CONVERSION OF HIGH CARBON REFINERY BY-PRODUCTS

Cooperative Agreement No.: DE-FC22-93BC14809
Contractor Name and: The M.W. Kellogg Company, 601 Jefferson Avenue, Address Houston, Texas 77002-7990
Date of Report: April 26, 1996
Award Date: October 02, 1993
Anticipated Completion Date: September 29, 1996
Government Award for: Current Fiscal Year $1,063,667
Principal Investigators: Satyan Katta
Gunnar Henningsen
Yung-Yi Lin
Jim O'Donnell
Project Manager: E.A. Zuech
Bartlesville Project Office
Reporting Period: January 1, 1996 - March 31, 1996

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.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Summary of Technical Progress

The Transport Reactor Test Unit (TRTU) was commissioned to conduct studies on pyrolysis of Rose Bottoms using spent FCC (Fluid Catalytic Cracker) catalyst as the circulating medium and gasification of this carbon over a temperature range of 1600 to 1700°F. The Rose Bottoms (Residuum Oil Supercritical Extraction) was produced in the Rose unit. Studies were done in the Bench Scale Reactor Unit (BRU) to develop suitable catalyst formulations and to study the steam reforming of methane and propane in support of the experiments to be conducted in the TRTU. Studies were also conducted on gasification of coke breeze, petroleum cokes and carbon deposited on FCC catalyst. The catalytic effect of potassium on gasification of these solids was studied. Studies were conducted in the CFS (cold flow simulator) to investigate flow problems experienced in the TRTU. Results from these studies are presented in this report.

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 of ROSE Bottoms following modifications/repair/commissioning of TRTU and preparation of ROSE Bottoms in Kellogg’s ROSE pilot plant facility. Task 32 - TRTU modifications to the solids flow valve were to have been completed. Actual accomplishments are described below.

The planned work hours for this period were 4216. The actual work hours were 2120.

Task 31: The BRU was used to develop data on optimum preparation/operation of the carbon-alkali catalyst in preparation for runs on ROSE Bottoms and petroleum coke in the TRTU. TRTU modifications were implemented based on CFS operational data. The pyrolysis of ROSE Bottoms, prepared from Hondo crude oil, is planned for the 3rd quarter. Low temperature partial oxidation (LTPOX) tests on a blend of Rose Bottoms and light cycle oil using FCC catalyst and K-impregnated FCC catalyst will be conducted in the 3rd quarter. Gasification of this carbon will use potassium carbonate (K₂CO₃) as the catalyst. Coke slurry runs are also planned for the 3rd quarter of 1996.

Task 32: Studies were done in the CFS to investigate the flow problems experienced in the TRTU and the required modifications for the TRTU and the solids control valve were established based on these studies. The TRTU modifications have been completed after CFS findings were incorporated into the redesign of the TRTU.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
Summary of Technical Progress

The Transport Reactor Test Unit (TRTU) was commissioned to conduct studies on pyrolysis of Rose Bottoms using spent FCC (Fluid Catalytic Cracker) catalyst as the circulating medium and gasification of this carbon over a temperature range of 1600 to 1700°F. The Rose Bottoms (Residuum Oil Supercritical Extraction) was produced in the Rose unit. Studies were done in the Bench Scale Reactor Unit (BRU) to develop suitable catalyst formulations and to study the steam reforming of methane and propane in support of the experiments to be conducted in the TRTU. Studies were also conducted on gasification of coke breeze, petroleum cokes and carbon deposited on FCC catalyst. The catalytic effect of potassium on gasification of these solids was studied. Studies were conducted in the CFS (cold flow simulator) to investigate flow problems experienced in the TRTU. Results from these studies are presented in this report.

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 of ROSE Bottoms following modifications/repair/commissioning of TRTU and preparation of ROSE Bottoms in Kellogg's ROSE pilot plant facility. Task 32 - TRTU modifications to the solids flow valve were to have been completed. Actual accomplishments are described below.

The planned work hours for this period were 4216. The actual work hours were 2120.

Task 31: The BRU was used to develop data on optimum preparation/operation of the carbon-alkali catalyst in preparation for runs on ROSE Bottoms and petroleum coke in the TRTU. TRTU modifications were implemented based on CFS operational data. The pyrolysis of ROSE Bottoms, prepared from Hondo crude oil, is planned for the 3rd quarter. Low temperature partial oxidation (LTPOX) tests on a blend of Rose Bottoms and light cycle oil using FCC catalyst and K-impregnated FCC catalyst will be conducted in the 3rd quarter. Gasification of this carbon will use potassium carbonate (K₂CO₃) as the catalyst. Coke slurry runs are also planned for the 3rd quarter of 1996.

Task 32: Studies were done in the CFS to investigate the flow problems experienced in the TRTU and the required modifications for the TRTU and the solids control valve were established based on these studies. The TRTU modifications have been completed after CFS findings were incorporated into the redesign of the TRTU.
STUDIES ON PYROLYSIS/GASIFICATION/CATALYST FORMULATION IN BRU

Introduction

The main objective of the gasification and hydrocarbon reforming studies undertaken in the BRU is to develop and show that selected catalyst formulation(s) can catalyze the carbon gasification and reform CH₄, propane and higher hydrocarbons in the presence of steam over a temperature range of 1400 to 1600°F at high conversion without producing any unsaturates in a fluidized bed. The same successful formulation will then be used in the TRTU to show the process on a larger scale in a continuous mode. The experiments done in the TRTU recently with K-impregnated FCC catalyst showed that this catalyst formulation was not effective in cracking naphtha. It appears that, based on Exxon studies¹, the potassium needs to be impregnated on the carbon matrix itself and that both potassium and carbon are needed for the catalytic effect. The FCC catalyst, on which about 15% carbon was deposited in the TRTU, was impregnated with K₂CO₃ solution using incipient wetting technique and then dried.

These studies were done in support of low temperature partial oxidation studies planned for the 3rd quarter. Gasification of untreated and K-impregnated coke breeze and carbon deposited on FCC catalyst were studied in the BRU at about 1600°F and 60 to 100 psig. The steam reforming of CH₄ and propane was studied in the BRU with untreated and K-impregnated FCC catalysts coated with carbon and mixtures of FCC catalyst and K₂CO₃. The carbon-coated FCC catalyst was obtained in the TRTU during naphtha pyrolysis studies.

Experimental

A simplified flow schematic and a detailed description of the BRU test facility were given in the last quarterly report. It consists of a 2.067-in. inside diameter (i.d.) section of 10-in. height and an expanded section of 3.068-in. i.d. of 12-in. height. Product gas leaving the reactor is sent to a water-cooled condenser and then to a particulate filter. An on-line GC is connected to the BRU for gas analysis in carbon gasification studies. This GC requires 12 min to complete the gas analysis. A different GC is used for experiments involving propane and higher hydrocarbons to analyze the concentration of hydrocarbons and carbon oxides (CH₄, C₂H₄, C₂H₆, CO, CO₂, H₂, N₂ and the unsaturates) in the effluent gas of the BRU by using gas sample bags. The BRU facility can be operated at temperatures up to 1950°F at pressures up to 450 psig. The catalyst used in these studies is K₂CO₃ in granular form. A narrow size distribution for the various carbonaceous solids and the catalyst was used for the experimental studies. Prior to experiments in the BRU, fluidization of the various mixtures was studied in a cold flow model of the BRU.
Steam Reforming of Methane/Propane

Steam reforming of methane and propane was studied in the BRU with different catalyst formulations over a temperature range of 1500 to 1700°F at 100 psig. The objective was to develop suitable catalyst formulations and to determine optimum operating conditions to maximize the gasification rate and to steam reform the hydrocarbons without producing any unsaturates.

The effect of steam-carbon molar ratio on methane conversion was studied with untreated coke breeze and a mixture of C-coated FCC catalyst and K$_2$CO$_3$ (50 wt%). This mixture is expected to yield about 15 wt% excess potassium based on the assumption that Al$_2$O$_3$ and SiO$_2$ present in the FCC catalyst react with K$_2$O to form potassium aluminosilicate (K$_2$O-Al$_2$O$_3$.SiO$_2$). Potassium present in the bed may not be available to catalyze the methane-steam reaction unless it is in excess. The C-coated FCC catalyst was produced previously during naphtha pyrolysis studies and contains about 13.5 wt% carbon.

Steam reforming of methane was studied in the presence of untreated coke breeze at 1600°F and 100 psig at steam-carbon molar ratios of 2, 1 and 0.5. This test was intended to establish a base line for the methane conversion and to compare with that of the reaction in the presence of K-doped coke breeze. Methane conversion was negligible except during an initial period. The initial methane conversion may be attributed to the catalytic behavior of the reactor wall that contains nickel. The surface of the reactor wall appears to have been passivated after a short period of operation.

Steam reforming of propane was studied in the presence of C-coated FCC catalyst both with and without K$_2$CO$_3$ (40 wt%) to study the catalytic behavior of the mixture on propane conversion at steam-carbon molar ratios of 1.0 and 0.5. The potassium in the mixture reduced the amount of unsaturates formed significantly.

Carbon Gasification Studies

Carbon gasification rates of untreated and K-impregnated coke breezes were studied at temperature of 1600°F and pressure of 100 psig in tests. Potassium was impregnated by soaking coke breeze in an aqueous solution of K$_2$CO$_3$ and then drying it. The results of these two experiments show a moderate catalytic effect of potassium on the carbon-steam reaction.

The gasification rate of carbon deposited on FCC catalyst at 1600°F is about 0.0016 min$^{-1}$ compared to about 0.017 min$^{-1}$ obtained for the mixture of C-coated FCC catalyst and K$_2$CO$_3$ (50% by wt) showing that the potassium was highly catalytic to the steam-carbon reaction.

Carbon gasification of a mixture of C-coated FCC catalyst and K$_2$CO$_3$ was studied at 1700°F. A gasification rate of 0.08 min$^{-1}$ was obtained for this mixture. At the end of this
test, 50 gm of C-coated FCC catalyst was added to the bed and gasification was conducted at 1600°F to find out if the potassium remaining in the bed was still active and mobile to catalyze the carbon-steam reaction. A gasification rate of 0.02 min⁻¹ was obtained showing that the potassium present in the original fluid bed was mobile and active. An additional amount of 50 gm of C-coated FCC catalyst was added to the bed and gasification conducted at 1600°F. A gasification rate of 0.02 min⁻¹ was obtained in this test confirming the earlier observation that the potassium present in the original fluid bed was still mobile and active. The carbon gasification rate of this solid at 1600°F without any catalytic effect was determined previously as 0.002 min⁻¹.

The gasification rate of delayed petroleum coke (produced in a Midwestern oil refinery) was studied with and without K₂CO₃ over a temperature range of 1630 to 1700°F. The size distributions used for the petroleum coke and K₂CO₃ particles were 140x270 mesh and 32x60 mesh, respectively. An increase in the catalyst concentration from 33 to 66% did not affect the carbon gasification rate. The potassium did not catalyze the carbon-steam reaction for this petroleum coke. This may be attributed to the significant gasification rate of the uncatalyzed coke. This is in contrast to the gasification rate of the C-coated FCC catalyst in the presence of K₂CO₃.

The gasification rate of petroleum coke from Lyondell/Citgo Refinery was studied at 1650°F and 100 psig both with and without potassium. There is no significant difference between the two results showing that the potassium did not catalyze the gasification rate of this coke. This is attributable to the high reactivity of the coke. Some agglomerates were formed in the tests where potassium was present. The formation of agglomerates may be attributed to the lack of any ash in the petroleum coke. This observation is in contrast to the tests with coke breeze where no agglomerates were formed that is believed to be due to the significant amount of ash present in the coke breeze.

A summary of the reaction rates obtained with various carbonaceous solids in the BRU is presented in Table 1.

Table 1. Gasification rates of various solids in the BRU

<table>
<thead>
<tr>
<th>Carbonaceous Solid</th>
<th>Gasif. Rate 1600°F, 1/hr</th>
<th>Gasif. Rate 1700°F, 1/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-coated FCC catalyst w/o K₂CO₃</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>C-coated FCC catalyst with K₂CO₃</td>
<td>2.7</td>
<td>4.68</td>
</tr>
<tr>
<td>Petroleum coke (delayed) + K₂CO₃</td>
<td>-</td>
<td>0.78</td>
</tr>
<tr>
<td>Coke breeze</td>
<td>0.12</td>
<td>-</td>
</tr>
<tr>
<td>Lyondell/Citgo Petroleum coke + K₂CO₃</td>
<td>-</td>
<td>0.96</td>
</tr>
<tr>
<td>K-impregnated coke breeze</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>Mixture of coke breeze + K₂CO₃</td>
<td>-</td>
<td>1.23</td>
</tr>
</tbody>
</table>
Conclusions

The following conclusions may be made from the studies on gasification of carbon deposited on FCC catalyst, petroleum cokes and coke breeze and steam reforming of hydrocarbons done in the BRU:

Gasification Studies

- The addition of potassium to C-coated FCC catalyst catalyzed the carbon gasification rate by ten fold. The addition of fresh C-coated catalyst to a bed containing $K_2CO_3$ showed the mobility of potassium to catalyze carbon gasification. No agglomeration of bed solids was observed.

- Based on tests with coke breeze, physical mixing of catalyst with carbon seems better than solution impregnation of the catalyst in the coke breeze. A catalyst concentration of 0.99 wt% appears to be the best of all the concentrations studied with coke breeze. This low concentration of potassium did not result in the formation of any agglomerates of solids and is, therefore, the recommended level. The addition of CaCO$_3$ to a mixture of coke breeze and $K_2CO_3$ did not result in any significant enhancement of gasification rate, but caused bed agglomeration.

- The addition of $K_2CO_3$ to either of the petroleum cokes did not catalyze the carbon gasification reaction. The gasification rate of both uncatalyzed petroleum cokes is relatively high and, so, the addition of potassium did not enhance the gasification rate.

Steam Reforming of Hydrocarbons

- The steam reforming of methane at the conditions studied was negligible both in the presence of coke breeze and C-coated FCC catalyst. The presence of potassium did not affect the conversion of methane.

- The steam reforming of propane was increased by the presence of potassium in the fluidized bed. The amount of unsaturates in the product gas was reduced significantly by the presence of potassium in the bed.

STUDIES IN COLD FLOW SIMULATOR

Introduction

In two of the TRTU runs conducted in late 1995, the solid flow was found to be some what unstable. Slugging in the riser was common as inferred from the pressure drop
readings. The feed conversion was not complete and some feed accumulated in the downstream recovery section because of poor contact between gas and solid. The plug valve was at the bottom of the standpipe to control the solid circulation rate. The solid flowrate seemed independent of the control valve opening and slight valve adjustment often gave large changes in solid circulation. Thus, cold flow model studies were undertaken. The CFS has nearly the same configuration and dimensions as the TRTU to investigate these problems. A sketch and a detailed description of the CFS were provided in the last quarterly report. It consists of a standpipe, a mixing zone, a riser and a cyclone and a Y-leg connecting the standpipe and the mixing zone.

Findings/Recommendations

Studies were done in the CFS to explore and understand the fluidization phenomena in a circulating bed and some unique behavior about the TRTU. The following deficiencies of the TRTU, sometimes inherent in a small-scale design, were identified and implemented besides some observations:

- The standpipe needs to be operated in a moving bed mode, for which the aeration gas cannot exceed a certain amount of flow, to prevent gas bubbles from growing to the size of the standpipe. Otherwise, it may cause slugging of the bed and result in poor solid circulation.

- Solid flowrate was found to be nearly independent of the opening of the solid control valve. It was removed from the solid flow path so that it does not interfere with solid flow.

- The location of the primary feed nozzle must be higher than the bottom of the Y-leg to prevent any primary feed gas from flowing into the Y-leg. The sharp turn (at the mixing zone) of the Y-leg must be smooth to ease solid flow from the Y-leg to the mixing zone. The secondary feed nozzle should be at the bottom of the transition between the mixing zone and the riser. Also, the secondary feed jet should be confined to the main solid stream instead of being directed to the opposite tube wall.

- The aeration tap at the bottom of the standpipe needs to be used to help solid flow from the standpipe to the Y-leg. The second one on the Y-leg is meant to control the solid flow in the Y-leg. The third one placed just below the Y-joint serves to control solid flow from the Y-leg to the mixing zone. The control of flowrates through these aeration taps is vital to the control of solid circulation rate. The required flow ranges at standard conditions for the three aeration taps for proper operation of the unit have been established as follows:

  (1) Aeration at Standpipe bottom: 0.50 to 1.50 ft³/hr
  (2) Aeration at bottom of Y-leg: 0.50 to 1.50 ft³/hr
  (3) Aeration at bottom of mixing zone: 0.35 to 0.55 ft³/hr
• A slip ratio of 2.0 was determined in the CFS based on measurement of solid circulation rate.

• The velocity of the primary feed gas has a direct impact on the stability of the mixing zone and the riser. In the CFS, it was found that the minimum velocity required to develop a stable turbulent fluidized bed in the mixing zone is 7.2 ft/sec. This is equivalent to 4.3 ft/sec for the hot unit assuming that the same drag force is required to transport solids in both cases. Because the gas-solid flow patterns in the TRTU cannot be predicted from the cold flow studies, the minimum superficial velocity of the primary feed gas needs to be reconfirmed during the startup of the TRTU.

• The riser bed density needs to be controlled such that it does not exceed 2.5 lb/ft³ by adjusting the aeration gas flowrate to avoid slugging caused by cyclone choking or its unsteady back pressure. With this constraint and with a slip of 2.0 found in the cold flow unit, the allowable highest solid circulation rate was about 500 to 600 lb/hr. This is another important criterion that needs to be considered during the operation of TRTU.

COMMISSIONING OF TRTU

The rework/repair of the new TRTU started right after the completion of the cold flow model testing. The unit was modified from the original design based on the observations and measurements made in the cold flow model testing. Several important modifications have been implemented in the unit. First, the solid control valve has been set at a full-open position to eliminate the restriction, thus improving the solid circulation rate. Secondly, the oxidant injection nozzle has been moved up to a new location that is slightly above the Y-joint. As a result, the possibility of reverse gas flow occurring in the Y-leg is eliminated. In addition, the cyclone dipleg has been extended by one foot. This not only enhances the cyclone performance but improves the stability of the standpipe as well. The standpipe is operated as a moving bed and, so, the aeration gas flowrate to the standpipe has been reduced to a minimum.

An improved technique of wrapping heating wire on the pipe and a more uniform power supply control scheme have been used along the solids circulation loop for better temperature control and safer operation. All electrical connections and the mechanical connections including feeds, purges, and fluidization nozzles were completed near the end of 2nd quarter.

As part of commissioning, the test unit was slowly heated without solid circulation. After the unit reached a temperature of about 800°F, a couple of hot spots in the mixing zone and several cold spots in the middle section of the riser and at the lower part of the standpipe were detected. These cold and hot spots resulted in a relatively high average differential temperature in the unit (DT - the difference in average skin temperatures of the riser side and the standpipe side). This is an important consideration in the operation of
the unit since an increase in average DT increases the stress on the unit. This condition frequently triggered an alarm system that, in turn, automatically shut off the electrical heaters.

Because of the difficulty experienced in controlling the reactor skin temperature profile, the heater control design was modified. A detailed analysis of the heating system led to the conclusion that each section of the heating elements needed a separate TIC (temperature indicating controller) for its independent temperature control. In addition, the current to each section of the heating elements should be adjustable to prevent the heaters from overheating. After the new temperature control scheme was implemented, the heaters could bring the unit to a desired temperature and hold it without causing any hot or cold spots at temperatures up to 1650°F. After the unit reached temperature 800°F, a leak test for the hot system was conducted at pressure of 45 psig. The average leak rate was found to be less than 3 psi/hr. Upon the completion of all rotameter installations, the differential pressure indicators and related bleed lines were checked and found in good working order. The unit was ready for solid circulation at the end of 2nd quarter.

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BRU</td>
<td>bench-scale reactor unit</td>
</tr>
<tr>
<td>C-coated</td>
<td>carbon-coated</td>
</tr>
<tr>
<td>CFS</td>
<td>cold flow simulator</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>LTPOX</td>
<td>Low Temperature Partial oxidation</td>
</tr>
<tr>
<td>ROSE</td>
<td>Residuum Oil Supercritical Extraction</td>
</tr>
<tr>
<td>TIC</td>
<td>Temperature Indicating Controller</td>
</tr>
<tr>
<td>TRTU</td>
<td>Transport Reactor Test Unit</td>
</tr>
</tbody>
</table>

Reference