

## HYDROPROCESSING OF STUART (AUSTRALIAN) OIL SHALE

R.M. Baldwin and W.L. Frank  
Chemical and Petroleum-Refining  
Engineering Department  
Colorado School of Mines  
Golden, CO 80401

G.L. Baughman  
Colorado School of Mines Research Institute  
Golden, CO 80401

C.S. Minden  
Southern Pacific Petroleum, N.L.  
Salt Lake City, UT 84103

### ABSTRACT

Research on production of shale oil by direct hydrogenation of oil shale has been conducted in batch stirred autoclave reactors. The objective of the work has been to elucidate the effect of operating variables on conversion of organic carbon, and the resulting yield structure (oil/gas). Yields of oil and gas (hydrocarbon and carbon oxide) have been quantified for hydroprocessing over a wide range of operating conditions using both pure hydrogen donor and pyrolysis oil solvents. The effects of temperature, reaction time, pressure, hydrogen partial pressure, and solvent characteristics on yield structure are described.

### INTRODUCTION

Oil may be extracted from oil shale by a number of different techniques. Of the several procedures available, only pyrolysis has received the attention required to develop a commercial processing technology (1). Direct hydrogenation, or hydrogenation in vehicle oils, is a well developed technology for conversion of coal to liquid fuels, but application of this technique to oil shale is far less well developed. 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 (4,5,6,7). 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).

The objective of the work described in this paper is to investigate the effect of direct hydrogenation operating conditions on the yield of oil and gas from an Australian oil shale (Stuart A). These data were developed from batch autoclave experiments using both pure hydrogen donor solvents (tetralin), and solvents derived by fractionation of a pyrolysis oil. Conditions employed for reaction include use of a vehicle oil (solvent), and temperatures substantially lower than those used in hydrogasification technologies (e.g. HYTORT).

### EXPERIMENTAL APPARATUS AND METHODS

All experiments for this study were performed in a 300 cc batch stirred autoclave reactor (Autoclave Engineers, Inc.). A schematic of the reactor and associated piping are shown in Figure 1. The reactor system was modified to include a sample injector. Two modes of operation were available with this apparatus: 1) true batch and, 2) injection, in which shale was

introduced directly into the pre-heated, pre-pressurized reactor.

Shale from the upper part of the Kerosene Creek seam in the Stuart Deposit was wet ground in a rod mill, sieved to 100% minus 74 micron (minus 200 mesh), and dried prior to use. A Fischer Assay of the feed shale for this study is shown in Table 1. Two different types of solvents were employed for the study; 1,2,3,4-tetrahydronaphthalene (tetralin) was used as a hydrogen donor solvent and later two fractions from a pyrolysis oil were employed as non-donor solvents. The pyrolysis oil was provided by Geokinetics, Inc., and was produced from a bench-scale retorting run on Stuart A shale. Hydrogen used was industrial grade from a local supplier.

Reaction products were analyzed by several different techniques. Reaction product gases were analyzed on a Carle Model 111-H gas chromatograph to determine hydrogen, hydrocarbon gases (through C5), and carbon oxide gases. Liquids were separated by acetone washing of the product slurry, and soxhlet extraction of the residue with a solution of 50% benzene plus 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.

#### DISCUSSION OF RESULTS

The first phase of the program dealt with a series of preliminary runs intended to investigate the effect of temperature, time, and total pressure on the yield structure using tetralin as the solvent. Robinson and Cummins (12) have described an oil shale conversion scheme where use of hydrogen donors such as tetralin is shown to be beneficial, and tetralin has long been used as a "standard" solvent in coal liquefaction studies where hydrogen donor

moieties are desired. Results of these preliminary runs are shown graphically in Figure 2. As can be seen, temperature has a pronounced effect on the extent of conversion. No effect of total pressure was seen in these runs, although the high solvent-to-shale ratio employed (10/1) may have masked that effect, if present. Pressures shown on the isotherms are initial (cold) hydrogen partial pressures, which translate to pressures at temperature of approximately 1000 and 1500 psi for starting pressures of 300 and 800 psi. These data were obtained with the reactor used in the true batch mode, and thus the reaction times shown are confounded by heat-up and cool-down times. One run was performed with helium rather than hydrogen in the gas phase, and organic carbon conversion was found to be unchanged. This demonstrates that molecular hydrogen need not be present in the gas phase, as long as good hydrogen donors are present in the liquid phase. Tetralin is a known free radical quencher, and thus is a very effective hydrogen transfer agent for this purpose.

The second phase of the project employed the reactor in the injection mode so that the kinetics of the reaction could be investigated. Experiments were performed at temperatures of 375, 400, and 425 C, and reaction times of 10 and 60 minutes. Starting pressure for each run was 800 psi (hydrogen pressure). Results of these runs are shown in Figure 3. As may be seen, the rate of the reaction is highly temperature dependent. An equilibrium conversion of approximately 92% was approached at 425 C, one hour residence time. The yield structure for the 60 minute data from these runs is shown in Table 2. These data illustrate one of the major advantages of this type of processing vs. standard high-temperature retorting: an extremely high selectivity for formation of oils is obtained. Simulated distillation of the product oil from the run at 425 C showed approximately 62% of the shale oil to boil below 343 C (650 F), and 44% of the shale

oil to be in the diesel oil range (425-600 F).

The third phase of the project was designed to investigate organic carbon conversion and process selectivity using solvents that more nearly resembled a process-derived recycle solvent. For this purpose, pyrolysis oil generated by retorting of a sample of Stuart A shale was fractionated in a spinning band distillation column. Three fractions were generated: light gas oil (420-610 F), heavy gas oil (610-735 F), and residuum (735+). The autoclave reactor was run in the true batch mode at temperatures of 400, 425, and 450 C, with an initial pressure of 800 psi (hydrogen). Reaction time was 60 minutes in each case, and both light and heavy gas oil fractions were used as solvents. Liquid products of the reaction were characterized by simulated distillation as above. Typical results of the runs are shown in Figure 4, and in Table 3. Figure 4 presents the simulated distillation envelopes from reaction in heavy gas oil solvent in comparison with the boiling range of the pyrolysis oil used to generate the solvent. As shown, temperature has a pronounced effect on the quality of the resulting shale oil, and considerable in-situ upgrading is indicated by the shifts in the envelopes. Results in light gas oil were similar to those shown in Figure 4. The residuum material was not employed as solvent in that very little of this type of material was shown to be produced in the first phases of the project. Summarized in Table 3 are the process selectivities in both light and heavy gas oil. As was the case with tetralin solvent, very high organic carbon conversions and selectivities to oil were obtained. Increasing the temperature resulted in increasing organic carbon conversion, but decreasing selectivity to oil formation, thus an optimum in temperature is suggested in this range. From the data collected, it is apparent that a temperature of approximately 425 C promotes maximum oil yield. The pyrolysis oil fractions employed as solvents

in this portion of the work were composed of largely normal paraffins, with some iso-paraffins, olefins, and monocycloparaffins present as well. The ability of these moieties to donate hydrogen is, however, limited. As proof, one run was made with helium in the gas phase rather than hydrogen, and with heavy gas oil as the solvent. Conversion of organic carbon was reduced by a factor of almost 4 when no molecular hydrogen was present in the reactor.

#### CONCLUSIONS

The research described above serves to highlight three major advantages of extracting shale oil by hydroprocessing vs. conventional pyrolysis. First, organic carbon conversions may be raised to very high values, with 90%+ readily attained at relatively mild operating conditions. Secondly, the process selectivity to oil is greatly enhanced. Since only small amounts of hydrocarbon gases are formed during reaction, hydrogen consumption at these high selectivities is not primarily for formation of gaseous saturates, but rather for hydrocracking and upgrading of the oil extracted. Finally, and most importantly, the oil quality as measured by simulated distillation is superior to any oil generated by pyrolytic retorting. This finding, and the remarkable selectivity for products in the diesel, kerosene, and jet fuel boiling range, indicates that further investigation into hydroprocessing technologies applied to oil shale is warranted.

#### ACKNOWLEDGEMENT

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

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", Bureau of Mines R.I. 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 1,327,572, Jan. 6, 1920.
5. Hampton, H., "Hydrocarbons from Bituminous Shale-Like Material", U.S. Patent 1,668,898, May 8, 1928.
6. Fisher, A., "Pyrolytic Conversion and Coking of Finely Divided Bituminous Material and Hydrocarbon Oil", U.S. Patent 2,073,367, March 9, 1937.
7. Buchan, F.E., "Processing Oil Shale", U.S. Patent 2,487,788, November 15, 1949.
8. Jensen, H.B., Barnet, W.I., and Murphy, W.I.R., "Thermal Solution and Hydrogenation of Green River Oil Shale", U.S. Bureau of Mines Bulletin 533, 1953.
9. Gregoli, A.A., "Fluidized Bed Hydroretorting of Oil Shale", U.S. Patent 4,075,081, February 21, 1978.
10. Patzer, J.F., "Recovery of Oil from Oil Shale", U.S. Patent 4,238,315, December 9, 1980.
11. Greene, M.I., "Process for Hydrogenation/Extraction of Organics Contained in Rock", U.S. Patent 4,325,803, April 20, 1982.
12. Robinson, W.E., and Cummins, J.J., "An Oil Shale Conversion Process Using Carbon Monoxide and Water", Laramie Energy Technology Center TPR-75/1, 1975.

FIGURE 1  
Reaction System Schematic

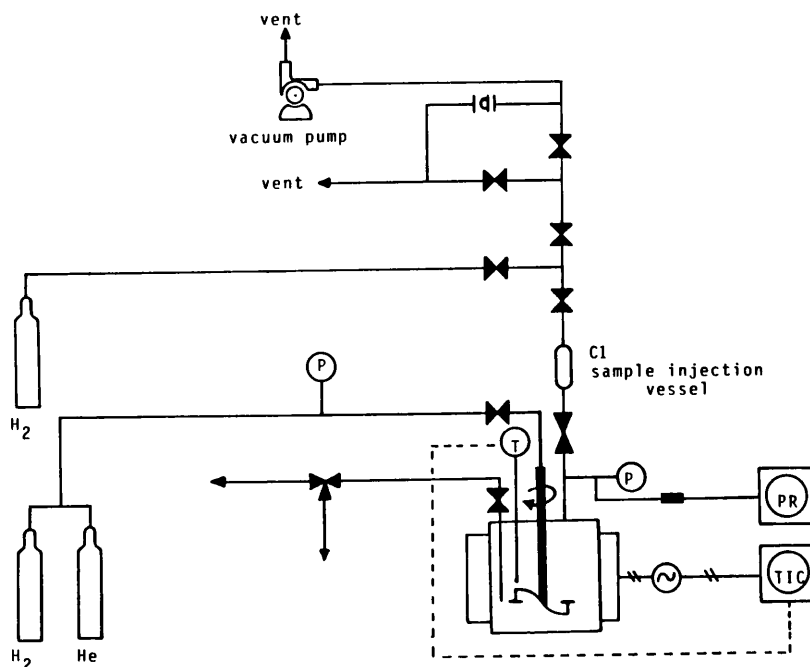


FIGURE 2  
Organic Carbon Conversion

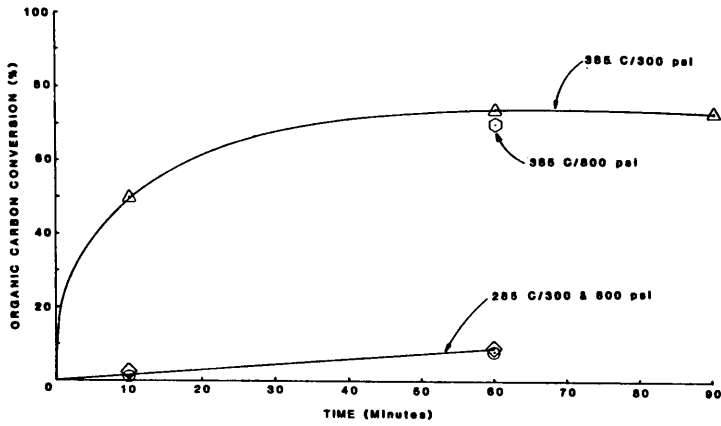


FIGURE 3  
Reaction Rate Data

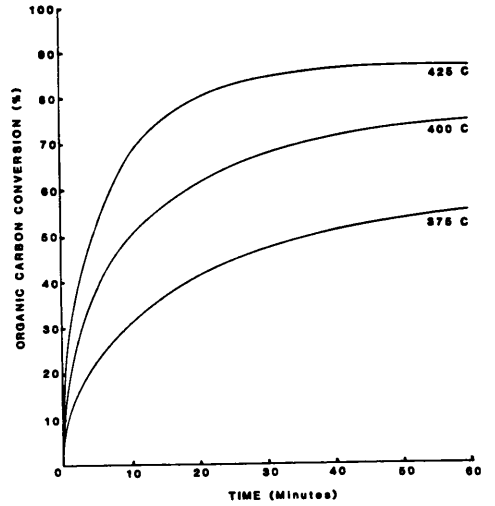


FIGURE 4  
Boiling Range Distributions in Pyrolysis Oil Solvents

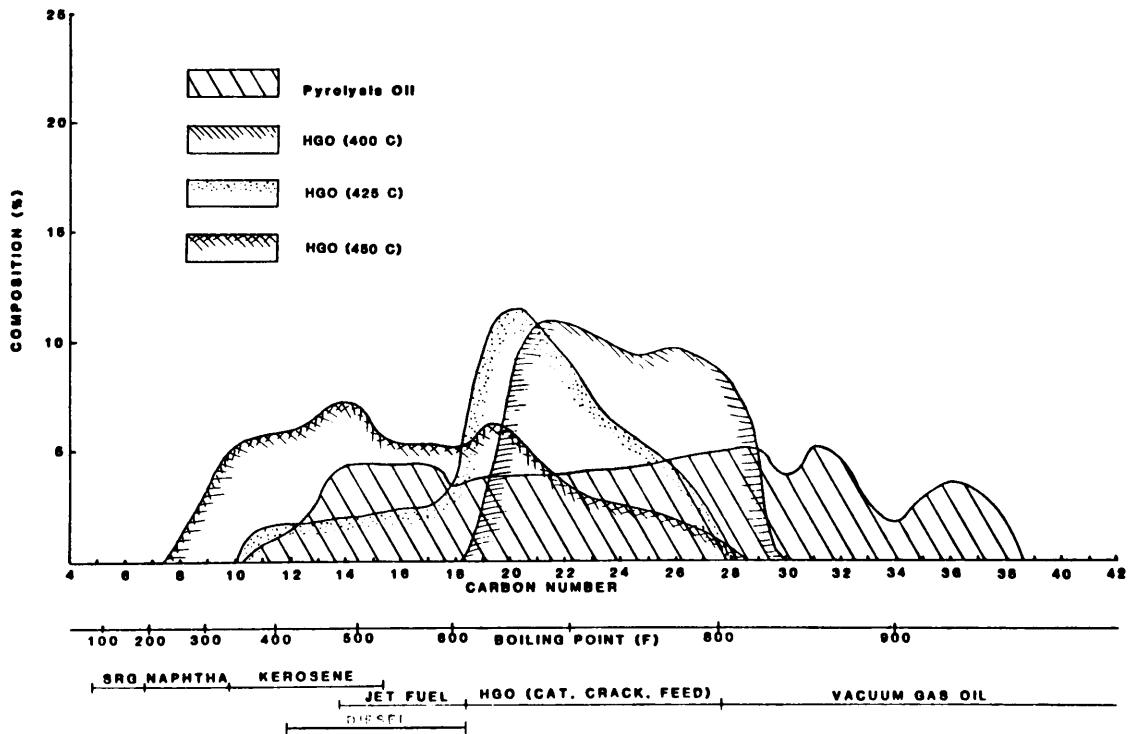


TABLE 1

FISCHER ASSAY OF FEED SHALE

<u>sample</u>	<u>gal/ton water</u>	<u>gal/ton oil</u>	<u>wt% gas + loss</u>
Stuart A	11.4	25.4	5.00

Analysis performed at Colorado School of Mines Research Institute

TABLE 2

YIELD STRUCTURE AND PROCESS SELECTIVITY IN TETRALIN

<u>TEMP( C)</u>	<u>%OCC</u>	<u>%ICC</u>	<u>%TCC</u>	<u>%HC GAS</u>	<u>%CO<sub>x</sub> GAS</u>	<u>%OIL</u>	<u>% FISCHER ASSAY</u>
375	55.2	24.8	53.4	0.59	3.53	95.87	102
400	75.6	16.9	72.3	0.78	3.26	95.96	139
425	87.2	17.8	83.2	1.77	3.67	94.56	158

%OCC = % conversion of organic carbon to oil+gas

%ICC = % conversion of inorganic carbon

%TCC = % conversion of total carbon

%HC GAS = % conversion of total carbon to C<sub>1</sub>-C<sub>5</sub> hydrocarbon gases

%CO<sub>x</sub> GAS = % conversion of total carbon to carbon monoxide + carbon dioxide

%OIL = % conversion of total carbon to C<sub>5</sub> + oil

ALL RUNS AT 60 MINUTES RESIDENCE TIME, 800 PSI INITIAL H<sub>2</sub> PRESSURE.

TABLE 3

YIELD STRUCTURE AND PROCESS SELECTIVITY IN PYROLYSIS OIL VEHICLES

<u>TEMP( C) AND VEHICLE</u>	<u>%OCC</u>	<u>%ICC</u>	<u>%TCC</u>	<u>%HC GAS</u>	<u>%CO<sub>x</sub> GAS</u>	<u>%OIL</u>	<u>%FISCHER ASSAY</u>
400 LGO	75.4	40.6	73.6	5.5	5.3	89.3	133
HGO	69.7	26.2	67.5	4.9	2.2	92.9	128
425 LGO	87.0	38.7	84.6	11.2	4.9	83.4	144
HGO	87.9	38.1	85.6	13.4	5.9	80.6	139
450 LGO	87.4	44.7	84.9	30.0	5.9	63.9	110
HGO	88.4	39.5	85.9	20.4	6.7	72.9	127

LGO = Light Gas Oil

HGO = Heavy Gas Oil