG-DOE-13406, Rockwell Internatl. Corp. (1983).