

NITROGEN AND SULFUR IN RAW AND REFINED SHALE OILS

Richard E. Poulson

Energy Research and Development Administration
Laramie Energy Research Center, Laramie, Wyoming 82071

INTRODUCTION

Raw Green River Formation shale oils contain significantly higher concentrations of some heteroatoms than most petroleum fractions of a similar distillate range. The nitrogen content of shale oils often runs twice that in a petroleum and therefore may require special refining methods. Removal of heteroatoms from shale oil is important because of (1) the potential for air pollution from their combustion products and (2) the susceptibility of modern refining catalysts to degradation, especially by nitrogen compounds. In addition to high heteroatom content, shale oils by and large have pour points too high for pipelining. In a shale-oil industrial process some sort of upgrading or partial refining is usually planned for reducing heteroatom content and improving fluidity to attempt to make shale oil compatible with existing petroleum processing facilities.

This paper reviews and discusses the work since the first Synthetic Liquid Fuels Act (1944) relating to heteroatom and heterocompound content of shale oils produced from Green River Formation of Colorado, Utah, and Wyoming oil shales. The work includes heteroatomic composition data for raw shale oils (crudes and distillates from various retorting processes) and their products in various stages of refining. Refining methods to be discussed include early upgrading processes involving distillation, delayed-recycle coking, thermal visbreaking, and acid and base or solvent extraction. Finally, modern hydrodenitrogenation (HDN) work with shale oil and related materials will be presented and heterocompound-type data for some refined and partially refined products will be discussed along with related analytical techniques.

It is apparent in reviewing the refining of shale oil that the nitrogen level has been the primary index of refining with respect to heteroatom content. This is not only because of the severe nitrogen effect in catalyst degradation¹ but also because of the persistence of nitrogen relative to sulfur and oxygen in the course of modern refining. For this reason data on sulfur and oxygen heterocompounds in shale oils are lacking in most cases.

DISCUSSION

Effect of Retorting Process on Heteroatom Content

One advantage in use of shale oil as a feed is that once a set of retorting parameters is found giving a desired and stable retorting operation the feed produced could be quite constant in its properties. All shale oils are not alike, however. Jensen² has shown that retorting processes in which the oil shale is more slowly heated in general correlate with oil products having increased amounts of naphtha plus light distillate fractions. In these fractions the aromatic content remains constant, but the saturate-olefin ratio increases. An approximate index to these effects is the specific gravity or pour point of the oil. In table 1 we see properties of crude shale oils produced by various retorting methods arranged from top to bottom in order of decreasing specific gravity or pour point. We see that the nitrogen level decreases in the same order but that the sulfur level only decreases appreciably in the lower half of the table.

As pointed out by Jensen² the retorting parameters that control the character of shale oils, largely, are shale size, combustion zone velocity, and effective retorting temperature. If this is

TABLE 1. - Properties^a of crude shale oils

Retort type	Retorting Index or T °F	Specific gravity, 60/60° F	Pour point, °F	Nitrogen, wt-pct	Sulfur, wt-pct
Gas combustion ³	1,200 ^b	0.943	85	2.13	0.69
Fischer assay ³	900 ^b	.918	70	1.95	.64
150-Ton batch ²	---	.909	60	1.59	.94
USBM in situ-4 ²	---	.885 ^d	40	1.36	.72
Equity Oil in situ ⁴	750 ^c	.825 ^d	-20 ^d	.53	.49

^a - References in table refer to properties of oils. ^b - Retorting index. ^c - Temperature of injected fluid. ^d - Properties of oil produced in laboratory simulation of process.⁴

carried a step further, it can be pointed out that these are not independent parameters and that effective retorting temperature itself may suffice to classify retorting methods.

Jacobson^{5,6} has defined a retorting index with dimensions of temperature which relates to the severity of oil-shale pyrolysis. The index is derived from the ethylene:ethane ratio in the retort product gas. The retorting index is listed in table 1 for the gas combustion retort and the Fischer assay retort along with the measured temperature of the injected fluid used in the Equity Oil in situ process. We see at least qualitatively that these temperatures are in a systematic order.

To see that the oils with unknown retorting temperatures or indexes also probably fall in a logical order based on particle size, let us consider each process very briefly. The gas combustion retort,⁷⁻¹¹ heated by internal combustion is fed crushed-screened shale of about 3-inch dimensions. The Fischer assay retort^{7,12} uses small sized shale crushed to pass 8 mesh screen but is externally heated at a controlled moderately low rate. The 150-ton batch retort^{7,13-15} uses mine-run shale with blocks as large as 3 ft x 4 ft x 5 ft and is heated by internal combustion. The USBM in situ oil¹⁶⁻¹⁸ was a combustion-retorted oil produced in fractured shale between injection and recovery wells. The Equity Oil in situ oil^{4,19} was produced by recycling of hot natural gas, at a controlled temperature, into an oil-shale formation. All of the combustion-type retorts were of the forward burning type where gas plus oil moves countercurrently to oil shale. Except for the Fischer assay retort which is a controlled temperature retort, the increase in particle size is down table 1 corresponding with decreasing heating rate. It is probable that the USBM in situ experiment with poorly controlled combustion had a higher effective temperature than the controlled nonoxidative Equity Oil process. Very high temperature retorted oils²⁰⁻²⁵ which by their very high aromatic content indicate a high degree of pyrolysis of the oil itself do not fit the above oversimplified pattern.

In summary, nitrogen and sulfur levels are both affected by the retorting method. Nitrogen level varies over a wider range than sulfur level and follows the specific gravity, pour point, and probably effective retorting temperature down for these oils. There is then potential for control of the nitrogen level in a crude shale oil through retorting. Whether the method of retorting adopted might be an economic approach to denitrogenation will not be pursued in this review. It depends undoubtedly on many factors, chief of these being probably the desired end use of the oil, whether for petroleum-type feedstock, direct fuel production or for chemicals, and the efficiency of resource recovery sought.

Composition of Raw Shale Oils

Much of the early shale-oil characterization work was on a shale oil from an NTU (Nevada-Texas-Utah) retort which was an aboveground internal combustion batch-type retort.²⁶ Cady and Seelig²⁷ have shown that an NTU crude may contain as much as 61 percent heterocompounds of which about 60 percent are nitrogen compounds, 10 percent sulfur compounds, and 30 percent oxygen compounds. Thus only 39 percent of this oil is hydrocarbons. These proportions will vary some depending on the retorting scheme; but in any case, the heterocompounds form a significant part of the potential source of hydrocarbons. The work in identification of specific heterocompound types and heterocompounds in an NTU shale-oil naphtha²⁸ and in a heavy gas oil²⁹ has been summarized by Dinneen and others.³⁰⁻⁴⁰ Others studying light gas oil fractions and other distillates have supplemented this work.⁴¹⁻⁴³ The naphtha and heavy gas oil represent the extremes of molecular weight in the distillates. Having nitrogen compound-type analyses for these extreme fractions with supplementary information on light distillate fractions allows interpolation to aid in compound-type assessment throughout the shale-oil distillate range. Sulfur and oxygen compound-type analyses have been done only for the naphtha distillate region.

In the following generalized discussion, the description of a compound type will be construed to include also homologous and benzologous series members depending on boiling range--e.g., pyridinic-type N includes pyridine, quinoline, acridine, alkylpyridines, etc.

Sulfur

In table 2⁴⁴ we see that for a crude shale oil the sulfur distribution is rather uniform throughout the boiling ranges but that nitrogen is more concentrated as the fractions get heavier. We have already seen in table 1 that the type of retorting seems to have only a second-order effect on sulfur level in the crude. The refractory nature of the sulfur⁴⁵ may be accounted for by the fact that most of the sulfur is in thiophene types^{28,44} as shown in table 3 for a naphtha fraction.

Oxygen

The oxygen in a shale-oil crude may run 0.5 to 2 percent. Much of the oxygen in a naphtha,²⁸ light distillate,⁴³ and gas oil²⁹ appears as phenols with minor amounts of carboxylic acids. Benzofuran was found in small amounts in the nonacidic portion of the naphtha.²⁸ It was shown

TABLE 2. - Sulfur and nitrogen contents of distillates from a Green River Formation crude shale oil⁴⁴

Fraction	Nominal boiling range, °F	Nitrogen, percent by wt	Sulfur, percent by wt
Naphtha	<400	1.17	0.77
Light distillate	400-600	1.24	.83
Heavy distillate	600-800	1.60	.79
Residuum	>800	2.04	.70

that light distillates from different retorting processes can vary in their oxygen content and its distribution.⁴³ For one in situ produced oil, oxygen appears to be accounted for largely in the tar acids. For one aboveground retorted oil it appeared that two-thirds of the oxygen was unaccounted for by tar acids implying the presence of other forms of oxygen possibly amidic type,^{41,43} or other as yet unclassified types.

TABLE 3. - Type sulfur in Green River Formation shale-oil naphtha⁴⁴

Sulfur type	Percent of total sulfur
Elemental	0
Thiol	4
Disulfide	2
Sulfide (includes cyclics)	19
Residual (includes thiophene type)	75

Nitrogen

The principal nitrogen-containing species in shale oils are pyridine types and pyrrole types. In pyridinic types the single aromatic ring type appears to predominate over multiple ring types through wide distillate ranges. In pyrrolic types multiaromatic rings tend to predominate as boiling range increases.^{29,41} Small amounts of amides,⁴¹ arylamines,⁴⁶⁻⁴⁸ and nitriles^{28,35} have been detected. Much of the nitrogen in shale-oil distillates is basic enough to titrate in acetic anhydride ($pK_a > -2$)^{28,41-43} and be extracted by acidic agents as shown in table 4.⁴² In addition appreciable acidic material containing oxygen or nitrogen is titratable in pyridine ($pK_a < 12$) and is extractable from the lighter distillates by basic reagents as shown. The relative amounts of various nitrogen types and their basicities observed for a shale-oil light distillate are shown in table 5.⁴¹

TABLE 4. - Polar materials by different methods for a 150-ton batch retort shale oil⁴²

Method	Nominal distillate cut		
	Naphtha IBP to 400° F	Lt. distillate 400° F to 600° F	Gas oil 600° F to 1,000° F
	Bases, wt-pct		
Titration: Weak, ^a very weak ^b	7.1, 3.6	13.1, 2.4	27.9, 0.0
Ion-exchange extraction	10.2	12.8	24.3
Aqueous extraction	11.2	11.5	12.0
	Acids, wt-pct		
Titration: Weak, ^c very weak ^d	1.0, 3.9	0.8, 5.6	0.3, 8.0
Ion-exchange extraction	4.2	3.3	1.1
Aqueous extraction	5.0	3.7	1.2

^a $pK_a = +8$ to $+2$. ^b $pK_a = +2$ to -2 . ^c $pK_a = +3$ to $+10$. ^d $pK_a = +10$ to $+12$.

Products from Early Refining Processes

Because of the waxy, viscous nature of shale oils from conventional retorting processes and the high pour point and heteroatom content along with the low light-end content, it was apparent from the outset that some sort of hydrocarbon-conversion process was required for shale-oil utilization. Early work centered on thermal processing (visbreaking, recycle cracking, and coking) along with chemical treatment to remove objectionable compounds in an attempt to improve gasoline and distillate fuel content and stability of shale oil.⁴⁹⁻⁵⁴ These methods were chosen because of the

TABLE 5. - Summary of nitrogen-type analysis of a shale-oil light distillate (400° to 600° F)⁴¹

Nitrogen type	Percent of total nitrogen
Weak bases (pKa = +8 to +2)	
Alkylpyridines	43
Alkylquinolines	22
Very weak bases (pKa = +2 to -2)	
Alkylpyrroles (N-H)	10
Alkylindoles (N-H)	9
Cyclicamides (pyridones, quinolones)	3
Anilides	2
Unclassified	7
Nonbasic (pKa < -2) corrected for pyrroles and indoles	4

availability of these processing facilities in all refineries, because of the poor economic aspect of hydrogenation at the time, and the lack of suitable catalysts which could stand up to the high nitrogen concentrations encountered in shale oil.

Thermal Methods

Visbreaking of shale oil or cracking with recycle can produce a low pour point shale oil with increased light end content. Recycle delayed coking can further increase the light end content as shown in table 6 but does not affect the nitrogen and sulfur concentrations appreciably.⁵⁴

TABLE 6. - Recycle delayed coking of crude shale oil to various endpoints⁵⁴

	Crude feed	Nominal distillate endpoint		
		650° F	750° F	850° F
Yields, vol-pct	--	77	87	89
Sulfur, wt-pct	0.74	0.63	0.61	0.63
Nitrogen, wt-pct	2.01	1.65	1.90	1.95
		<u>Light end yields</u>		
IBP-350° F, vol-pct	1.5	5.5	9.0	19
350-550° F	18	87	36	36

Chemical Methods

Chemical treatment of shale oils can be very effective in nitrogen removal. One such treatment consisting of successive contacting at 100° F with 15 weight-percent NaOH, 20 weight-percent H₂SO₄, 100 percent H₂SO₄, and then neutralization with 3 volume percent NaOH produced a diesel fuel from a shale-oil light gas oil as shown in table 7.⁵⁰ The sulfur level, however, is nearly unaffected. Although similar treatment of naphtha fractions may produce very low

TABLE 7. - Result of chemical treatment^a of shale-oil recycle delayed-coker distillate light gas oil (400° to 670° F)⁵⁰

	Raw oil	Treated oil (diesel fuel)
Yield, vol-pct	100	67.0
Sulfur, wt-pct	0.84	0.74
Nitrogen, wt-pct	1.66	.085
Tar acids, vol-pct	3.4	.3
Tar bases, vol-pct	13.0	0

^a Treatment consists of 15 percent by weight NaOH, 20 percent by weight H₂SO₄, 100 percent H₂SO₄ (22.8 lb/bbl), and 3 volume percent NaOH to neutralize, then redistill to restore end-point. Treating temperature about 100° F.

nitrogen gasolines, these may still have a few tenths percent sulfur present. Diesel fuels from various solvent extractions of light oils showed greatly improved nitrogen levels with little effect on sulfur levels much the same as acid base treated oil in table 7.

The loss of distillate shown in table 7 illustrates a problem with chemical refining of shale oil. Undoubtedly quite effective nitrogen and oxygen compound removal could be achieved with various reactants or solvents, but it is unlikely that improvement in sulfur level would be obtained because of the chemical similarity of thiophene-type compounds to the hydrocarbon matrix. If all heterocompounds were removed from a crude shale oil, as much as 60 percent of the oil might be removed.²⁷

Summary

It was shown by the Bureau of Mines in 1949⁵¹ that adequate gasolines and diesel fuels could be produced from shale oil by methods like those just discussed. However, there were at least three good reasons for continuing research in refining of shale oil. First, the losses in raw material involved in extraction of heterocompounds represent great waste unless a ready use exists for the extracted materials. Secondly, the demand for very low nitrogen stocks for refining to high octane fuels was increasing. Finally, the pressure from an environmental standpoint for extremely low sulfur fuels was increasing steadily.

Products from Modern Refining Processes

Fortunately a by-product of the demand for higher octane fuels was hydrogen from petroleum catalytic reforming processes. The economics of hydrogen utilization began to look favorable as a means of improving the quality of shale oils and the research emphasis swung to hydrogenation. In 1947 Union Oil was successful, on a pilot plant basis, in catalytic hydrosulfurization of high thiophenic sulfur-type coker distillates from Santa Maria Valley crude petroleum.⁵⁵ Since then, aided by the increasing availability of hydrogen, much work has been done in refining shale oil via hydrogenation one way or another.⁵⁶⁻⁷⁵ Shale-oil crude was analogous to this petroleum crude in that sulfur was present largely as thiophenes and distributed uniformly throughout the distillate ranges.⁵⁵ As it turned out, both sulfur and nitrogen could be removed from shale oil effectively by catalytic hydrogenation. Production of potentially high quality fuels and refinery feedstocks has been achieved in many cases.

The question of which method of HDN is best of course depends on the individual case-- i.e., what is the feed and what are the desired products. Knowledge of the types and kinetics in

HDN of heterocompounds remaining in refined and partially refined shale oils could be of value in optimizing refining processes. Nitrogen level alone is only a partial criterion of the degree of hydrogenation that has taken place. Various deleterious heterocompounds appear to be removed at different rates for a given set of conditions as discussed below. To date little data concerning the nature and reactivity of the heterocompounds in refined shale oils have appeared in the literature of shale-oil refining.

Sulfur and Oxygen

In the hydrodesulfurization of Santa Maria Valley petroleum crude by Union Oil, all types of sulfur present (mercaptan, sulfide, and thiophenic) appeared to be removed at the same rate.⁵⁵ Little compound-type information relating to hydrodesulfurization or hydrodeoxygenation has been reported in shale-oil refining studies however. This is probably because it has been found in refining of shale oils by catalytic hydrogenation that both sulfur and oxygen are removed before desired nitrogen levels are attained. In cases where results suggest otherwise, it is not always apparent whether analytical interference from elemental sulfur might not have been a factor. Elemental sulfur is formed readily as an interference by air oxidation of hydrogen sulfide. Inadvertent air contact with hydrogenated distillates before thorough washing has been accomplished may complicate evaluation of low organic sulfur levels. (Elemental sulfur may be removed from oils by extraction with metallic mercury⁷⁶⁻⁷⁷ or in some cases with aqueous sulfite solution.⁷⁸) In addition, direct low-level oxygen analyses are not readily available in most laboratories. From these properties of sulfur and oxygen, it can be understood why nitrogen level has been the index usually used in shale-oil heterocompound removal studies.

Nitrogen

In an attempt to work out some of the HDN reaction kinetics, several shale-oil HDN studies have been made in which nitrogen-type analyses were presented.^{46-48,73,75,79-81} Studies have been made on pure nitrogen compounds occurring in shale oils and also on low-level nitrogen oils "spiked" with some of these nitrogen compounds.⁸²⁻⁸⁵ Work in this area has been aided by the simple nitrogen-type analysis described by Koros, et al.,⁴⁶ extended by Silver, et al.^{47,48} and by Poulson, et al.^{41,81}

This analytical method for nitrogen types uses elemental analysis, nonaqueous titrimetry, infrared spectrophotometry, and visible colorimetry to define several nitrogen types: 1° and 2° alkylamine, 3° amine (pyridine and other), arylamine, pyrrolic N-H, α - or β -unsubstituted pyrrolic (excluding carbazoles), amide, and miscellaneous very weak base and nonbasic nitrogen types. Further subdivisions are possible depending on which groups are represented in a given sample. As hydrogenation progresses, oxygenated types disappear so rapidly that specific compound-type assignments become simpler. Some examples of uses of this analysis and the nature of hydrodenitrogenated shale oils are shown below followed finally by a summary of the principal nitrogen types in a premium shale-oil syn crude having 0.025 percent nitrogen.

Pyridines Versus Pyrroles

This analysis has been used to resolve a fundamental conflict in shale-oil refining literature; which is easier to hydrodenitrogenate, pyridinic types or pyrrolic types? Researchers were split about equally on each side of this question. Using an analytical scheme similar to the one just described, Frost and Jensen⁷³ were able to rationalize the conflicting reports. Working with crude shale oil over a wide range of temperature and hydrogen pressure, they showed denitrogenation of pyridinic types was faster than for pyrrolic types at low temperature and pressure, but the other way round for more severe conditions of temperature and pressure.

Anilines in Shale Oils

The reaction sequence for denitrogenation of indoles and carbazoles proposed by Flinn, et al.^{83,84} contains approximately a dozen competing or consecutive reactions. Reactants, intermediates, and products run the gamut from nonbasic to strongly basic nitrogen types. Anilines are postulated as intermediates as they are also in a denitrogenation sequence proposed for quinolines by Doelman and Vlugter⁸⁵ and Koros, et al.⁴⁶ Anilines would arise from saturation of the heteroring in a fused ring compound followed by rupture of the bond between nitrogen and the aliphatic carbon.

One-Step HDN

Although anilines themselves have been shown to be readily hydrodenitrogenated,⁸³⁻⁸⁵ they have been observed in severely hydrodenitrogenated shale oils. Brown⁷⁹ found that 33 percent of the tar bases in a hydrocracked recycle shale-oil naphtha were anilines at 95 percent denitrogenation. Koros, et al.,⁴⁶ Silver, et al.,^{47,48} and Frost⁷⁵ found a few percent aniline-type nitrogen in shale oils which had up to 98 percent denitrogenation levels. All these results were based on one-step HDN processes whereby anilines formed by the processes just described above would appear directly in the products, probably as lighter boiling compounds as a result of hydrocracking.

Multistep HDN

In addition to the one-step syncrude described above, Frost, using a multistep HDN process with the same crude shale-oil feed and denitrogenating to a similar level, produced a syncrude with a different nitrogen-type distribution.^{74,81} The multistep process, based on an NPC proposed scheme,⁸⁶ involves continuous catalytic hydrogenation of three individual distillate fractions from a crude shale oil with the inclusion of products from delayed coking of the residuum in the distillate fractions. Anilines were completely absent from this syncrude product but did show up in intermediate products.

In table 8 the heteroatom composition of these two syncrudes is reviewed, as discussed by

TABLE 8. - Nitrogen and sulfur in shale-oil syncrudes and distillate fractions⁷⁵

	Nitrogen, ppm		Sulfur, ppm	
	Multistep	One-step	Multistep	One-step
Syncrude	250	225	5	6
Naphtha	1	83	8	3
Light oil	79	200	1	5
Heavy oil	935	513	9	5

Frost⁷⁵ in this symposium, and is compared through the distillate ranges. Light nitrogen compounds are virtually absent from the multistep syncrude illustrating the difference of a multistep process compared to a single-step process.

Premium Syncrude

Residual nitrogen types in a shale-oil premium syncrude (multistep syncrude above) heavy oil (550° to 850° F) were determined by Poulson, Frost, and Jensen⁸¹ using the above-described classification scheme supplemented by mass spectrometry. This heavy oil contained 935 ppm nitrogen which was 90 percent of the total nitrogen in the syncrude. The total nitrogen concentration

in the whole syncrude was 250 ppm and resulted from over 98 percent nitrogen removal from the crude shale-oil feed. The general nitrogen-type analyses are shown in table 9. In pyrrolic types,

TABLE 9. - Summary of nitrogen types in a heavy oil (550° to 850° F)^a from a multistep shale-oil syncrude^b 81

	N, pct of total in oil
<u>Pyrrolic-type nitrogen</u>	
Three aromatic rings	30
One or two aromatic rings	25
<u>Pyridinic-type nitrogen</u>	
Two aromatic rings	15
One aromatic ring	30

^a Total N = 935 ppm. ^b Total N = 250 ppm.

three aromatic ring compounds (carbazoles) predominate and in pyridinic types one aromatic ring compounds (pyridines) predominate, much as in a raw shale-oil heavy gas oil.²⁹ A slight olefin interference makes the exact pyridine:quinoline ratio somewhat uncertain in table 9, however.

In table 10 the neutral and very weak-base nitrogen types are summarized for this heavy oil which represents 90 percent of the nitrogen in the syncrude. Pyrroles and indoles appear to be N-unsubstituted and highly ring-alkyl substituted. Carbazoles in this oil are about evenly split between N-substituted and N-unsubstituted types.

TABLE 10. - Summary of neutral and very weak base nitrogen types in the heavy oil (550° to 850° F)^a from a multistep shale-oil syncrude^b 81

Nitrogen-type compounds	N, pct of total in fraction
<u>N-unsubstituted pyrroles (or indoles)</u>	29.0
α - or β -unsubstituted	6.8
α - or β -substituted	22.2
<u>Carbazoles</u>	71.0
N-unsubstituted	34.4
N-substituted	36.6

^a Total N = 935 ppm. ^b Total N = 250 ppm.

In summary HDN is effective in heteroatom removal from shale oils and its use has been and is being studied widely. Optimum processing conditions for denitrogenation of shale oils depend on the individual case but probably have not been determined for many situations. Little information on nitrogen types in refined or partially refined shale oils has been reported. A relatively simple analytical scheme can produce nitrogen-type compound data of aid in mechanistic interpretations of denitrogenation reactions in shale oils.

SUMMARY

Crude Green River Formation shale oils contain large amounts of heterocompounds containing nitrogen, sulfur and/or oxygen. Shale oils produced in low temperature retorting processes seem to have lower nitrogen levels paralleling lower specific gravities and pour points. The effect of retorting on sulfur level is not as clear. Sulfur occurs principally as thiophenic-type compounds. Oxygen occurs mainly as phenols with minor amounts as carboxylic acids, amides, ethers, or other unidentified types. Nitrogen occurs principally as pyridinic type and pyrrolic type with small amounts of amide types, nitriles, and other unidentified types. Refining of shale oil by thermal methods and chemical or solvent extraction processes reduces nitrogen levels appreciably, but sulfur level is not affected much. Refining of shale oil by processes involving hydrogenation can be effective in producing extremely low level nitrogen, sulfur, and presumably oxygen fuels and feedstocks.

The susceptibility of oils to HDN depends on the nature of the nitrogen compound types present and the hydrogenation scheme employed. The nature of the nitrogen compound types remaining at low levels after upgrading of shale oil gives evidence of the reaction mechanisms involved. Some available analytical techniques can give nitrogen compound-type information relating to mechanisms of hydrodenitrogenation.

ACKNOWLEDGMENT

The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U.S. Department of the Interior, and the University of Wyoming.

REFERENCES

1. Mills, G. A., E. R. Boedeker, and A. G. Oblad. Chemical Characterization of Catalysts. I. Poisoning of Cracking Catalysts by Nitrogen Compounds and Potassium Ion. *J. Am. Chem. Soc.*, v. 72, 1950, pp. 1554-1560.
2. Jensen, H. B., R. E. Poulson, and G. L. Cook. Preprints, Div. Fuel Chem., ACS, v. 15, No. 1, 1971, pp. 113-121.
3. Dinneen, G. U., C. S. Allbright, and J. S. Ball. Comparison of Brazilian and Colorado Shale Oils. *Chem. Eng. Data*, v. 2, No. 1, 1957, pp. 91-95.
4. Hill, G. R., D. J. Johnson, L. Miller, and J. L. Dougan. *Ind. and Eng. Chem., R & D*, v. 6, 1967, pp. 52-59.
5. Jacobson, I. A., A. W. Decora, and G. L. Cook. Retorting Indexes for Oil-Shale Pyrolyses from Ethylene-Ethane Ratios of Product Gases. Preprints, Div. Fuel Chem., ACS, v. 19, No. 2, 1974, pp. 183-191.
6. Jacobson, I. A., A. W. Decora, and G. L. Cook. Retorting Indexes for Oil-Shale Pyrolyses from Ethylene-Ethane Ratios of Product Gases. *BuMines RI 7921*, 1974, 22 pp.
7. Hendrickson, T. A. Oil Shale Processing Methods. *Colo. School of Mines Quart.*, v. 69, No. 2, 1974, pp. 45-69.
8. Matzick, A., R. O. Dannenberg, J. R. Ruark, J. E. Phillips, J. D. Lankford, and B. Guthrie. Development of the Bureau of Mines Gas-Combustion Oil-Shale Retorting Process. *BuMines Bull.* 635, 1966, 199 pp.

9. Ruark, J. R., H. W. Sohns, and H. C. Carpenter. Gas Combustion Retorting of Oil Shale Under Anvil Points Lease Agreement: Stage I. BuMines RI 7303, 1969, 109 pp.
10. Ruark, J. R., H. W. Sohns, and H. C. Carpenter. Gas Combustion Retorting of Oil Shale Under Anvil Points Lease Agreement: Stage II. BuMines RI 7540, 1971, 74 pp.
11. Cameron, R. J., and B. Guthrie. Oil from Shale. Chem. Eng. Prog., v. 50, 1954, pp. 336-341.
12. Hubbard, A. B. Automated Fischer Retorts for Assaying Oil Shale and Bituminous Materials. BuMines RI 6676, 1965, 19 pp.
13. Harak, A. E., A. Long, Jr., and H. C. Carpenter. Preliminary Design and Operation of a 150-Ton Oil Shale Retort. Colo. School of Mines Quart., v. 64, No. 4, 1970, pp. 41-56.
14. Carpenter, H. C., and H. W. Sohns. Development of Technology for In Situ Oil Shale Processes. Colo. School of Mines Quart., v. 69, No. 2, 1974, pp. 143-169.
15. Harak, A. E., L. Dockter, A. Long, and H. W. Sohns. Oil Shale Retorting in a 150-Ton Batch-Type Pilot Plant. BuMines RI 7995, 1974, 31 pp.
16. Burwell, E. L., H. C. Carpenter, and H. W. Sohns. Experimental In Situ Retorting of Oil Shale at Rock Springs, Wyoming. BuMines TPR 16, June 1969, 8 pp.
17. Burwell, E. L., T. E. Sterner, and H. C. Carpenter. Shale Oil Recovery by In Situ Retorting--A Pilot Study. J. Petrol. Technol., v. 22, 1970, pp. 1520-1524.
18. Burwell, E. L., T. E. Sterner, and H. C. Carpenter. In Situ Retorting of Oil Shale (Results of Two Field Experiments). BuMines RI 7783, 1973, 41 pp.
19. Hill, G. R., and P. Dougan. The Characteristics of a Low Temperature In Situ Shale Oil. Colo. School of Mines Quart., v. 62, No. 3, 1967, pp. 75-90.
20. Brantley, F. E., R. J. Cox, H. W. Sohns, W. I. Barnet, and W.I.R. Murphy. High Temperature Shale Oil (Production and Utilization). Ind. Eng. Chem., v. 44, 1952, pp. 2641-2647.
21. Dinneen, G. U., J. R. Smith, and C. W. Bailey. High Temperature Shale Oil (Product Composition). Ind. Eng. Chem., v. 44, 1952, pp. 2647-2650.
22. Sohns, H. W., E. E. Jukkola, R. J. Cox, F. E. Brantley, W. G. Collins, and W.I.R. Murphy. Entrained-Solids Retorting of Colorado Oil Shale (Equipment and Operation). Ind. Eng. Chem., v. 47, 1955, pp. 461-464.
23. Tihen, S. S., J. F. Brown, H. B. Jensen, P. R. Tisot, N. M. Melton, and W.I.R. Murphy. Entrained-Solids Retorting of Colorado Oil Shale (Product Yields and Properties). Ind. Eng. Chem., v. 47, 1955, pp. 464-468.
24. Sohns, H. W., E. E. Jukkola, and W.I.R. Murphy. Development and Operation of an Experimental Entrained Solids, Oil-Shale Retort. BuMines RI 5522, 1959, 45 pp.
25. Dinneen, G. U. Effect of Retorting Temperature on the Composition of Shale Oil. Chem. Eng. Prog., v. 61, 1965, pp. 42-47.

26. Cattell, R. A., Boyd Guthrie, and L. S. Schramm. Retorting Colorado Oil Shale--A Review of the Work of the Bureau of Mines, U.S.D.I. *Oil Shale and Cannel Coal*, v. 2, Inst. Petrol., London, 1951, pp. 345-399.
27. Cady, W. E., and H. S. Seelig. Composition of Shale Oil. *Ind. Eng. Chem.*, v. 44, 1952, pp. 2636-2641.
28. Dinneen, G. U., R. A. Van Meter, J. R. Smith, C. W. Bailey, G. L. Cook, C. S. Allbright, and J. S. Ball. Composition of Shale Oil Naphtha. *BuMines Bull.* 593, 1961, 74 pp.
29. Dinneen, G. U., G. L. Cook, and H. B. Jensen. Estimation of Types of Nitrogen Compounds in Shale-Oil Gas Oil. *Anal. Chem.*, v. 30, 1958, pp. 2026-2030.
30. Ball, J. S., G. U. Dinneen, J. R. Smith, C. W. Bailey, and R. Van Meter. Composition of Colorado Shale-Oil Naphtha. *Ind. Eng. Chem.*, v. 41, 1949, pp. 581-587.
31. Smith, J. R., C. R. Smith, and G. U. Dinneen. Separation of Nitrogen Compounds by Adsorption from Shale Oil. *Anal. Chem.*, v. 22, 1950, pp. 867-870.
32. Janssen, A. G., E. R. Schierz, R. Van Meter, and J. S. Ball. Isolation and Identification of Pyrrole and 2-Methylpyrrole from Shale Oil. *J. Amer. Chem. Soc.*, v. 73, 1951, pp. 4040-4041.
33. Thorne, H. M., W.I.R. Murphy, J. S. Ball, K. E. Stanfield, and J. W. Horne. Characteristics and Utilization of Oil Shale and Shale Oil. *Ind. Eng. Chem.*, v. 43, 1951, pp. 20-27.
34. Thorne, H. M., W.I.R. Murphy, K. E. Stanfield, J. S. Ball, and J. W. Horne. Green River Oil Shales and Products. *Oil Shale and Cannel Coal*, v. 2, Inst. Petrol., London, 1951, pp. 301-344.
35. Van Meter, R. A., C. W. Bailey, J. R. Smith, R. T. Moore, C. S. Allbright, I. A. Jacobson, Jr., V. M. Hylton, and J. S. Ball. Oxygen and Nitrogen Compounds in Shale-Oil Naphtha. *Anal. Chem.*, v. 24, 1952, pp. 1758-1763.
36. Dinneen, G. U., J. S. Ball, and H. M. Thorne. Composition of Crude Shale Oils. *Ind. Eng. Chem.*, v. 44, 1952, pp. 2632-2635.
37. Dinneen, G. U. Shale Oil--What Is It? *Petrol. Refiner*, v. 33, 1954, pp. 113-116.
38. Thorne, H. M., and J. S. Ball. The Composition of Crude Shale Oils. Chapter 5 in *The Chemistry of Petroleum Hydrocarbons*, B. T. Brooks, et al., eds., Reinhold Publishing Corp., N. Y., 1954, pp. 63-82 in v. 1.
39. Dinneen, G. U., J. R. Smith, R. A. Van Meter, C. S. Allbright, and W. R. Anthony. Application of Separation Techniques to a High-Boiling Shale Oil Distillate. *Anal. Chem.*, v. 27, 1955, pp. 185-190.
40. Thorne, H. M. Retort Oil Shale for Chemicals. *Petrol. Refiner*, v. 35, 1956, pp. 155-160.
41. Poulson, R. E., H. B. Jensen, and G. L. Cook. Nitrogen Bases in a Shale-Oil Light Distillate. Preprints, Div. Petrol. Chem., ACS, v. 16, No. 1, 1971, pp. A49-A55.

42. Poulson, R. E., H. B. Jensen, J. J. Duvall, F. L. Harris, and J. R. Morandi. Determination of Compound Types in Complex Mixtures Using Subtraction and Gas Chromatographic Readout. *Analysis Instrumentation*, v. 10, Instrument Society of America, 1972, pp. 193-201.
43. Morandi, J. R., and R. E. Poulson. Nitrogen Types in Light Distillates from Aboveground and In Situ Combustion Produced Shale Oils. *This Symposium*.
44. Dinneen, G. U. Sulfur and Nitrogen Compounds in Shale Oil. *Proc. Amer. Petrol. Inst.*, v. 42 (VIII), 1962, pp. 41-44.
45. Carpenter, H. C., and P. L. Cottingham. A Survey of Methods for Desulfurizing Residual Fuel Oil. *BuMines IC 8156*, 1963, 29 pp.
46. Koros, R. M., S. Bank, J. E. Hofman, and M. I. Koy. Hydrodenitrogenation of Shale Oil. *Preprints, Div. Petrol. Chem., ACS*, v. 12, No. 4, 1967, pp. B165-B174.
47. Silver, H. F., N. H. Wang, H. B. Jensen, and R. E. Poulson. Denitrification Reactions in Shale Gas Oil. *Preprints, Div. Petrol. Chem., ACS*, v. 17, No. 4, 1972, pp. G94-G100.
48. Wang, N. H. Hydrodenitrification Reactions in Shale. M.S. Thesis, University of Wyoming, 1973.
49. Lankford, J. D., and C. F. Ellis. Shale Oil Refining. *Ind. Eng. Chem.*, v. 43, 1951, pp. 27-32.
50. Lankford, J. D., and Boyd Morris. Refining of Colorado Shale Oil. A Review of Work by the Bureau of Mines, U.S.D.I. *Oil Shale and Cannel Coal*, v. 2, *Inst. Petrol.*, London, 1951, pp. 500-532.
51. Annual Report of the Secretary of the Interior, Part II: Oil from Oil Shale. *BuMines RI 4652*, 1950, 70 pp.
52. Annual Report of the Secretary of the Interior, Part II: Oil from Oil Shale. *BuMines RI 4866*, 1951, 86 pp.
53. Annual Report of the Secretary of the Interior, Part II: Oil from Oil Shale. *BuMines RI 4943*, 1952, 70 pp.
54. Annual Report of the Secretary of the Interior, Part II: Oil from Oil Shale. *BuMines RI 5119*, 1955, 115 pp.
55. Berg, C., W. E. Bradley, R. I. Stirton, R. G. Fairfield, C. B. Leffert, and J. H. Ballard. Catalytic Desulfurization of High-Sulfur Stock by the Cobalt Molybdate Process. *Chem. Eng. Progress, AIChE Trans.*, 1947, pp. 1-12.
56. Carver, Harold E. Conversion of Oil Shale to Refined Products. *Colo. School of Mines Quart.*, v. 59, No. 3, 1964, pp. 19-38.
57. Clarke, E. L., R. W. Hiteshue, H. J. Kandiner, and B. Morris. Hydrogenation of Shale-Oil Coker Distillate. *Ind. Eng. Chem.*, v. 43, 1951, pp. 2173-2178.
58. Smith, W. M., T. C. Landrum, and G. E. Phillip. Hydrogenation of Shale Oil. *Ind. Eng. Chem.*, v. 44, 1952, pp. 586-589.

59. Pelipetz, M. G., M. L. Wolfson, H. Ginsberg, and E. L. Clark. High Pressure Hydrogenation of Crude Shale Oil. *Chem. Eng. Prog.*, v. 48, No. 7, 1952, pp. 353-356.
60. Cottingham, P. L., J. C. Antweiler, L. G. Mayfield, R. E. Kelley, and W. P. Coker. Hydrofining Thermally Cracked Shale-Oil Naphtha. *Ind. Eng. Chem.*, v. 48, 1955, pp. 1146-1151.
61. Carpenter, H. C., C. B. Hopkins, R. E. Kelley, and W.I.R. Murphy. A Method for Refining Shale Oil. *Ind. Eng. Chem.*, v. 48, 1956, pp. 1139-1145.
62. Crecelius, R. L., E. O. Kindschy, E. R. White, P. L. Cottingham, and W.I.R. Murphy. Recycle Hydrogenated Shale-Oil Crude. *Petrol. Refiner*, v. 35, 1956, pp. 171-175.
63. Cottingham, P. L., E. R. White, and C. M. Frost. Hydrogenating Shale Oil to Catalytic Reforming Stock. *Ind. Eng. Chem.*, v. 49, 1957, pp. 679-684.
64. Carpenter, H. C., and P. L. Cottingham. Evaluation of Catalysts for Hydrogenating Shale Oil. *BuMines RI 5533*, 1959, 29 pp.
65. Frost, C. M., H. C. Carpenter, C. B. Hopkins, Jr., S. S. Tihen, and P. L. Cottingham. *BuMines RI 5574*, 1960, 17 pp.
66. Benson, D. B., and L. Berg. Catalytic Hydrotreating of Shale Oil. *Chem. Eng. Prog.*, v. 62, No. 8, 1966, pp. 61-67.
67. Hellwig, K. C., S. Fergelman, and S. B. Alpert. Upgrading Fuels by the H-Oil Process. *Chem. Eng. Progress*, v. 62, No. 8, 1967, pp. 71-74 and *Colo. School of Mines Quart.*, v. 62, No. 3, 1967, pp. 123-132.
68. Cottingham, P. L., and H. C. Carpenter. Hydrocracking Prehydrogenated Shale Oil. *Ind. Eng. Chem. Proc. Design and Dev.*, v. 6, No. 2, 1967, pp. 212-217.
69. Montgomery, D. P. Refining Pyrolytic Shale Oil. *Preprints, Div. Petrol. Chem., ACS*, v. 13, No. 2, 1968, pp. F58-F70.
70. Lessley, G. E., H. F. Silver, and H. B. Jensen. Thermal Cracking of Shale Gas Oil Under a Hydrogen Atmosphere. *Preprints, Div. Petrol. Chem., ACS*, v. 15, No. 4, 1970, pp. A84-A92.
71. Frost, C. M. Refining of Crude Shale Oil Produced by In Situ Retorting. *Preprints, Div. Fuel Chem., ACS*, v. 16, No. 1, 1972, pp. 73-87.
72. Frost, C. M., and P. L. Cottingham. Hydrogenating Shale Oil at Low Space Velocity. *BuMines RI 7738*, 1973, 9 pp.
73. Frost, C. M., and H. B. Jensen. Hydrodenitrogenation of Crude Shale Oil. *Preprints, Div. Petrol. Chem., ACS*, v. 18, No. 1, 1973, pp. 119-128.
74. Frost, C. M., R. E. Poulson, and H. B. Jensen. Production of Synthetic Crude from Crude Shale Oil Produced by In Situ Combustion Retorting. *Preprints, Div. Fuel Chem., ACS*, v. 19, No. 2, 1974, pp. 156-168.

75. Frost, C. M., and R. E. Poulson. Nitrogen Types in Syncrudes from In Situ Crude Shale Oil. This Symposium.
76. Ball, J. S. Determination of Sulfur Types in Petroleum Distillates. BuMines RI 3591, 1941, 60 pp.
77. Rall, H. T., C. J. Thompson, H. J. Coleman, and R. L. Hopkins. Sulfur Compounds in Crude Oil. BuMines Bull. 659, 1972, 187 pp.
78. ASTM Book of Standards, Part 17, Method D267-61T, "Chemical Analysis of Rubber Products," 1964, pp. 153-154.
79. Brown, Dennis, D. G. Earnshaw, F. R. McDonald, and H. B. Jensen. Gas-Liquid Chromatographic Separation and Spectrometric Identification of Nitrogen Bases in Hydrocracked Shale Oil Naphtha. Anal. Chem., v. 42, 1970, pp. 146-151.
80. Silver, H. F., N. H. Wang, H. B. Jensen, and R. E. Poulson. A Comparison of Shale Gas Oil Denitrification Reactions Over Co-Mo and Ni-W Catalysts. Preprints, Div. Fuel Chem., ACS, v. 19, No. 2, 1974, pp. 147-155.
81. Poulson, R. E., C. M. Frost, and H. B. Jensen. Characteristics of Synthetic Crude Produced by In Situ Combustion Retorting. Preprints, Div. Fuel Chem., ACS, v. 19, No. 2, 1974, pp. 175-182.
82. Hartung, G. K., D. M. Jewell, O. A. Larson, and R. A. Flinn. Catalytic Hydrogenation of Indole in Furnace Oil. J. Chem. Eng. Data, v. 6, 1961, pp. 477-480.
83. Flinn, R. A., O. A. Larson, and H. Beuther. The Kinetics of Hydrodenitrogenation. Preprints, Div. Petrol. Chem., ACS, v. 17, No. 1, 1962, pp. 163-172.
84. Flinn, R. A., O. A. Larson, and H. Beuther. How Easy is Hydrodenitrogenation. Hydrocarbon Process and Petrol. Refiner, v. 42, No. 9, 1963, pp. 129-132.
85. Doelman, J., and J. C. Vlughter. Model Studies on the Catalytic Hydrogenation of Nitrogen-Containing Oils. Proc. Sixth World Petroleum Congress, Section III, 1963, pp. 247-256.
86. National Petroleum Council. U.S. Energy Outlook, v. 2, 1972, p. 80.