

## EFFECTS OF SCALE-UP ON OIL AND GAS YIELDS IN A SOLID-RECYCLE FLUIDIZED BED OIL SHALE RETORTING PROCESS

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### BACKGROUND

Fluidized bed pyrolysis of oil shale in a non-hydrogen atmosphere has been shown to significantly increase oil yield in laboratory-scale reactors compared to the Fischer assay by many workers.(1,2,3,4) The enhancement in oil yield by this relatively simple and efficient thermal technique has led to the development of several oil shale retorting processes based on fluidized bed and related technologies over the past fifteen years.(5,6,7,8) Since 1986, the Center for Applied Energy Research (CAER) has been developing one such process, KENTORT II, which is mainly tailored for the Devonian oil shales that occur in the eastern U.S.(9) The process contains three main fluidized bed zones to pyrolyze, gasify, and combust the oil shale. A fourth fluidized bed zone serves to cool the spent shale prior to exiting the system. The autothermal process utilizes processed shale recirculation to transfer heat from the combustion to the gasification and pyrolysis zones. The CAER is currently testing the KENTORT II process in a 22.7-kg/hr process-development unit (PDU).

### INTRODUCTION

Fluidized bed pyrolysis increases oil yield by reducing the extent of secondary coking and cracking reactions which result in carbonaceous deposition and gas production. The fluidizing gas dilutes the shale oil vapors and sweeps them quickly out of the bed of pyrolyzing shale to reduce both thermal cracking and solids-induced coking and cracking. Fluidized beds, in the case of oil shale retorting, offer an advantage over gas-swept fixed bed reactors because there is little gas/solid contact in the bubble phase of a fluidized bed. Assuming similar fluidization characteristics, the extent of secondary reaction (i.e. oil loss) is affected by bed depth, solid type, and temperature as it is in any gas/solid reaction. For small fluidized beds the bed depth is shallow, so secondary reactions are minimal. Since it is unpractical to increase a fluidized bed to commercial scale by only increasing the cross-sectional area without also increasing the height, an unavoidable increase in secondary reactions will occur with scale up. The extent of this increase can only be reliably determined by experiment because of the difficulty in modeling fluidized bed contacting. Even at the laboratory scale, significant differences in oil yield have been observed as a result of retort size. Rubel and Carter (10) observed that oil yields from a 7.6-cm diameter fluidized bed pyrolyzer were approximately 13% less than the oil yields from an otherwise similar 3.8-cm diameter fluidized bed retort. Increased gas production in the larger retort confirmed that secondary reactions had increased in this study.

Another factor that contributes to high oil yield in small laboratory scale retorts is that the heat for pyrolysis is provided by preheated gas and/or through the walls by an external furnace. In these retorts the nascent shale oil vapors experience contact with

an isothermal and homogenous mixture of pyrolyzing shale. Because processed shale is recycled in commercial-scale retorting schemes, however, the particles in the pyrolysis zone are not homogeneous and may potentially contribute to greater rates of secondary oil-loss reactions compared to pyrolyzed shale particles which have not been additionally processed. Rubel et al. (11) and Coburn and Morris (12) have found that carbon deposition from shale oil vapors is more rapid on combusted shale than pyrolyzed shale. While Udaja et al. (13) found combusted and pyrolyzed shales to have similar propensities for carbon deposition, they also noted that the pyrolyzed shale had a much higher surface area than the combusted oil shale. In general, it appears that oil shale which has had residual carbon burned off via combustion or gasification tends to have higher capacity for carbon deposition. This is consistent with the notion of the "coke clock", first identified by Voorhies (14) in the fluid catalytic cracking literature, where carbon deposits more slowly on cracking catalysts as time of exposure increases (i.e., at higher levels of carbon on the catalyst). Therefore, the oil yield potential of large-scale fluidized bed retorts is potentially affected not only by their size but also by the concentration and composition of recycled shale in the pyrolysis zone.

#### EXPERIMENTAL

Apparatus. A 7.6-cm diameter, 2.3-kg/hr fluidized bed reactor system has been used extensively at the CAER as a small prototype of the KENTORT II process (15,16) and as an apparatus to study the kinetics of coking and cracking of shale oil vapors over processed shales. (17,18) The prototype is enclosed in electric furnaces to preheat the system and to compensate for heat losses. The PDU (see Figure 1 for flow diagram), on the other hand, operates nearly autothermally and relies on a propane burner to preheat the air entering the combustor and an electric furnace to superheat the steam which fluidizes the cooling, gasification, and pyrolysis zones. In a commercial system the energy for preheating these streams would be recovered in part from cooling and condensing the hot gases and vapors exiting the system. Electric heat tapes surround the pyrolysis zone of the PDU, but provide little net heat to the system. In almost all respects the oil collection systems of the prototype and the PDU are similar. The temperature is reduced in stages which results in a crude fractionation of the oil product. The oil collected in the air-cooled heat exchanger and electrostatic precipitator (ESP) is heavy and viscous and is termed "heavy oil." The oil condensed downstream in the water-cooled condenser is low boiling and is termed "light oil."

Oil Shale Samples. There were two master samples of oil shale that were used in this work. Both are from the Cleveland Member of the Ohio Shale in northeastern Kentucky and are similar in nature except for kerogen content. The average shale analysis for the KENTORT II prototype was: 16.7% C, 2.0% H, 0.7% N, 1.7% S, and 74.5% ash, and the average analysis for the PDU was: 11.3% C, 1.1% H, 0.7% N, 1.8% S, and 82.5% ash. Each master sample was prepared to a size distribution of - 0.85mm +0.25mm.

Operating Conditions. The prototype was run in three different modes of operation: 1) gas heating, 2) gas/solid heating w/o combustion, and 3) gas/solid heating w/combustion. Gas heating runs were performed to establish baseline oil yield data, and the unit was run with and without the combustor in the gas/solid-heating mode to observe the significance of combusted shale on product yields. Throughout the test series, the pyrolysis zone temperature was held at 530-540°C because this temperature

was found to maximize oil yield for this type of shale in a fluidized bed.(19) The gasifier temperature ranged from 750 to 850°C and the combustor from 850 to 910°C. The shale recycle ratio between the gasifier and the pyrolyzer was varied from 1.3:1 to 2.6:1 (recycled shale:raw shale).

Due to its design, the PDU can only operate with all three zones functioning and with shale recycling to transfer heat to the pyrolysis zone. The temperature regimes achieved are similar to those in the prototype: pyrolysis 500-540°C, gasification 700-800°C, and combustion 750-900°C. Due to its larger size, the solid-recycle ratio between the gasifier and pyrolyzer is higher for the PDU and has been recorded in the range of 3:1 to 5:1.

## RESULTS AND DISCUSSION

In the gas-heating mode of operation for the prototype, oil yields averaged 129% of the Fischer assay oil yield by weight. Under the most severe solid-recycle conditions (i.e. high recycle rate and temperature) in the second mode of operation, less than 15% oil loss was recorded. Under these conditions approximately 60% of the heat required for pyrolysis was supplied by recirculating shale from the gasification zone. The study was rather inconclusive in determining whether solid-recycle rate or temperature was the more influential parameter; however, it appeared that higher recycle-solid temperatures caused greater oil yield loss. The addition of the combustor to the operation of the prototype did not significantly affect the oil yield. The excess carbon in the shale following pyrolysis and gasification was not completely combusted because the combustion zone was purposefully starved of oxygen. The recycle loop between the combustor and gasifier was undersized, so the heat generated in the combustor with air as the oxidant could not be removed fast enough to maintain the combustor at a materials-safe temperature. Therefore, nitrogen was blended with air to fluidize the combustion zone resulting in partial combustion of the residual carbon. Since the burn out of carbon was not complete, the effect of combusted shale on oil yield in this case was probably masked.

The composite oil produced in the prototype is a heavy, viscous and aromatic material which is composed of 70% "heavy oil" as was described in the experimental section.(20) The character of the oil indicates that minimal secondary cracking and coking has occurred as compared to the oils produced from Fischer assay. There was evidence of increased secondary reactions by a somewhat improved oil quality for the oils produced in the solids-recycle modes of operation. These oils displayed higher H/C ratios, lower viscosities, lower average molecular weights, and an improved boiling range distribution.

Unfortunately, at the time of this writing, complete analyses from the recently successful runs of the KENTORT II PDU are not available, and it is not possible to make quantitative oil yield comparisons to the prototype results. It is fairly certain, however, that the oil yields on a carbon conversion basis are lower than the prototype. A shift to a lighter composite oil is evident because approximately 60% of the total has been collected as "heavy oil." The loss of "heavy oil" is consistent with increased secondary oil-loss reactions because the heaviest and most aromatic fractions are most susceptible to carbon deposition and gas production.

## FUTURE WORK

Most PDU runs that have been completed to date have been prematurely shortened because of various mechanical difficulties (ESP failure is most frequent). Therefore, more PDU runs are planned that will attain the design steady-state operating period of ten hours. This amount of time is required so that the solids in the system will reach a steady state composition. Due to the nature of the start-up procedure, all zones of the reactor are composed of combusted shale when raw shale is first introduced. While we do not have a method of on-line oil yield measurement, it is likely that oil generation during this start-up period is very low.

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## REFERENCES

1. Rubel, A.M., Margolis, M.J., Haley, J.K., and Davis, B.H., 1983 Eastern Oil Shale Symposium Proceedings, 1983, IMMR83/089, University of Kentucky, Lexington, KY.
2. Richardson, J.H., Huss, E.B., Ott, L.L., Clarkson, J.E., Bishop, M.O., Gregory, L.J., and Morris, C.J., Lawrence Livermore National Laboratory, 1982, UCID-19548.
3. Wallman, P.H., Tamm, P.W., and Spars, B.G., ACS Symp. Series 163, 1981, 93.
4. Bissel, E.R., Burnham, A.K., and Braun, R.L., I and EC Proc. Des. Dev., 1985, 24, 381.
5. Gwyn, J.E., Roberts, S.C., Hinds, Jr., G.P., Hardesty, D.E., and Johnson, G.L., Thirteenth Oil Shale Symposium Proceedings, 1980, Colorado School of Mines, Golden, CO.
6. Tamm, P.W., Bertelsen, C.A., Handel, G.M., Spars, B.G., and Wallman, P.H., Energy Progress, 1982, 2 (1), 37.
7. Cena, R.J. and Thorsness, C.B., 25th Oil Shale Symposium Proceedings, 1992, Colorado School of Mines, Golden, CO.
8. Dung, N.V. and Yip, V., Fuel, 1990, 69, 1129.
9. Carter, S.D., 1987 Eastern Oil Shale Symposium Proceedings, 1987, University of Kentucky, Lexington, KY.
10. Rubel, A.M. and Carter, S.D., American Chemical Society Preprints, 1984, Div. of Fuel Chemistry, Vol. 29, No. 3, pp. 202-208.
11. Rubel, A.M., Rimmer, S.M., Keogh, R., Robl, T.L., Carter, S.D., and Derbyshire, F.J., Fuel, 1992, 71, 1427.
12. Coburn, T.T. and Morris, C.J., Fuel, 1991, 70, 1362.
13. Udaja, P., Duffy, G.J., and Chensee, M.D., Fuel, 1990, 69, 1150.
14. Voorhies, Jr., A., Ind. Eng. Chem., 1945, 37 (4), 318.
15. Carter, S.D., Robl, T.L., Rubel, A.M., and Taulbee, D.N., Fuel, 1990, 69, 1124.
16. Carter, S.D., Robl, T.L., and Taulbee, D.N., Fuel, 1991, 70, 1347.
17. Carter, S.D. and Taulbee, D.N., Fuel, 1992, 71, 1421.
18. Carter, S.D., Taulbee, D.N., and Robl, T.L., Fuel, 1993, 72, 851.
19. Carter, S.D. and Taulbee, D.N., Fuel Processing Technology, 1985, 11, 251.
20. Taulbee, D.N. and Carter, S.D., Fuel, 1991, 70, 1245.

