CONVERSION OF HIGH CARBON REFINERY BY-PRODUCTS

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Objective

The overall objective of the project is to show that a partial oxidation system, which utilizes a transport reactor, is a viable means of converting refinery wastes, byproducts, and other low-value materials into valuable products. The primary product would be a high quality fuel gas, which could also be used as a source of hydrogen.

The concept involves subjecting the hydrocarbon feed to pyrolysis and steam gasification in a circulating bed of solids. Carbon residues formed during pyrolysis, and metals in the feed, are captured by the circulating solids returned to the bottom of the transport reactor. Air or oxygen is introduced in this lower zone and sufficient carbon is burned, sub-stoichiometrically, to provide the necessary heat for the endothermic pyrolysis and gasification reactions. The hot solids and gases leaving this zone pass upward to contact the feed material and continue the gasification process.
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Tests were conducted in the Transport Reactor Test Unit (TRTU) to study gasification and combustion of Rose Bottoms using the spent FCC (Fluid Catalytic Cracker) catalyst as the circulating medium at temperature of 1690°F. The Rose (Residuum Oil Supercritical Extraction) Bottoms was produced in the Kellogg's Rose unit. Studies were done in the Bench Scale Reactor Unit (BRU) to characterize petroleum coke with respect to pyrolysis and agglomeration tendency upon heating to 1800°F. Studies were conducted in the CFS (Cold Flow Simulator) to determine the various aeration flowrates required for satisfactory circulation of petroleum coke in the TRTU. Results from these studies are presented in this report. A dry solid feed system was developed and tested for use in the fourth quarter.

WORK PLAN

In the second quarter, the work plan called for accomplishing the following work as part of tasks 31 and 32: Task 31 - TRTU tests were to have been carried out on processing ROSE Bottoms (ROSE Bottoms was prepared in Kellogg's ROSE pilot plant facility). Task 32 - Cold flow simulator (CFS) testing on petroleum coke and testing of a coke feeder was planned. Actual accomplishments are described below.

The planned work hours for this period were 3178 hr. The actual work hours were 2596 hr.

Task 31: The pyrolysis and gasification of ROSE Bottoms, prepared from Hondo crude oil, were performed in the 3rd quarter. Low temperature partial oxidation (LTPOX) tests on a blend of Rose Bottoms and light cycle oil (LCO) using FCC catalyst and K-impregnated FCC catalyst was conducted. Gasification of this carbon utilized potassium carbonate (K\textsubscript{2}C\textsubscript{O\textsubscript{3}}) as the catalyst. The BRU was used to study agglomeration tendencies of petroleum coke upon heating to 1800°F. Petroleum coke runs in the TRTU are now planned for the 4th quarter of 1996.

Task 32: Studies were done in the CFS to investigate the circulation of petroleum coke and to determine the aeration flows required to operate the TRTU with these solids. A solid feeder consisting of a vertical screw was designed, fabricated and tested successfully on the CFS.

TRTU OPERATIONS

Introduction

Results of TRTU test using Rose Bottoms blend and operating in a nonadiabatic gasification mode are discussed below.
The rework/repair of the TRTU was completed by the end of March. As part of commissioning, several modifications were made to the hydrocarbon feed system, notably, retracting the feed nozzle tip to the tube wall and adding steam to the hydrocarbon feed line as well as addition of a steam shroud to improve the operation. In the second week of April, the unit was brought to a steady operation at 1650°F and 85 psig.

By the middle of April, both solid circulation and the operation of hydrocarbon feed system were found to be satisfactory and testing was begun to process the Rose Bottoms. In a one-hour long run, LCO was first pumped into the unit for 25 min followed by a continuous injection of Rose Bottoms blend for 35 min. The feed system was flushed again with LCO for another 5 min. At the conclusion of this run, it was found that the bed material (circularing solids) had been coated with about 9 wt% carbon.

After a couple of runs that were intended to explore the advantages of alkali addition and for testing different configurations of the hydrocarbon feed system, the TRTU was restored to an operable condition for further testing of the Rose Bottoms. The details on and test results obtained from processing the Rose Bottoms are given below.

**Rose Bottoms Blend**

The Rose Bottoms used in the test was prepared from Hondo 650°F+ resid. This heavy material (bottom of the barrel) containing primarily asphaltenes and is pumpable at 300°F (with a kinematic viscosity of ~1000 centistokes at this temperature).

In a trial, it was found that the Rose Bottoms could not be fed through the feed pump even though the feed line temperature had been maintained at an adequate level. To reduce the resistance to flow, it was decided to blend 4 parts of ROSE Bottoms with 1 part of LCO as a "modified" feed for testing. This feed is referred to as the "blend" in this report. The blend contains about 10 wt% of H₂ and 88.5 wt% of carbon.

**TRTU Operation with ROSE Bottoms**

The TRTU was filled with 10 lb of FCC catalyst while it was maintained at a temperature of 1400°F. After adjusting the main gas flows and critical aeration gases, solid circulation in the unit gradually approached steady state with the mixing zone bed density at 16 lb/ft³ and the riser bed density in the range of 8 to 10 lb/ft³. The reactor back pressure was set at 50 psig to prevent the steam from condensing in the hydrocarbon feed line. Air was introduced into the riser section at a flow rate of 40 SCFH for about 30 min to burn off the hydrocarbon residue left over from previous runs as a precaution against coking. During air injection, an appreciable amount of CO₂ (~1 vol%) was found in the effluent gas. The unit was then gradually heated from 1400 to 1650°F over a period of 4 hr.

After the TRTU was heated to an average temperature of 1650°F, 1 lb of makeup catalyst was added to the unit to maintain the solid inventory close to 10 lb. The
temperature controllers on the hydrocarbon feed storage tank and feed line were set at 300 °F. Steam was introduced into the unit through both the oxidant and the feed nozzles. The steam injection, however, tended to disturb the riser bed density. The main gas flows and the aeration gas flows had to be adjusted again to stabilize the TRTU and maintain the riser bed density in the range of 8 to 10 lb/ft³. At this time, the standpipe DP was slightly below 80 in. of water. The air feed was 10 SCFH while the fluidization N₂ to the mixing zone was set at 140 SCFH and the booster N₂ to the riser was set at 165 SCFH.

The Rose Bottoms blend was introduced at a rate of 3.5 lb/hr. The introduction of the hydrocarbon feed into the unit has resulted in a substantial increase in the riser bed density. In order to maintain a solid circulation rate at less than 1500 lb/hr, all the aeration gas flows were turned down to a minimal level in addition to adjusting the main gas flows. This resulted in a stable operation that lasted about 40 min during which the on-line GC analysis was conducted and a product gas sample was taken for off-line analysis.

After a steady operation for about 40 min, the differential pressure (DP) across the filter increased as a result of plugging. When the filters were switched to stabilize the unit, solid circulation was lost which led to the shutoff of Rose Bottoms feed. The unit was then cooled down to 1400°F, and solid samples were taken for analysis.

Results and Discussion

The duration of the run processing the Rose Bottoms blend lasted about 60 min, during which the unit has operated steadily for 40 min and then was unstable for 20 min as a result of loss of solid circulation. This is shown in Figs. 1, 2, and 3. During steady operation, the volumetric ratio of CO to CO₂ measured by the on-line CO and CO₂ analyzers was about 2 to 1 (Fig. 1) which is relatively constant over this time period. This measurement should be regarded as approximate. The CO/CO₂ ratio determined by the on-line GC was much higher, viz., 5 to 1 and is considered accurate. This high value is due to the low carbon conversion achieved here and is expected to decrease significantly at high carbon conversion. The concentration of free O₂ was negligible. These data show that the partial oxidation (POX) of hydrocarbons had occurred in the transport reactor. The temperature in the mixing zone was steady at about 1690°F. The process temperature decreased with the elevation along the riser (Fig. 2). The temperature was 1670°F at the entrance to the riser and then dropped to 1640°F at the top of the riser. This temperature profile along the riser indicates that the gasification (endothermic) reactions took place in the riser. The steam consumption has been verified by a material balance. The mixing zone bed density was in the range of 15 to 17 lb/ft³ while the riser bed density was about 10 lb/ft³ (Fig. 3) and the total transport gas flow was 340 SCFH. Assuming a slip of 2, the solid circulation rate was estimated to be 1565 lb/hr, which is close to the upper limit of the cyclone capacity.

A material balance on the data collected during the steady 40-min period has been made to estimate the carbon conversion. The catalyst inventory in the circulation loop was estimated to be 9 lb while the carbon deposited on the catalyst was determined to be 9.2
wt% and the steam consumption was 1.4 lb. The C₅⁺ and other heavy hydrocarbons (not measured) amounted to about 1.87 lb. Some of the unconverted heavy hydrocarbons appeared to have been carried over to the filters causing filter plugging. Only 22 wt% of the hydrocarbon contained in the feed was converted into fuel gas as a result of short run time. Steady state with respect to carbon was not achieved as the carbon input was much higher than carbon consumption. The LHV of the final product gas was estimated to be 110 BTU/ft³ if carbon conversion of 90% could be achieved.

As mentioned above, about 40 min after the start of the Rose Bottoms blend into the unit, the differential pressure across the filter increased rapidly. This rapid buildup of the filter DP appeared to be caused by some unconverted heavy hydrocarbons, which deposited on the sintered metal surface. This was later established by an examination of the plugged filter. The material balance around the circulation loop also confirmed a substantial amount of unconverted hydrocarbons. The hydrocarbon carryover can be attributed to a lower reactor temperature than what is required to crack the hydrocarbons completely. The reactor has to be operated at 1800°F or higher and the filter must be maintained at much higher than 600°F to eliminate plugging of filters.

The pressure imbalance over the TRTU, happened during the course of switching filters, might have upset the reactor system contributing to loss of solid circulation as indicated by a low riser bed density (Fig. 3). After the unit was cooled down, it was observed that the cyclone skin temperature was much higher compared to other components in the circulation loop indicating that some solids had hung up in the cyclone section. Thus, the loss of solid circulation might be a result of choking the cyclone. As mentioned earlier, the solid circulation rate has reached the upper limit of the cyclone design capacity (1500 lb/hr). It may be necessary to use a smaller solid inventory than 10 lb used here to eliminate this problem.

General Comments

The following comments may be made based on the test with the Rose Bottoms blend:

- This test has demonstrated the viability of the concept (discussed in Objectives). The Rose Bottoms blend has been successfully converted into a fuel gas through both partial oxidation and steam-carbon gasification in the unit.

- The heating value of the product gas can be enhanced to an acceptable level by increasing the carbon utilization to 90% or higher.

- To improve the operability and stability of the unit, the operating temperature needs to be increased to 1800°F or higher and the solid inventory needs to be reduced.
STUDIES IN COLD FLOW SIMULATOR (CFS)

The flow properties of petroleum coke (40x140 mesh) were studied in the CFS in preparation for processing this solid in the TRTU. The CFS data obtained with petroleum coke were used to predict its fluidization characteristics in the TRTU. The test results and data interpretation are discussed in this section. The CFS was operated with petroleum coke with approximately 9 lb of solid inventory.

The CFS was operated at a steady state with three aeration flows, namely FI-199 (aeration to bottom of mixing zone), FI-400 (aeration to the Y-leg), and FI-305 (aeration to standpipe) set at 1.0, 1.30 and 0.2 SCFH, respectively while the main gas flows FI-100 (flow to the mixing zone) and FI-101 (transport flow to the riser) were maintained at 250 and 40 SCFH. At this set of flow conditions, the CFS was operated steadily for more than 4 hr. The bed density of the riser was 3.3 lb/ft³ which corresponds to a solid circulation rate of about 1000 lb/hr (without the slip). Mixing zone bed density could not be measured because of a malfunction of the DP indicator. The results were found to be reproducible when the test was repeated. The CFS results obtained on petroleum coke are compared with those obtained on FCC catalyst in Table 1. The petroleum coke required more aeration gas to the Y-leg compared to the FCC catalyst.

<table>
<thead>
<tr>
<th>Flow Setting</th>
<th>FI-199</th>
<th>FI-400</th>
<th>FI-305</th>
<th>FI-100</th>
<th>FI-101</th>
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</thead>
<tbody>
<tr>
<td>FCC Cat.</td>
<td>0.35</td>
<td>0.10</td>
<td>0.10</td>
<td>200</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.25</td>
<td>0.15</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Pet. Coke</td>
<td>1</td>
<td>1.3</td>
<td>0.2</td>
<td>250</td>
<td>40</td>
</tr>
</tbody>
</table>

Estimation of Flowrates for Processing Petroleum Coke in TRTU

The CFS required 250 SCFH of gas flowing to the mixing zone to maintain a stable turbulent bed. The equivalent superficial velocity is 6.3 ft/sec which gives a drag coefficient of 2.1. At 1800°F and 60 psig, the drag coefficient is estimated to be 5.0 and the corresponding superficial velocity is 4 ft/sec. This is the desirable gas velocity to be used in the mixing zone for the TRTU hot test with petroleum coke.

The required total flow for transport, bleed (for the DP sensing legs), and aeration is about 60 SCFH. The mixing zone gas velocity will be increased from 4 to 7 ft/sec to increase the reactor throughput. The feed gas to the mixing zone is air. The O₂ consumption is assumed to be as per reaction (1) which gives a consumption rate of about
3 lb/hr of petroleum coke (based on 95 wt% carbon content) and the steam-carbon gasification is expected to consume 1.4 lb/hr of carbon based on a measured gasification rate of 1.0 lb/lb/hr. Thus, the total consumption rate of petroleum coke is estimated to be 4.4 lb/hr. The product gas flow rate is 1.2 lbmol/hr (392.9 ACFH) which gives a riser gas velocity of about 30 ft/sec. The lower heating value (LHV) of the product gas is calculated to be 96.6 BTU/ft³ at standard conditions based on a predicted gas composition (CO-22.3%, CO₂-6.5%, H₂-9.3%, balance - N₂). The overall flow requirements for this test are summarized in Table 2.

\[
\begin{align*}
3 \text{C} + 2 \text{O}_2 & \rightarrow \text{CO}_2 + 2 \text{CO} \quad (1) \\
\text{C} + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2 \quad (2)
\end{align*}
\]

<table>
<thead>
<tr>
<th>Flows</th>
<th>Flow Rate</th>
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<tbody>
<tr>
<td>Air to the mixing zone</td>
<td>284 SCFH</td>
</tr>
<tr>
<td>Aeration and bleed N₂</td>
<td>20 SCFH</td>
</tr>
<tr>
<td>Trans. N₂ to coke feed line</td>
<td>40 SCFH</td>
</tr>
<tr>
<td>Coke feedrate</td>
<td>4.4 lb/hr</td>
</tr>
<tr>
<td>Steam feedrate</td>
<td>1.3 lb/hr</td>
</tr>
</tbody>
</table>

**Solid Feed System**

A dry petroleum coke feed system, consisting of a low speed air motor, a vertical screw and a pressurized feed hopper, was developed and tested successfully on the cold flow model. The solid flowrate was found to be a function of the DP (between the hopper and solid injection location) when the screw speed was maintained constant. It was then installed on the TRTU for experiments to be conducted in the fourth quarter. A sketch of the dry solid feed system is shown in Fig. 4.

The solids’ feeder was installed and tested on the TRTU using the following operating conditions and the procedure:

- N₂ supply pressure to motor: 5 psig
- Speed of screw: 60 rpm
- Aeration flow to feed hopper: 6 scfh at 100 psig
- Differential pressure above solids and solid injection location: 10 in. of water
Solids were charged to the feed hopper by stopping the screw feeder (if running) and closing the isolation valves No.1 and No. 2. The vent was kept open while charging solids to the hopper. After the hopper was filled with solids, the vent was closed and the isolation valve No.2 was opened. When at system pressure, isolation valve No.1 was opened and the screw feeder was started. (If the screw feeder is operated while the isolation valve No.1 is closed, the solids in the hopper tend to get packed and cause problems in solid flow later.)

Slurry Feed System

An alternative feed system (slurry) was assembled using a peristaltic pump and by developing a stable slurry. It was tested and discarded after it was shown that settling of slurry in the discharge line caused repeated pluggage.

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>BRU</td>
<td>bench-scale reactor unit</td>
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<tr>
<td>CFS</td>
<td>cold flow simulator</td>
</tr>
<tr>
<td>DP</td>
<td>differential pressure</td>
</tr>
<tr>
<td>FCC</td>
<td>fluid catalytic cracker</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatograph</td>
</tr>
<tr>
<td>K-impregnated</td>
<td>potassium-impregnated</td>
</tr>
<tr>
<td>LHV</td>
<td>lower heating value</td>
</tr>
<tr>
<td>LTPQX</td>
<td>Low Temperature Partial oxidation</td>
</tr>
<tr>
<td>ROSE</td>
<td>Residuum Oil Supercritical Extraction</td>
</tr>
<tr>
<td>SCFH</td>
<td>volumetric flowrate, ft³/hr at standard conditions</td>
</tr>
<tr>
<td>TRTU</td>
<td>Transport Reactor Test Unit</td>
</tr>
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