

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

REACTIVITY OF OIL SHALE TOWARDS SOLVENT HYDROGENATION

By

R. M. Baldwin, D. P. Bennett and R. A. Briley
Chemical Engineering Department, Colorado School of Mines, Golden, Colorado 80401

INTRODUCTION

Oil may be extracted from oil shale by a number of different techniques. Of the several procedures available, only pyrolysis (retorting) has received the attention required to develop a commercial processing technology (1). Direct hydrogenation, or hydrogenation in slurry systems, is a well developed technology for conversion of coal to liquid fuels, but application of this technique to oil shale has only recently begun to receive attention. Kerogen in oil shale is known to be relatively insoluble in most organic solvents at their normal boiling points, but when oil shale is heated to temperatures above 600 K, the organic matter in shale may be solvent extracted in high yield (2, 3). Several early patents describe solvent processing of torbanite and other shale-like materials at elevated temperatures both with and without hydrogen gas atmospheres (4-7). In an extensive study, Jensen et al. (8) reported on hydroprocessing of a Green River oil shale in both batch and continuous reactors. Their results indicated that very high organic carbon conversions could be attained. Recently, patents on direct hydrogenation processes in vehicle oils have been granted to Gregoli (9), Patzer (10) and Greene (11). Results on hydroprocessing of an Australian oil shale have also been published by Baldwin et al. (12).

The objective of the work described in this paper was to compare the effect of direct hydrogenation operating conditions on the yield of oil and gas from a sapropelic oil shale (Australian Stuart A) and a humic oil shale (Montgomery County, Kentucky). These data were developed from batch autoclave experiments using both a pure hydrogen donor solvent (tetralin) and non-donor solvents (toluene and 1-methylnaphthalene).

EXPERIMENTAL APPARATUS AND METHODS

All experiments for this study were conducted in a 300 cc batch stirred autoclave reactor, manufactured by Autoclave Engineers, Inc. A schematic of the reactor and associated piping are shown in Figure 1. Shales from the upper part of the Kerosene Creek seam in the Stuart Deposit and from the Cleveland Member, Ohio Shale, Montgomery County, Kentucky were wet ground in a rod mill, sieved to 100% minus 74 micron (minus 200 mesh) and vacuum dried at 40°C prior to use. The Stuart shale was beneficiated by de-sliming prior to grinding, while the Kentucky shale was essentially run-of-mine. Fischer Assays of the feed shales used for this study are presented in Table I. Two different types of solvents were used for this study; 1,2,3,4-tetrahydronaphthalene (tetralin) was used as a hydrogen donor solvent and toluene and 1-methylnaphthalene were employed as non-donor solvents. Hydrogen used was 95% H₂ with a 5% argon tracer added to facilitate gas made calculations.

TABLE I
FISCHER ASSAY, PARENT SHALES

	% Spent Shale	Product Yield			Oil, gpt	OCC ^b
		% Oil	% Water	% Gas+Loss		
Kentucky ^a	91.6	4.6	1.5	2.3	11.6	
Stuart ^a	72.4	16.3	5.3	6.0	44.0	44.7

a. Analysis performed by Commercial Testing and Engineering, Golden, CO.

b. OCC = organic carbon conversion, %.

Reaction products were analyzed by several different techniques. Reaction product gases were determined on a Carle model 111-H gas chromatograph, with hydrogen, hydrocarbon gases

(through C₅) and carbon oxide gases quantified. Liquids were separated by acetone washing of the product slurry and soxhlet extraction of the residue with a solution of 50% benzene/50% methanol. The liquids were analyzed by chromatographic simulated distillation on an HP model 5840 gas chromatograph to determine the boiling range and by elemental analysis on a Carlo-Erba elemental analyzer. The spent shale was analyzed for total and inorganic carbon using a Coulometrics system and then ashed in a muffle furnace. Hydrocarbons were speciated with an Extranuclear model EL mass spectrometer, interfaced to a Carlo-Erba model 4100 capillary column gas chromatograph. The GC/MS system was operated in the electron impact mode, at 70 eV.

DISCUSSION OF RESULTS

Results of the experimental runs on the shales are presented in Tables II through V. In all cases, data on organic carbon conversion (OCC) and oil yield (OY) are shown at the applicable reaction conditions. The data given for oil selectivity represent carbon conversion to oil, determined by a quantitative gas analysis followed by a carbon balance on the reaction system. The selectivity reflects the carbon conversion to oil, relative to total carbon converted (expressed as a percentage of the total carbon conversion). Discussion of these data follows.

TABLE II
EFFECT OF TEMPERATURE AND SOLVENT TYPE, STUART SHALE

Temperature	Solvent	
	Tetralin	1-Methylnaphthalene
350°C	OCC: 32.3	OCC: 43.6
	OY: 91.8	OY: 95.9
425°C	OCC: 83.3	OCC: 81.6
	OY: 93.9	OY: 91.2

OCC = organic carbon conversion, %

OY = oil yield, % of total carbon converted

All runs at 800 psi H₂ initial pressure, 1 hour nominal residence time, 1:1 solvent-to-shale ratio.

TABLE III
EFFECT OF TEMPERATURE AND SOLVENT TYPE, KENTUCKY SHALE

Temperature	Solvent	
	Tetralin	Toluene
375	OCC: 38.0	OCC: 44.0
	OY: 96.2	OY: 98.5
425	OCC: 79.6	OCC: 80.9
	OY: 95.1	OY: 95.1
450	OCC: 85.6	NA
	OY: 97.2	

All runs at 800 psi initial H₂ pressure, 1 hour nominal residence time, 2:1 solvent-to-shale ratio.

Temperature

Temperature effects both organic carbon conversion and selectivity for oil formation. For both shales studied, increasing temperature raises organic carbon conversion. However, in the case of Kentucky shale, the reactivity towards conversion in both the donor and non-donor solvents is lower. This is reflected in the conversions found at the lower temperature levels. In tetralin, conversion of organic carbon is approximately 32% at 350°C for Stuart shale, while comparable conversions are achieved for Kentucky shale at 375°C (38%). In the non-donor solvents, the same temperature sensitivity is seen. This is undoubtedly due to the relative reaction rates of the two shales, with the more paraffinic Stuart shale reacting quicker and, thus, giving higher yields of oil at lower temperatures. It should be noted that since the reactor was operated in the true batch

mode, the actual reaction time was different for runs made at 350° and 375°C. Approximately 5 to 8 minutes was required to heat the reactor from 350° to 375°C and, thus, the comparisons of temperature sensitivity are even more pronounced than indicated by the data due to this confounding effect of heat-up time. At the higher temperature levels, reaction time is sufficiently long that the reaction has proceeded essentially to completion and the temperature sensitivity and reactivity differences noted between the two shales at the lower temperature levels are no longer apparent.

TABLE IV

EFFECT OF SOLVENT AND HYDROGEN PARTIAL PRESSURE, STUART SHALE

Solvent	Gas Atmosphere			
	Hydrogen		Nitrogen	
	800	300	800	300 ^a
Tetralin	OCC: 83.3	OCC: 83.7	OCC: 77.9	OCC: 83.3
	OY: 93.9	OY: 92.2	OY: 90.8	OY: 90.7
1-Methylnaphthalene	OCC: 81.6	OCC: 68.6	NA	NA
	OY: 91.2	OY: 88.0		

a. Initial total pressure at room temperature.

All runs at 425°C, 1 hour nominal residence time, 1:1 solvent-to-shale ratio.

TABLE V

EFFECT OF SOLVENT AND HYDROGEN PARTIAL PRESSURE, KENTUCKY SHALE

Solvent	Gas Atmosphere			
	Hydrogen		Helium	
	800	300	800	300 ^a
Tetralin	OCC: 79.6	NA	OCC: 76.57	NA
	OY: 95.1		OY: 97.35	
Toluene	OCC: 80.9	OCC: 72.6	OCC: 44.01	NA
	OY: 95.1	OY: 95.9	OY: 91.59	

a. Initial total pressure at room temperature.

All runs at 425°C, 1 hour nominal residence time, 1:1 solvent-to-shale ratio.

Somewhat surprisingly, for both shales temperature has little effect on selectivity for oil formation. This could be due to the relatively low temperatures employed in the study, although even at 450°C, selectivity for oil formation in tetralin was extremely high. It is also possible that reactions responsible for hydrocarbon gas formation in this reaction system have very high activation energies, requiring temperatures in excess of 450°C in order to proceed at an appreciable rate. The hydrogen activity of the system could also be a factor here, especially in inhibiting free-radical cracking reactions. Selectivities are somewhat lower in the non-donor systems, or where an inert gas rather than hydrogen is used for the reaction gas atmosphere, but overall oil yields are extraordinarily high for this reaction system.

Organic carbon conversions for these shales retorted under Fischer Assay conditions are as reported in Table I. Comparison of these conversions with those shown in Tables II through V points out the extreme differences in carbon utilization between these two reaction schemes. While retorting leaves behind in excess of 50% of the organic carbon on the spent shale, hydroprocessing successfully converts in excess of 80% of the carbon and at lower temperatures with a resulting higher selectivity for oil forming reactions.

Solvent and Hydrogen Partial Pressure

Solvent type (hydrogen donor or non-donor) has a marked effect on carbon conversion, but only in the absence of gas phase molecular hydrogen. When molecular hydrogen is present in the reactor, organic carbon conversion and the yield structure are nearly independent of the type of solvent used. In the absence of gaseous hydrogen, however, the nature of the solvent becomes very important, with high conversions only obtainable using the hydrogen donor solvent (tetralin). This

interdependency of solvent efficacy with hydrogen partial pressure is most clearly shown in Tables IV and V, where data on runs made with variable gas atmospheres is shown. As may be seen, hydrogen in some form is required to achieve the level of organic carbon conversions being obtained under these reaction conditions. With neither molecular hydrogen in the gas phase or donatable hydrogen in the solvent, low carbon conversions (typically on the order of the pyrolysis yields at these temperatures) are realized.

Product Oil Characterization

Sample total ion intensity (TII) chromatograms for a shale oil produced by hydrogenation of Stuart shale are shown in Figure 2. The chromatograms represent the whole oil and several fractions generated by open column elution chromatography. Although work is still in progress on identification of individual components in the two oils, several general features have been elucidated by GC/MS. In the case of Stuart shale oil, the spectrum is dominated by a homologous series of normal paraffins, commencing at approximately C₇ and continuing past C₃₀. Clustered around each normal paraffin peak are two smaller peaks, which represent mono-olefinic hydrocarbons with the same carbon number as the paraffin. Between the paraffin/olefin clusters, the peaks shown on the chromatogram for Stuart shale are largely comprised of iso-paraffins with a low degree of branching, alkyl-substituted aromatics and cycloparaffins and nitrogen moieties.

Further separation work on the Stuart shale is in progress, with attention being given to specification of the nitrogen compounds present. To date, a homologous series of nitriles from C₇ through C₃₀ and nitrogen-containing heterocycles have been speculated. The nitrogen heterocycles are predominately alkyl-substituted pyrrolidines, quinolines and isoquinolines. No evidence of amines or amides has been found, although under the conditions of reaction, amides are most probably converted to nitriles. This could explain the high concentration of nitriles found in the product oil, as these species are not normally present in shale oils. Regtop et al. (13) have reported the identification of a nitrile series in a Fischer Assay oil from Rundle shale.

Identification of chemical species in the Kentucky shale oil by GC/MS also indicates a homologous paraffin series starting at C₉ and terminating at C₃₀ or higher. In this case, however, the product distribution is much more complex and is not dominated by the paraffin series to the extent of the Stuart shale oil. The remaining compounds seem to consist predominately of alkyl-substituted benzenes and cycloparaffins and nitrogen moieties.

Simulated chromatographic distillation of the product oils is being used to determine the effect of operating variables on the boiling range distribution. At this time, data analysis is incomplete, preventing a comprehensive evaluation of the differences in distillation characteristics. Preliminary comparisons with Stuart Fischer Assay oil indicate that the shale oil produced by this process has approximately the same boiling range distribution, even though the highest temperature experienced in producing the oil was some 75°C lower than the final Fischer Assay temperature (500°C).

CONCLUSIONS

The results of this study indicate that sapropelic shales, such as the Australian Stuart A, are moderately more reactive towards oil extraction by direct hydrogenation than humic shales. This result is not surprising considering the aromaticity and hydrogen deficiency of humic shales relative to sapropelic shales. Both types of shale exhibit the same sensitivity to solvent type and hydrogen partial pressure, with the humic shale showing a lower temperature sensitivity (e.g., slower rate of reaction). Finally, the product spectra are substantially different, as would be expected due to the differing source materials for the organics in these shales.

ACKNOWLEDGMENT

The authors would like to express their gratitude to Southern Pacific Petroleum, N. L., Sydney, Australia for financial support of this work.

Figure 1
Reaction System Schematic

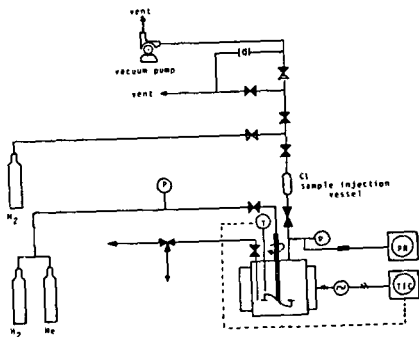
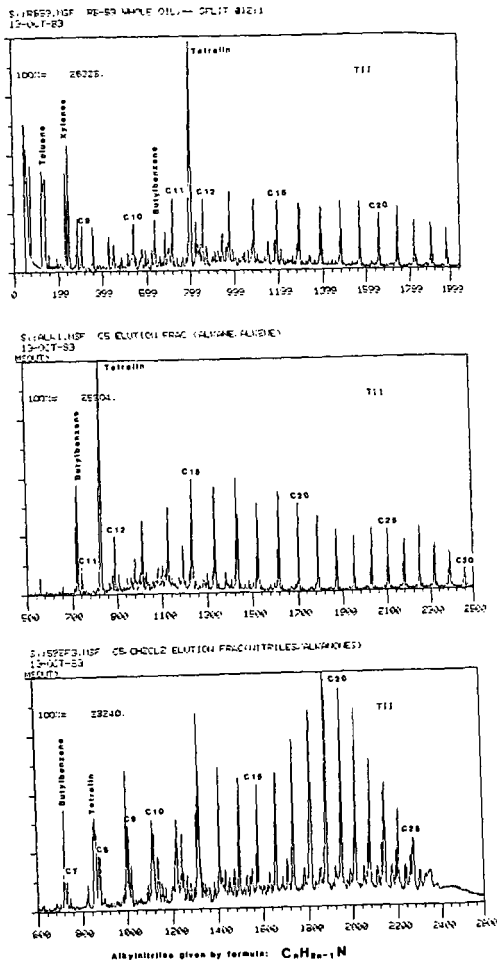


Figure 2
TII Chromatograms of Whole Shale Oil and Elution Fractions



LITERATURE CITED

- (1) Baughman, G. L., Synthetic Fuels Data Handbook, second edition, Cameron Engineers, Inc. (1978).
- (2) Gavin, M. J. and Aydelotte, J. T., "Solubilities of Oil Shales in Solvents for Petroleum", U. S. B. M. Report of Investigation 2313 (1922).
- (3) Dulhunty, J. A., "Solvent Extraction of Torbanite", Proc. Linnean Soc., New South Wales, vol. 67 (1942).
- (4) Ryan, H. D., "Bituminous Material from Shale", U. S. Patent 1327572, January 6, 1920.
- (5) Hampton, H., "Hydrocarbons from Bituminous Shale-Like Material", U. S. Patent 1668898, May 8, 1928.
- (6) Fisher, A., "Pyrolytic Conversion and Coking of Finely Divided Bituminous Material and Hydrocarbon Oil", U. S. Patent 2073367, March 9, 1937.
- (7) Buchan, F. E., "Processing Oil Shale", U. S. Patent 2487788, November 15, 1949.
- (8) Jensen, H. B., Barnett, W. I. and Murphy, W. I. R., "Thermal Solution and Hydrogenation of Green River Oil Shale", U. S. B. M. Bulletin 533 (1953).
- (9) Gregoli, A. A., "Fluidized Bed Hydroretorting of Oil Shale", U. S. Patent 4075081, February 21, 1978.
- (10) Pätzer, J. F., "Recovery of Oil from Oil Shale", U. S. Patent 4238315, December 9, 1980.
- (11) Greene, M. I., "Process for Hydrogenation/Extraction of Organics Contained in Rock", U. S. Patent 4325803, April 20, 1982.
- (12) Baldwin, R. M., Frank, W. L., Baughman, G. L. and Minden, C. S., "Hydroprocessing of Australian (Stuart A) Oil Shale", Proc. 16th Oil Shale Symp., Golden, CO (1983).
- (13) Regtop, R. A., Crisp, P. T. and Ellis, J., "Chemical Characterization of Shale Oil from Rundle, Queensland", Fuel, Vol. 61, February, 1982.