Hot-Recycled-Solid Pilot Plant—1991 Status Report

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ABSTRACT

At Lawrence Livermore National Laboratory, we are studying aboveground oil shale retorting and have developed the LLNL Hot-Recycled-Solid (HRS) process as a generic, second-generation, rapid pyrolysis retorting system in which recycled shale is the solid heat carrier. In 1984-87, we operated a 1-tonne/day HRS pilot plant to study retorting chemistry in an actual recirculation loop (Cena and Mallon, 1986). In 1989 we upgraded our laboratory pilot plant to process 4 tonne/day of commercially sized shale, allowing us, for the first time, to study pyrolysis and combustion using the full particle size. With the new facility we are able to produce enough oil for detailed characterization studies, to evaluate environmental consequences, and to begin answering the many bulk solid-handling questions concerning scale-up of the HRS process. In this paper we report on operations of our laboratory (4TU) pilot plant and plans for a field test unit (FTU) at approximately 100-tonne/day scale to be sited in the western United States.

INTRODUCTION

Laboratory Pilot Plant Description

Key components of a Hot-Recycled-Solid (HRS) retorting system are being studied at Lawrence Livermore National Laboratory (LLNL) in a 4-tonne/day laboratory facility designed to process commercially sized shale (7 mm top size). Identified schematically in Figure 1 are the five key components that comprise the HRS process—(1) delayed-fall combustor, with a five-second solid-residence time; (2) fluidized-bed classifier to control solid discharge and provide a pressure block to separate pyrolysis and combustion atmospheres; (3) high-throughput, short residence-time, fluid-bed mixer; (4) moving-packed-bed pyrolyzer with crossflow gas sweep and radial vapor removal; and (5) air pneumatic-lift pipe combustor.

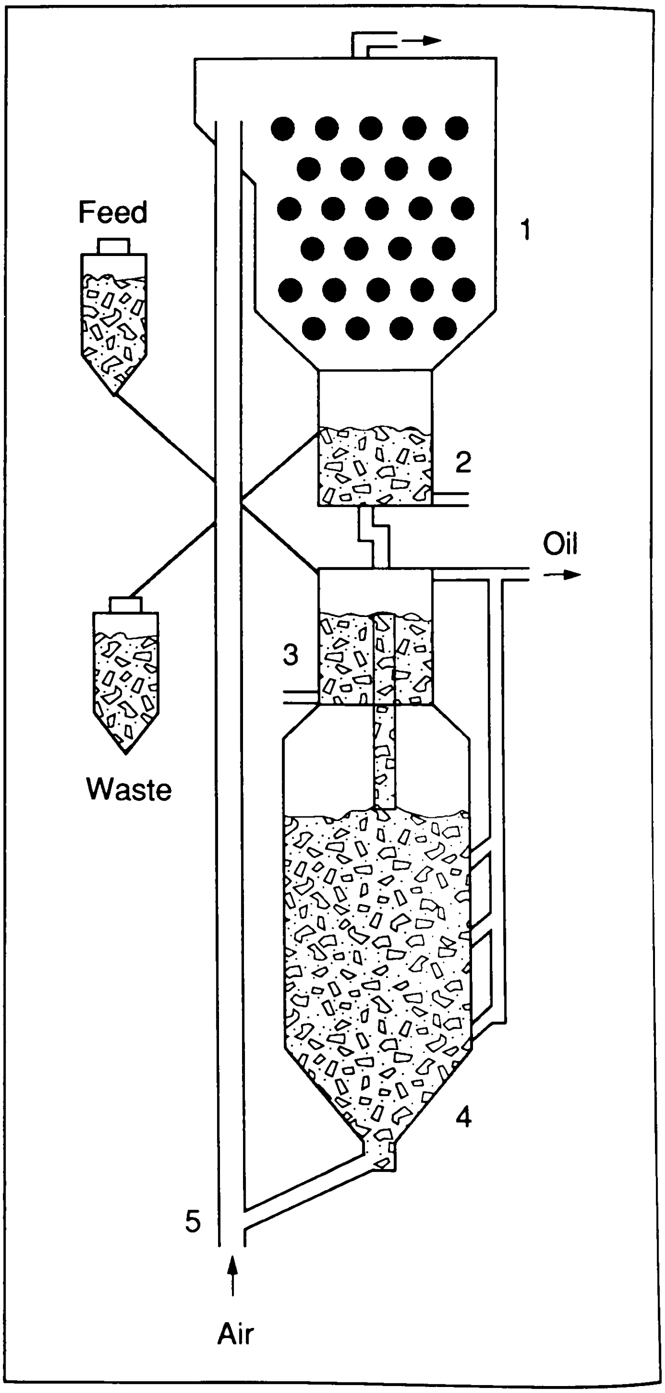

Figure 1 (right). Schematic of Hot-Recycled-Solid (HRS) process. 1, delayed-fall combustor; 2, fluid-bed classifier; 3, fluid-bed mixer; 4, packed-bed pyrolyzer; 5, air pneumatic lift pipe.

Pyrolysis Components

Fluid-Bed Mixer

Raw and recycled shale must be mixed to begin the pyrolysis process. We use a two-stage, 15-cm-diameter, fluid-bed mixer for our tests, with a nominal 30-second solid-residence time (Figure 2). The active bed height is 40 cm. By providing a short residence-time fluid-bed mixer followed by a moving-packed-bed pyrolyzer, we accomplish the following—(1) rapid mixing in a compact unit, (2) high gas sweep to recover generated oil, (3) reduced gas requirements compared to a fluid-bed mixer and pyrolyzer in one unit, (4) shale residence-time variations inherent in fluid beds mitigated by a downstream packed-bed pyrolyzer.

Packed-Bed Pyrolyzer

The kinetics of oil shale pyrolysis have been accurately measured in the laboratory (Coburn and others, 1988). Based on these results, a solid-residence time of less than 2 minutes is required at 500°C to complete pyrolysis. Concurrently, oil is lost during pyrolysis as a result of coking and cracking, which are functions of gas-solid contact time. In the pilot plant, shale leaving the mixer enters a 20-cm-diameter by 125-cm-high packed-bed pyrolyzer with circumferential gas removal (Figure 3). Because we use radial vapor removal, conditions of solid-residence time and gas-solid contact time are accomplished in our 4-tonne/day pyrolyzer that directly apply to any scale.* A residence time of 3 minutes is provided in our design at a recycled-shale to raw-shale ratio of 3:1. Shorter residence times are achieved simply by maintaining a lower bed level. Features include (1) uniform residence time of solid, (2) short path length for oil vapor removal, with direct applicability to larger scale, (3) smaller reactor volume (less voidage) and less gas sweep compared to fluid beds, (4) process flexibility to alter residence time (by changing bed height), and (5) excess surge volume to accommodate process upsets.

Combustion Components

Combustion kinetics in solid-recycle systems are poorly understood because of the complexity of the process. Shale combustion is sensitive to processing conditions, to residual carbon, hydrogen, and sulfur content, and to kinetics. Nitrogen-compound formation and destruction mechanisms in the presence of oxidized shale at low temperatures (500°C to 600°C) are poorly understood. In addition, during pneumatic transport, particle attrition, solid velocities, and other particle dynamics for mixed-particle systems are not well understood. Low-temperature combustion may result in significant carbon monoxide and unburned hydrocarbon emissions while possibly limiting nitrogen oxide and sulfur dioxide emissions.

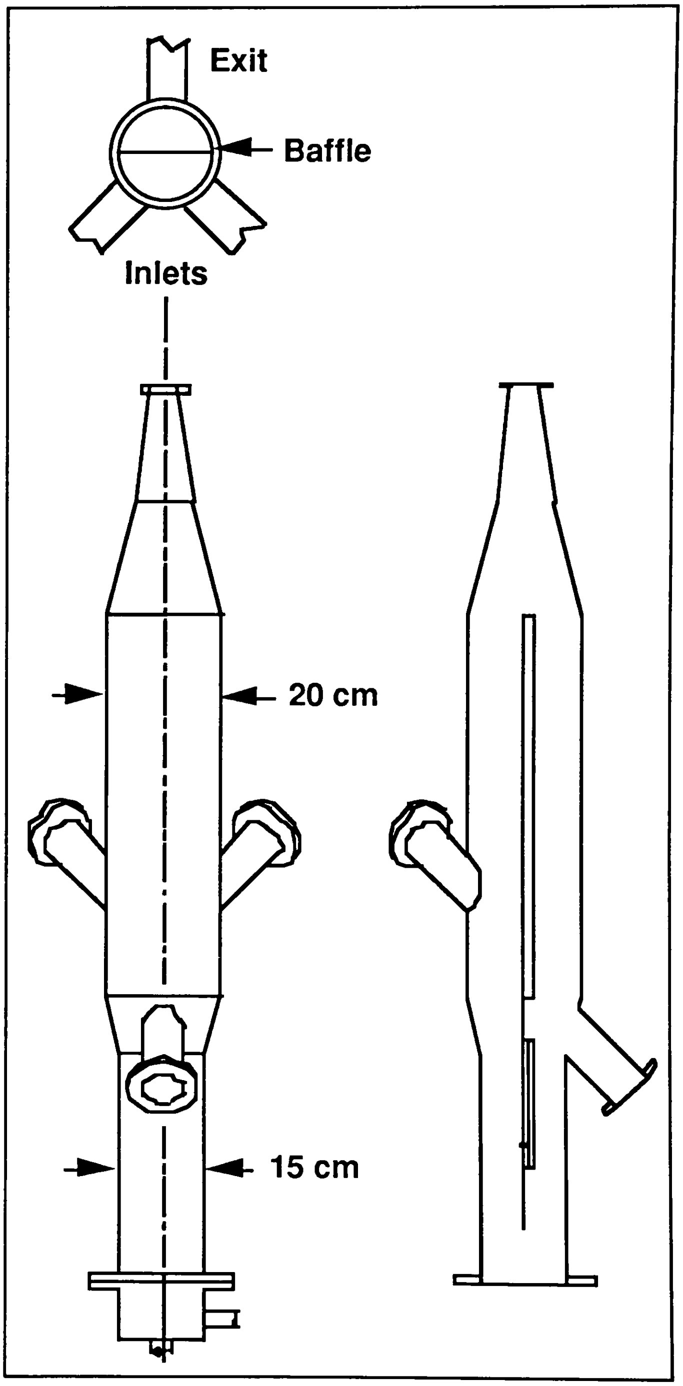

Figure 2. Schematic of two-stage fluid-bed mixer (front, side, and top views).

Air Lift-Pipe

We study combustion during pneumatic transport using a 5.4-cm-diameter lift-pipe system. The lift is designed to

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* It can be shown that gas-solid contact time in these systems is independent of vessel diameter.

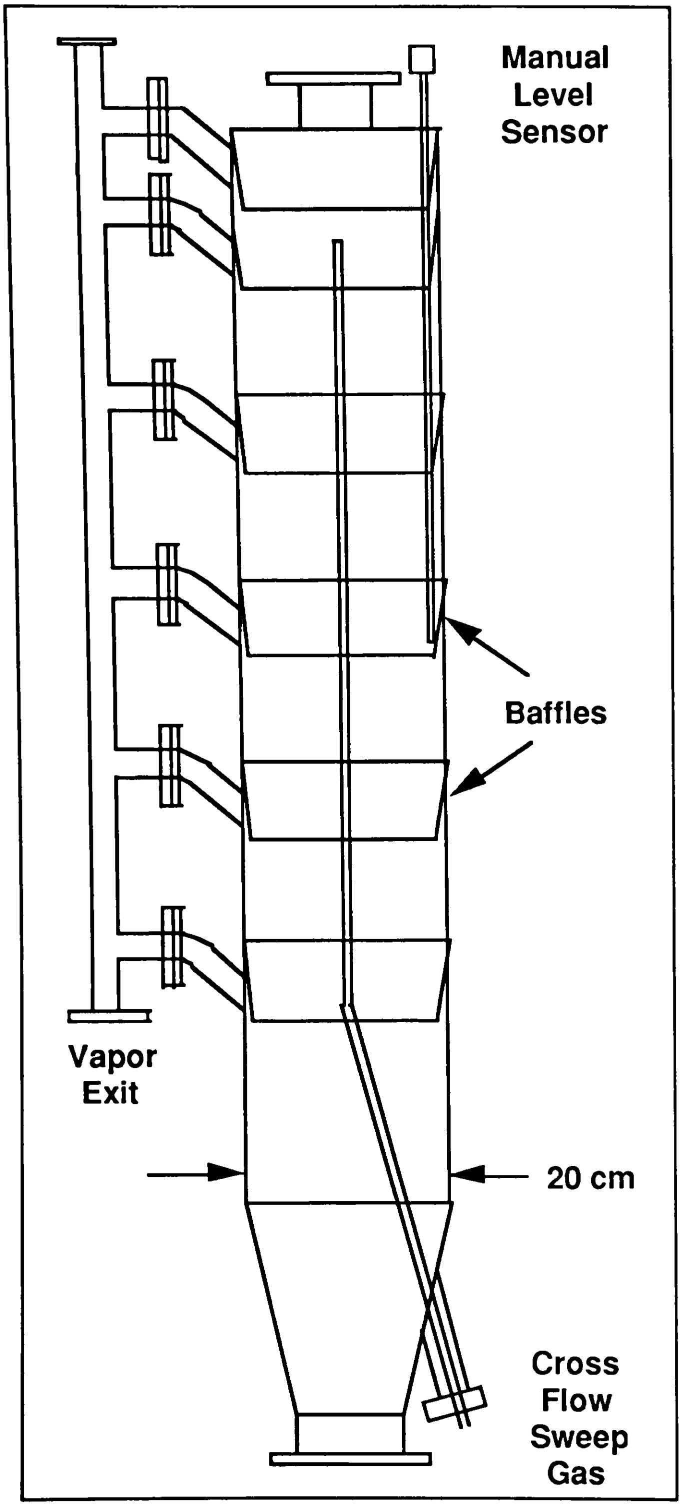

Figure 3. Schematic of packed-bed pyrolyzer, showing baffles, vapor exits, sweep gas injection, and manual level sensor.

combust a major portion of the char on the spent shale, with a slight excess of oxygen in the flue gas. Complete combustion of the largest particles will not occur in one pass through our combustion system. However, in our design, fines are preferentially discharged, and larger particles are recycled, providing multiple passes through the system to complete combustion.

Delayed-Fall Combustor

Following the lift, the solid tumbles through a delayed-fall combustor, consisting of a series of rods to inhibit free fall. Air is blown either cocurrent or countercurrent to the solid. The delayed-fall combustor (Figure 4) was designed with a 5-second solid-residence time and enough air to bring the solid to the desired recycle temperature. Based on mathematical modeling, cocurrent air injection appears more efficient because of longer retention time for fine shale. We will critically evaluate both processing options through operation of the pilot plant.

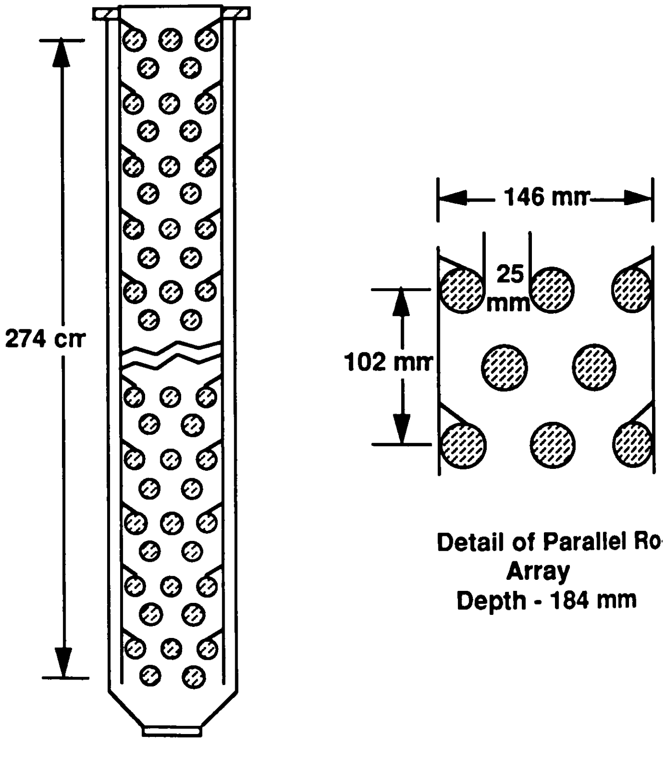

Figure 4. Schematic of delayed-fall combustor.

Fluid-Bed Classifier

After passing through the delayed-fall combustor, the solid falls into a fluid-bed classifier (Figure 5), which performs three main functions:

1. It provides solids discharge from the circulating loop in such a way that rejected material includes the smallest circulating particles.
2. It functions as a surge tank to smooth irregularities in solids loop flow.

3. It provides a pressure block to separate combustion and pyrolysis atmospheres.

The classifier can be fluidized with inert gas or with air. If air is used, combustion of residual char occurs. We designed the classifier with a shale-residence time of 40 to 120 seconds, depending on the height of the solid discharge.

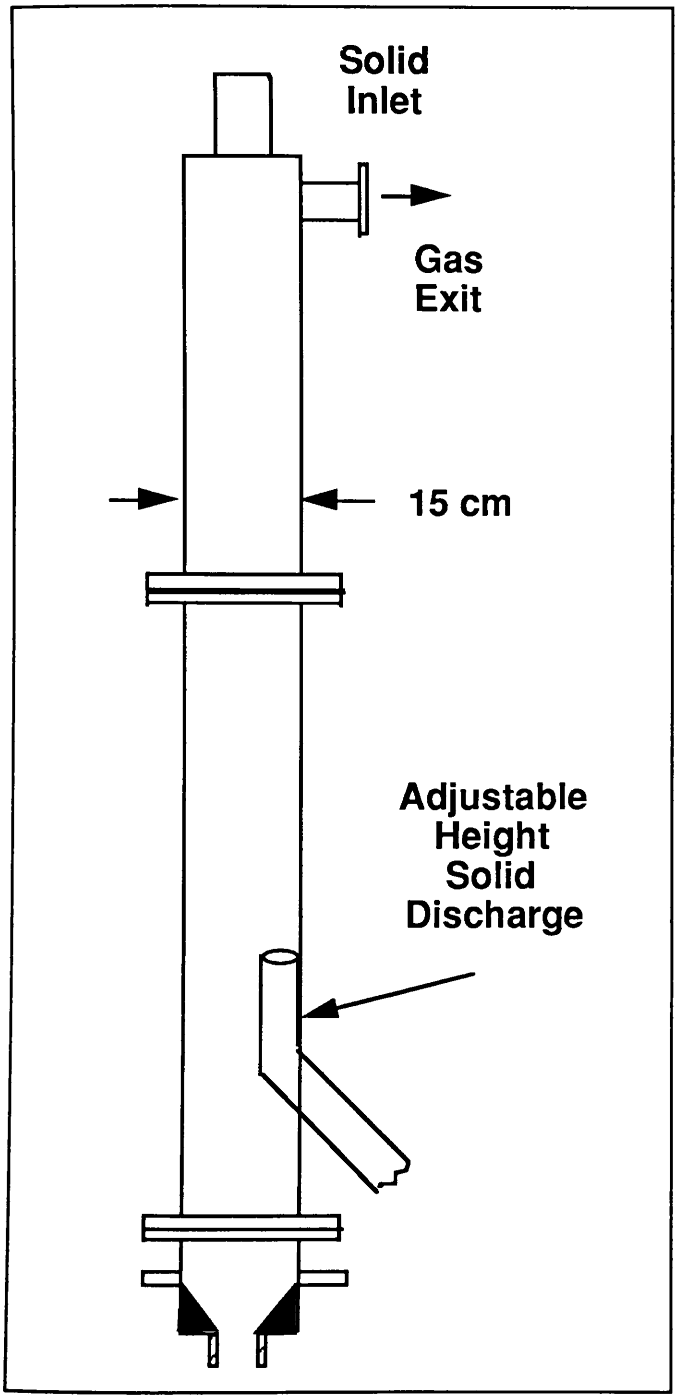

Figure 5. Schematic of fluid-bed classifier.

PILOT RETORT OPERATIONS AND TEST RESULTS

In our 4-tonne/day pilot plant we internally circulate 7.5 kg/min of shale around the process at a recycle/raw ratio of 3:1. Two L-valves are used for solids flow control, one positioned below the packed-bed pyrolyzer and the second below the fluid-bed classifier. Each valve contains a skid to interrupt the solid flow. The skid is equipped with a continuous and pulsed gas supply. Continuous gas flow keeps clear the jets located horizontally along the skid. Pulsed gas is controlled via a solenoid valve, which is opened approximately once per second. When the solenoid opens, the combined gas flow forces a quantity of solids off the skid and through the valve. Approximately 250 to 300 g of solids are moved for each 100-ms gas pulse. Thus, to obtain the design solid-flow rate of 7.5 to 10 kg/min (7.5 kg/min of recycled shale and 2.5 kg/min of raw shale), the L-valve is operated at 30 to 40 cycles/min.

During recirculation, as solid enters the lift pipe from the pyrolyzer L-valve, a surge in local pressure occurs proportional to the solids loading in the lift. Figure 6 shows a typical pressure response. We use this information to determine solid recirculation rate, discussed below.

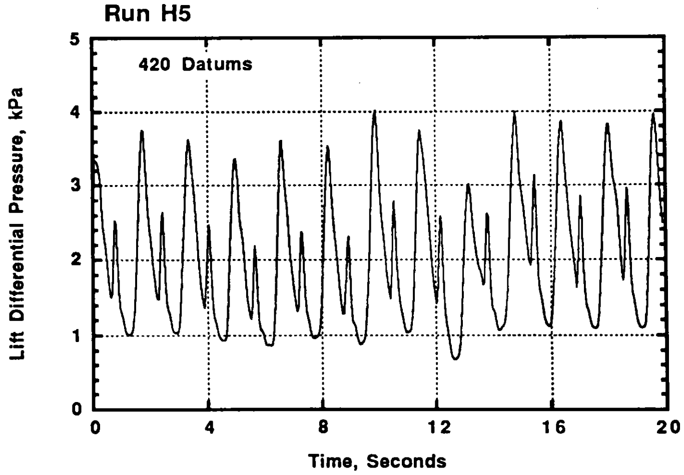

Figure 6. Lift-pipe pressure response to pulsed solid loading.

Solid Flow Measurement

Controlling the solid-flow rate is important to proper operation of the retort system. At the same time its measurement is difficult. In the pilot retort system provisions have been made for measuring solid flow at three points. Flow rates at two of these points, the raw shale feed and spent-shale discharge, are easily measured via changes in vessel weight.

A more difficult measurement is the total solids flow circulating within the system. To measure the solid-recirculation rate, we installed a star valve within the loop between the delayed-fall combustor and fluid-bed classifier. Flow rate is measured by controlling the rate of rotation of the valve so as to maintain a small constant head of material above the valve. Although operational, this star valve adds some complications to the system in that it is the only moving part in the hot, hostile environment, making it subject to failure. Furthermore, it presents a possible upset to the overall system if levels are not properly maintained. For these reasons, it would be advantageous to use some other means of monitoring total solids flow.

As it turns out, one of the basic process units, the lift pipe, has the potential of allowing measurement of solids based on the change in pressure, Δp, from the bottom to the top of the lift pipe. This pressure drop clearly is related to the solids loading in the lift, which in turn is related to the solids flow rate. Using a simple algorithm, the total solid flow rate in the lift, S, is given by:

$$S = \rho_s U A \quad (1)$$

where ρ_s is effective density of solid material in the lift, U is average solid velocity, and A is cross-sectional area of the pipe. If it is assumed that slip velocity of the solid does not depend on loading and that loading, ρ_s, is directly proportional to the increase in Δp with solids flow, then S can be given by:

$$S = K(\Delta p - \Delta p_0) \quad (2)$$

where K is a constant representing all constant parameters, and Δp_0 is the pressure drop with no solids flow. Based on measurements presented elsewhere (Cena and Thorsness, 1990), values of K vary from about 3 to 4, which should not be surprising because average solid velocity, U, certainly is some function of gas flow rate and operating temperature and pressure. Below, we compare solid flow using the rotary star valve with estimates using the lift Δp over the course of run H7.

Pilot-Plant Run Results

Seven engineering tests (H1–H7) have been completed to date in which 24-gal/ton Green River oil shale was processed; results for run H7 are presented here. For this run, lift gas was separated from the solid above the delayed-fall combustor, and the fluid-bed classifier was operated with air. As shown in Figure 7, we operated at two feed rates, 2 kg/min and 2.5 kg/min with a recycle ratio of 2.5:1 to 3:1. Comparison of the solid-recirculation rate using the star valve (DFC Solid) versus lift Δp (Lift Solid) was very good, using K of 4.1. Gas flows to the fluid beds, lift, and product are shown in Figure 8. The system operated stably with constant pressure maintained in the head space above

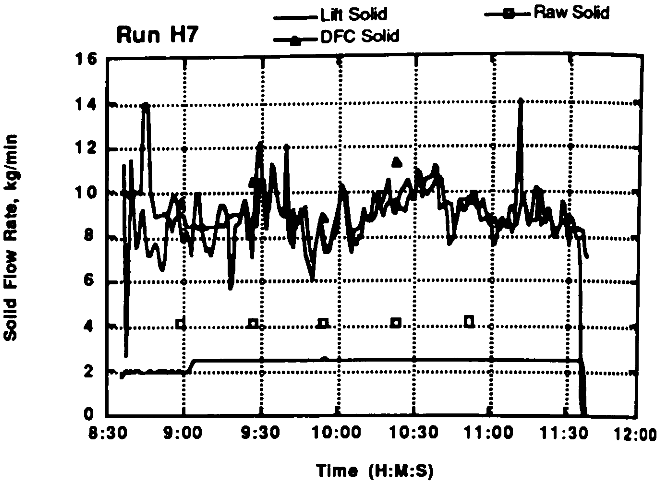

Figure 7. Solid flow of raw feed and recirculated solid for run H7.

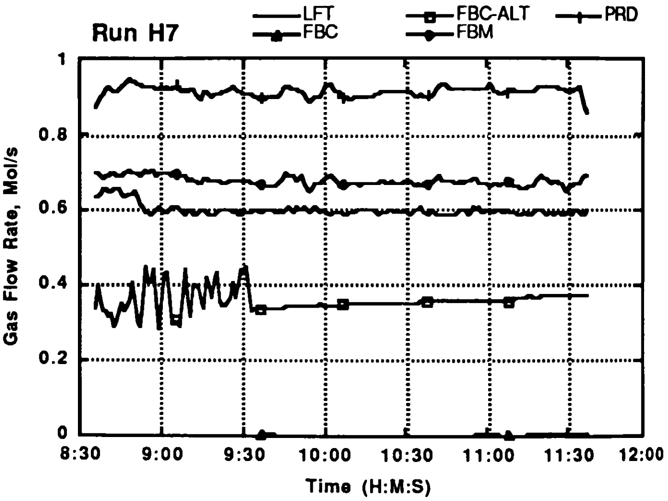

Figure 8. Gas flows in the fluid beds, pneumatic lift, and product collection system for run H7.

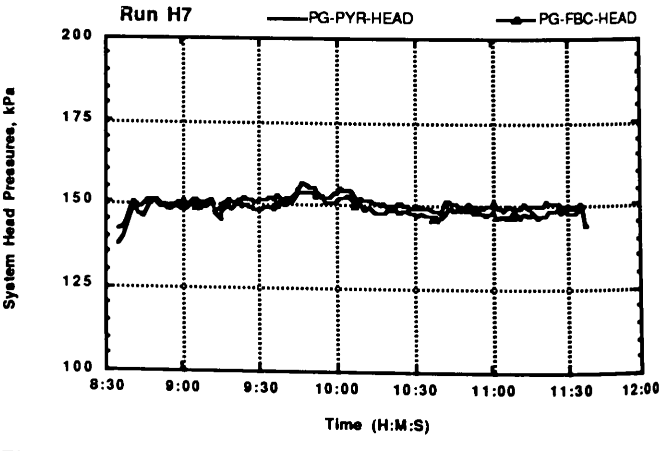

Figure 9. Head space pressures for run H7.

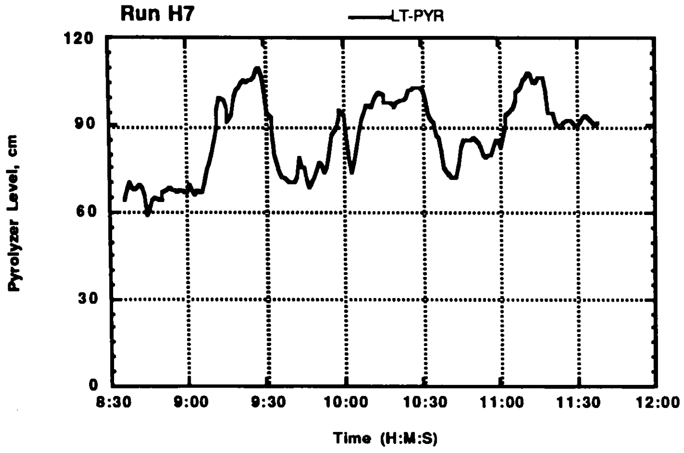

Figure 10. Pyrolyzer level maintained during run H7.

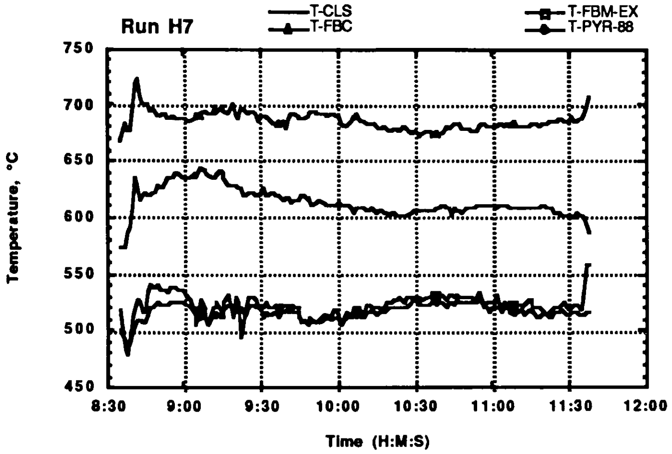

Figure 11. Temperatures measured around recirculation loop for run H7.

the pyrolyzer and fluid-bed classifier (Figure 9). With minor adjustments in back pressure and L-valve pulse rates, reasonably constant recirculation rates were obtained with variations in bed level (Figure 10) well within limits to complete pyrolysis. Finally, in Figure 11, temperatures around the recirculation loop—at the top of the pneumatic lift pipe (T-CLS), in the fluid-bed classifier (T-FBC), at the exit of the fluid-bed mixer (T-FBM-EX), and midway through the packed-bed pyrolyzer (T-PYR-88). Oxidized shale at 685°C was recirculated and mixed with the 105°C raw-shale feed to produce a 515°C equilibrium temperature in the mixer and pyrolyzer. During the period shown in the illustrations, 400 kg of raw shale were processed. Results from this and future runs will form the basis for determining overall operating characteristics and scale-up potential of the HRS process.

CONCLUSIONS

Successful pilot-plant operations have been achieved to date, with initial data reduction under way. We hope to complete a run series and quantify our results in the months to come. Based on these results, we will be able to begin detailed design of a larger field test of the HRS process at approximately 100-tonne/day scale, which we hope eventually will lead to commercialization of the process early in the next century. We are seeking government and private industry support to begin construction of a field test unit (FTU) in 1993 or soon after.

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