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EASTERN SHALE HYDRORETORTING

By

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INTRODUCTION

The Institute of Gas Technology (IGT), under a subcontract to HYCRUDE Corporation, participated in a feasibility study (Commercialization of the HYTORT Process), funded by Phillips Petroleum Company from December 1980 through May 1983. The overall objective of the Bench-Scale Unit (BSU) test program, which was one of the activities conducted, was to determine the effects of major process variables on conversion of organic carbon, yields and properties of oil and gas and consumption of hydrogen for hydroretorting of a specific Indiana New Albany shale. As part of the BSU program, an improved method was developed for measuring reactable organic oxygen in these shales, which resulted in greatly improved oxygen balances (1). The effects of particle size on product yields from hydroretorting a similar oil shale were measured in a high-pressure thermobalance unit and a semi-batch unit; the results of this work have been presented in earlier publications (2, 3).

Before the BSU hydroretorting tests were begun, a preliminary error-propagation analysis was performed to identify possible improvements in BSU measurements that could lead to better overall material and elemental balances. A list of additional potential sources of uncertainty (primarily due to the operating procedures used) was compiled. Based on the identification of these possible sources of uncertainty, additional equipment was ordered and installed and existing operating procedures and calculation methods were modified. The result was excellent overall material balance closures (100% $\pm$ 1%).

EQUIPMENT AND PROCEDURES

A flow diagram of the BSU after modification is shown in Figure 1. The BSU equipment consists primarily of a reactor with associated equipment for feeding and measuring the flow rates of feed shale and feed gas and for collecting and measuring the flow rates of residue shale, liquid product and product gas. Simple analog controllers are used to maintain reactor temperatures at the desired values, to maintain feed rates at constant values and to maintain the reactor pressure constant. Representative samples of the spent shale and feed and product gases are taken every 15 minutes during steady-state operation. The capacity of the unit is 250 lb/h of shale. Shale-gas contacting occurs in a truly continuous, countercurrent manner. Additional details of construction and operation of the BSU are available in earlier publications (4, 5).

The addition of mass flow meters (in series with orifice meters), a second product gas meter (in series with the first meter) and a helium tracer system contributed to improved gas flow measurements. The following equipment was added to improve product sampling and analyses:

- Sampling train for trace sulfur and nitrogen species
- "Cold Finger" for product gas freeze-out sample
- Steady-state product shale sampler
- On-line infrared gas analyzers
- On-line gas chromatograph
- Flash gas measurement system

Additional equipment installed to improve operation and data analysis included a closed-loop bed level control system, electronic feed and discharge screw RPM indicators, a multipoint digital pressure gauge (0.1% accuracy) and an electronic temperature profiler.

BSU TEST PROGRAM

Two "blank" or zeroing tests were conducted before the hydroretorting tests were begun. The first test was made with an "empty" reactor (at reaction temperature and pressurized with hydrogen) to determine the accuracy of the metered gas flows into and out of the reactor system. Gas flows were measured with an accuracy of $\pm 1\%$. The second test was similar to the first except that gravel was fed to the reactor to simulate shale movement without the complication of heat effects due to chemical reactions. Temperature controllers were also set to obtain a nearly linear temperature profile in the reactor. The results of this test indicated that solids flow rates could be measured with an accuracy of $\pm 0.25\%$.

Like oil hydrotreating and hydrocracking, oil shale hydroretorting requires that a large excess of hydrogen-rich gas be passed through the reactor. In commercial designs, this gas is recycled as a heat carrier. The quantity required for that purpose is such that only 8.5% of the hydrogen it contains actually reacts on one pass through the reactor. Therefore, determination of the level of chemical hydrogen consumption done in the obvious way (by subtracting the measured hydrogen gas flow rate leaving the reactor from that entering) can be subject to considerable uncertainty. This is because the resulting figure is a small difference between two large numbers. In order to provide measurements of chemical hydrogen consumption at an acceptable ($\pm 10\%$) level of confidence, it was necessary to obtain mutually-supporting measurements using several different and independent techniques as well as to improve the accuracy of the conventional methods.

Four methods were used to calculate H_2 consumption: the appearance of combined hydrogen in the product, forcing an oxygen balance, taking direct measurements (difference between H_2 fed and H_2 in the product) and using a helium tracer. The basis of each method is described below:

Appearance of Combined Hydrogen - The total chemically combined hydrogen in all reactants is subtracted from the total combined hydrogen in all products to obtain the chemical hydrogen consumption. This method depends on correct measurements of shale moisture contents and water production rates.

Forced Oxygen Balance - This calculational method assumes that oxygen analyses of feed and spent shale, oil and gas are correct. The hydrogen consumption is then calculated from the water yield which has been calculated by a forced oxygen balance.

Direct Measurement (by difference) - In this calculational procedure, the hydrogen (as H_2) flow rate in the product gas stream is subtracted from the hydrogen (as H_2) feed gas flow rate to determine hydrogen consumption. Improved accuracy is realized by duplication of gas flow metering equipment.

Helium Tracer - To utilize the helium tracer technique in the BSU test program, approximately 5 mole % of helium was dynamically blended with the BSU feed hydrogen. Ratios of He/H_2 in the feed and product streams were used to calculate hydrogen consumption.

The BSU hydroretorting test program was divided into three phases. Phase I was designed to investigate the effects of two independent variables, shale heat-up rate and maximum bed temperature, at two levels. In this phase, four replicate runs were also conducted. The replicate runs provided an indication of the experimental error and of the precision of the experiments. The implicit assumption here was that, by maintaining the same test procedures throughout the BSU program, the experimental error would remain constant. Phase II was designed to study the effects of lower maximum shale bed temperatures and shorter shale residence times. The experimental matrix was composed of two bed temperature levels at two shale residence times. Phase III was designed to investigate the combined effects of high shale mass flux, shale residence time at temperature, shale preheat and hydrogen partial pressure.

The properties of the Indiana New Albany shale employed in the study are shown in Table I.

TABLE I

CHARACTERISTICS OF FEASIBILITY STUDY SHALE

Shale source	Henryville, Indiana
Stratigraphic unit	Late Devonian (New Albany)
Pay thickness, ft	40
Organic carbon content, wt %	11.9 to 12.7
Fischer Assay oil yield, gal/ton	11 to 13

RESULTS AND CONCLUSIONS

Some standard deviations of selected resultant variables from the Phase I test results are shown in Table II. The reported standard deviations of the resultant variables incorporate both experimental uncertainty and the degree of precision in setting replicate run conditions. It is

important to note that the standard deviation of hydrogen consumption of ±170 SCF/ton of dry shale is within the desired accuracy limits of ±10%.

TABLE II

RESULTS OF STATISTICAL ANALYSIS OF PHASE I TEST DATA

Variable	Standard Deviation
Hydrogen consumption, SCF/ton[b]	170[a]
Gross oil yield, gal/ton[b]	0.3
Adjusted oil yield, gal/ton[b]	0.2
Carbon conversion, %	1.3
Selectivity to oil, $\left(\frac{\text{Oil}}{\text{Oil + Gas}}\right)$, %	0.9

a. Calculated by the forced oxygen balance method.
b. On a dry shale basis.

The Phase I test results clearly indicate that lower maximum bed temperatures (1000°F versus 1250°F) —

- Decreased hydrogen consumption
- Increased oil production
- Improved oil quality

API gravity and sulfur content were used as an index of oil quality. Use of lower heat-up rates (15°F/min versus 100°F/min) also favors increased oil production and improved oil quality but does not appear to affect the hydrogen consumption within the temperature range employed in Phase I of the program.

Figure 2 indicates the range of hydrogen consumption values calculated by the various methods for some typical BSU runs. The direct method for measuring hydrogen consumption tended to give values with greater variability from the mean values. This is typical of methods that involve the calculation of a relatively small difference between two large numbers. There was generally good agreement between the hydrogen consumption figures calculated by the above methods. Use of four different methods provided an excellent cross-check of the hydrogen consumption values and increased our confidence in the experimental results. Additionally, sufficient experimental and analytical data were generated from each BSU run, to enable identification of plausible reasons for occasional differences in calculated hydrogen consumption values.

Analysis of the Phase II results indicates that the higher maximum bed temperature (1000°F versus 850°F) had the following statistically significant effects:

- Increased oil production
- Increased carbon conversion
- Increased hydrocarbon gas yield

The use of a longer shale residence time (60 minutes versus 30 minutes) results in an increase in carbon conversion, the major part of which goes into an increase in hydrocarbon gas yield.

The final phase of the test program showed that the yield of oil product increased continuously as the hydrogen partial pressure was increased. This effect is depicted graphically in Figure 3. The BSU tests indicated that oil yields of up to 230% of the Fischer Assay yield can be achieved. It should be pointed out that these higher oil yields were achieved without an appreciable reduction in oil quality. Choice of a design hydrogen partial pressure for commercial operation was based on a cost tradeoff study of yields against pressure.

Another aspect of commercial importance is the effect of hydroretorting time (shale residence time) on the oil product yield. The BSU program results indicate that there is essentially no change in volumetric oil yield when the shale residence time is reduced from 60 minutes to 15 minutes. The relatively short shale residence time requirement means that retorts smaller than originally estimated may be used commercially. This results in reduced capital expenditures and lower operating costs.

The Phase III study addressed the specific commercial plant design areas identified by the Bechtel Group, Inc., as having the greatest potential for reducing product oil costs. The variables studied were mass flux, purge gas preheat and shale residence time. Because more than one variable was changed at a time, it was not statistically possible to isolate the individual effects of high shale mass flux and purge gas preheat from the Phase III test results. However, judicious selection of operating conditions provided acceptable design points for the conceptual commercial plant design.

The stability of HYTORT product shale oil (Table III) was evaluated (in terms of API

gravity, kinematic viscosity at 100°F, pour point and amount of precipitated solids) over a period of 16 weeks. Storage stability was evaluated under four separate sets of storage conditions. One group of samples was refrigerated at 4°C, a second sample set was held at 50°C (to accelerate any potential changes) and two groups of samples were stored at ambient temperature (25°C). An anti-oxidant (DuPont Anti-Oxidant No. 22) was added to one subsample of the two ambient temperature groups. All samples were shielded from light during storage. The results of the oil stability tests, shown in Table IV, indicate no significant change in properties over a 16-week period. Thus, HYTORT oil can be stored prior to upgrading for several months without significant degradation.

TABLE III

ANALYSIS AND PROPERTIES OF RAW HYTORT SHALE OIL USED IN STABILITY TESTS

Ultimate Analysis, Wt %	
Carbon	86.38
Hydrogen	10.24
Sulfur	1.28
Nitrogen	2.13
Ash	0.0
Viscosity, cSt @ 100°F	16.0
Specific Gravity (60/60°F)	0.968
API Gravity, ° API	14.7
Distillation, °F	
IBP	159
50%	653
EP	760
Heating value, Btu/lb	17,698
Pour point, °F	-25

TABLE IV

RESULTS OF HYTORT OIL STORAGE STABILITY TESTS

Storage Conditions	Analysis	Elapsed Time, Weeks 0	Elapsed Time, Weeks 16	Analytical Method Accuracy
Refrigerated (4°C)	API gravity, °API	14.7	14.6	±0.1
	Viscosity, cSt @ 100°F	16.0	17.6	±0.1
	Pour point, °F	-25	-20	±2.5
	Precipitated solids, ppm	40	45	±2.5
Ambient (25°C)	API gravity, °API	14.7	14.1	±0.1
	Viscosity, cSt @ 100°F	16.0	18.1	±0.1
	Pour point, °F	-25	-20	±2.5
	Precipitated solids, ppm	40	40	±2.5
Heated (50°C)	API gravity, °API	14.7	14.3	±0.1
	Viscosity, cSt @ 100°F	16.0	18.8	±0.1
	Pour point, °F	-25	-20	±2.5
	Precipitated solids, ppm	40	35	±2.5
Ambient (Anti-oxidant added)(25°C)	API gravity, °API	14.7	14.5	±0.1
	Viscosity, cSt @ 100°F	16.0	19.7	±0.1
	Pour point, °F	-25	-15	±2.5
	Precipitated solids, ppm	40	40	±2.5

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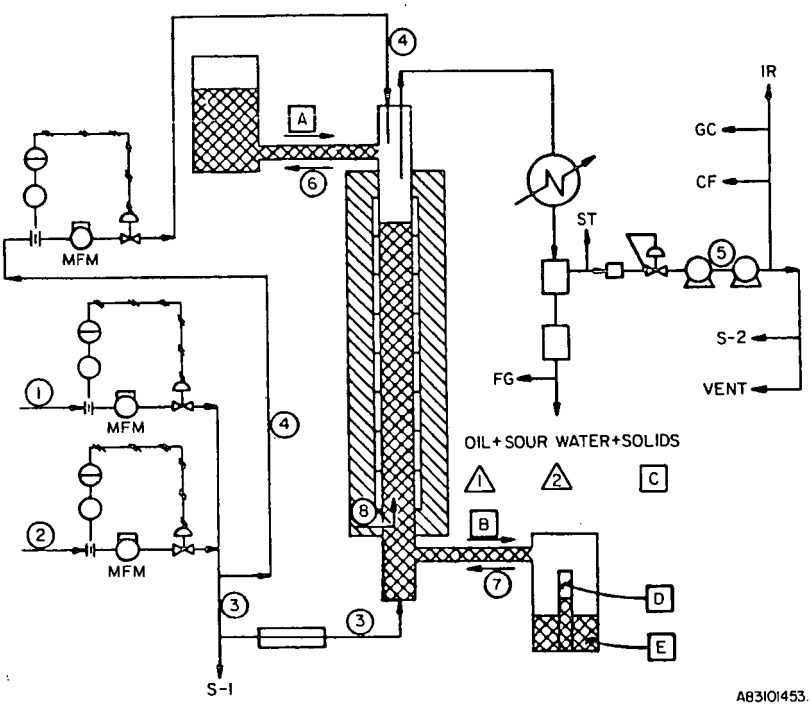

Figure 1. BENCH-SCALE UNIT (BSU)

LEGEND FOR FIGURE 1

① Main hydrogen supply to retort system
② Helium tracer supply to retort system
③ Pre-mixed hydrogen/helium flow to bottom of retort
④ Pre-mixed hydrogen/helium purge to top of retort
⑤ Product gas
⑥ Purge gas mixture
⑦ Pressurization gas mixture (H_2/He)
⑧ Purge nitrogen stream from shell to reactor
A Shale feed
B Shale discharge
C Solids in condensed liquids
D Spent shale sample from steady-state sampler
E Spent shale sample from residue receiver
1 Product oil
2 Sour water
S-1 Feed gas sample point
S-2 Product gas sample point
ST Sampling train
FG Flash gas system
CF Cold finger for freeze-out sample
GC Gas chromatograph
IR Infrared gas analyzers
Vent Product gas vent to atmosphere
MFM Mass flow meter

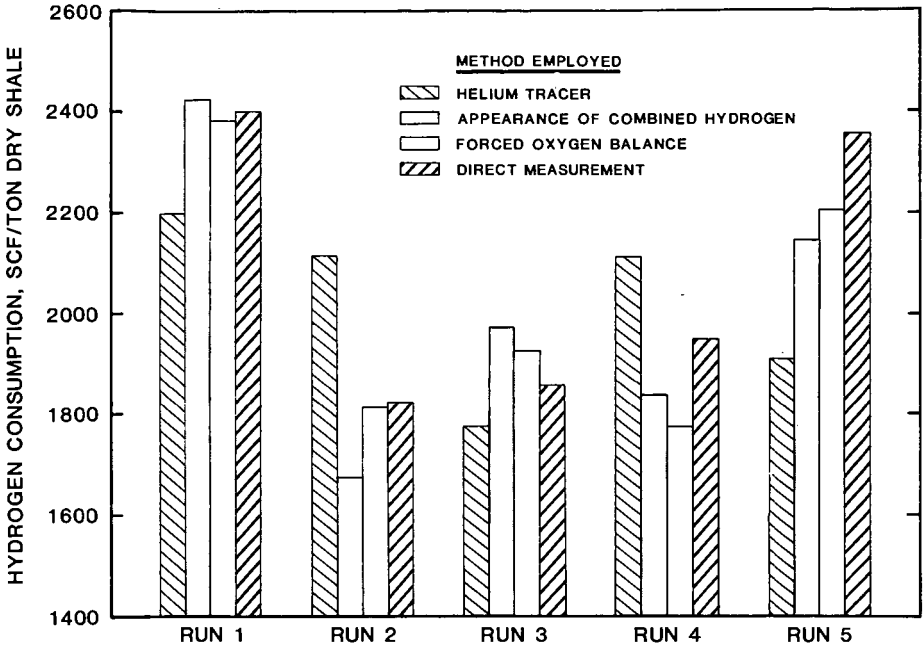

Figure 2. Comparison of hydrogen consumption calculated by various methods in selected BSU runs.

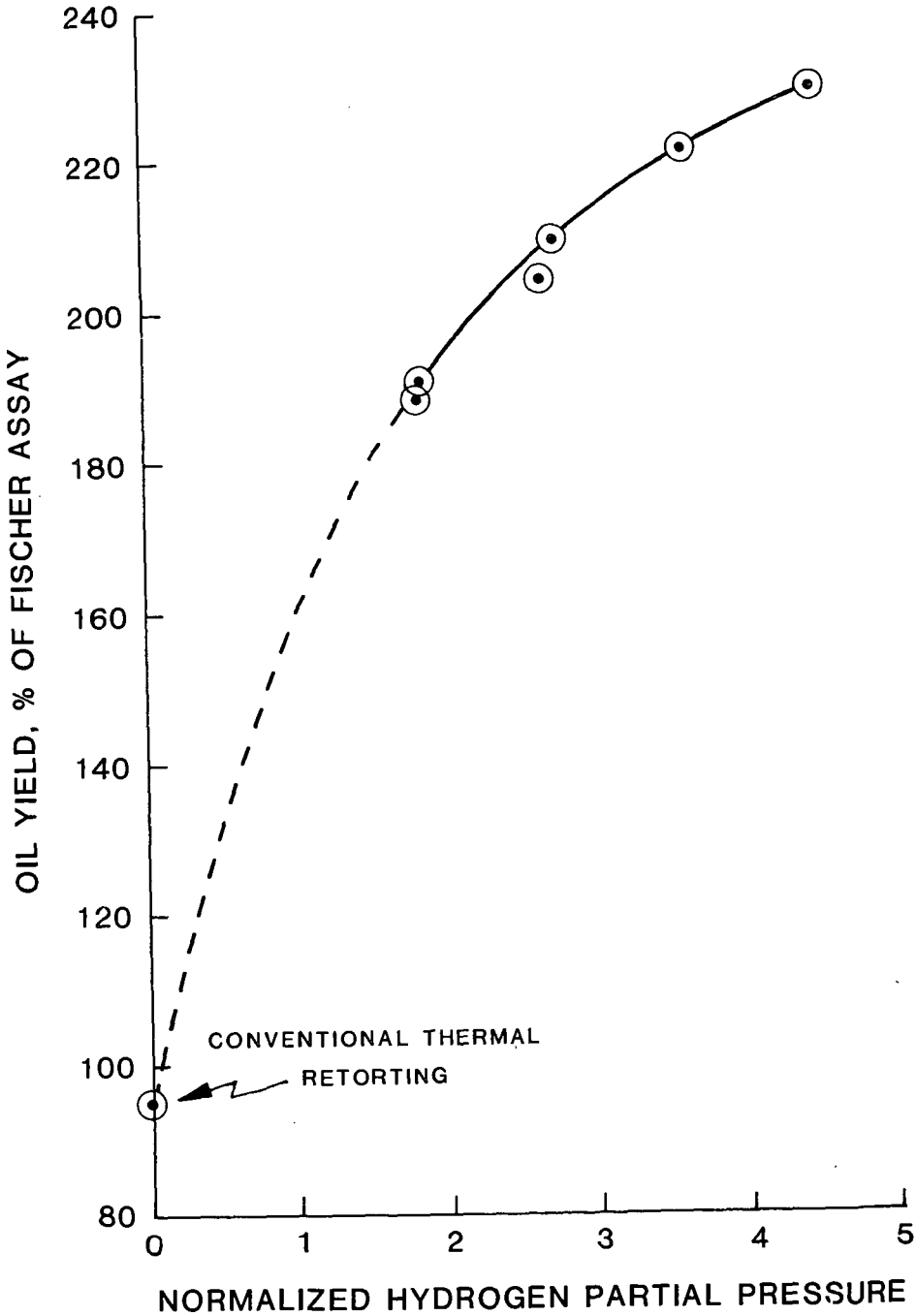

Figure 3. Oil yield (relative to Fischer Assay) as a function of hydrogen partial pressure.

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