2

CONTRACT TITLE AND NUMBER:
Bench-Scale Co-Processing
DE-AC22-87PC79818

DOE/PC/79818--T7

Date: February 19, 1992
Quarterly Report: No. 13
Reporting Period: 4/1/91 - 9/31/91

CONTRACTOR NAME:
UOP
25 E. Algonquin Road
Des Plaines, Illinois 60017-5017

AUTHORS: Carol A. Piasecki
John G. Gatsis

CONTRACT PERIOD: April 1, 1988 to March 31, 1992

DOE/PC/79818--T7

DE92 012557

QUARTERLY REPORT

This report, which is the 13th quarterly report for Contract DE-AC22-87PC79818, covers the two quarters from April 1991 to September 1991. The objective of this contract is to extend and optimize UOP's single-stage, slurry-catalyzed co-processing scheme. The current task is to complete a long-term operability run using a 0.05 wt-% Mo-based catalyst at approximately 460°C. The objectives of this run are to demonstrate that high-severity conditions can be run for an extended period of time (at least one month) and to collect enough product sample to do a complete Hempel fractionation and detailed characterization of the individual naphtha, distillate, and VGO cuts. This information will be used to reevaluate the engineering design and product upgrading scheme that was developed under the first co-processing contract (DE-AC22-84PC70002). During the current two quarters, the long-term operability study was unsuccessfully attempted several times. This report discusses these attempts.

Operations

Three attempts to complete the long-term operability study were completed during the current two quarters. All three attempts were ended prematurely because of various operational problems.

For the first two attempts, a modified start-up procedure was used. The plant was lined out to 425°C in a once-through mode of operation before the recycle of high-pressure separator (HPS) material was started. In the prior attempts, the reactor temperature was increased directly to 460°C in the presence of liquid recycle.¹ Most of the problems in these early attempts occurred during the start-up period. The purpose of starting with once-through operations was

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ANALYST 118 11/11/92

to avoid recycling under-converted material that is initially present and possibly causing plugging problems.

In the first attempt, sporadic level control in the HPS was experienced after the recycle was started. This behavior eventually (at 16 HOS) resulted in the plugging of the outlet of the HPS and the liquid recycle line. Because the products were not analyzed, this attempt was not given a run number.

Run 35 Operations

An additional modification was made with Run 35, which was the second attempt. A modified flush oil blend was used. Flush oil is used to start-up and to clean the plant. Starting in January 1991, a new flush oil was used because of the unavailability of the original flush oil. One possible explanation of the plugging problems may be an incompatibility of the new flush oil and our co-processing feed. Run 35 was completed with a modified blend that included the addition of 20 vol-% of a highly aromatic solution to the current refinery slurry oil being used.

Run 35 initially looked encouraging. However, a unique problem was experienced. The hydrogen recycle gas disperser developed a plug that could not be cleared. Consequently, the disperser was bypassed beginning with Period 13. The distribution of gas in the reactor was different and this difference may have altered the utilization of the hydrogen. Operations were maintained in this mode of operation.

During Period 18, a plugged recycle flowmeter was misdiagnosed. As a result, the feed was cut out of the plant, and the reactor temperature was decreased. When the feed was cut back in, level control problems were experienced in the HPS, and the outlet of the HPS plugged. The run was aborted. Plant upsets, especially with the HPS or the recycle line, often lead to other problems because solids begin to settle out when the liquid becomes stagnate.

Products from three periods of operations were examined. Two of the early periods (Periods 7 and 8) were analyzed and compared with a test period (Period 17) using the modified gas dispersion. The conversions and yields were similar for all of the periods, as shown in Table 1. Because the results from Period 17 were similar to the earlier periods, the modified gas distribution probably did not significantly alter the utilization of hydrogen.

Table 1
Run 35 Results at Approximately 465°C

	Period		
	7	8	17
Temperature	465	466	467
Conversions, wt-%			
Coal	89.2	91.0	89.0
C ₇ Insolubles	68.9	77.6	71.7
Nondist. (510°C+)	66.0	70.0	70.4
Yield, wt-%			
C ₅ -510°C+	67.9	68.1	65.8
510°C+	13.4	13.0	13.2

Much of the effort has been focused on trying to identify the cause and a solution to the problem. The operational records from January 1990 to the present were reviewed and a list of operational problems and action items was compiled. Two plant modifications were completed to try to minimize the frequently occurring operational problems prior to Run 36. The two major modifications addressed the following problems:

- Several occurrences of plugging in the HPS outlet were noted. The outlet was redesigned and repiped to make this section of pipe free draining.
- The 1/16 inch line in the recycle flowmeter frequently plugs due to the particulates in the solution. If the recycle meter is not bypassed quickly, the reactor can plug. An automatic bypass of the recycle flowmeter was added to minimize the time required to switch to the bypass system when the flowmeter begins to plug.

Run 36 Operations

Run 36 was the third attempt during the current two quarters to complete the long-term operability study. The operational approach for this run was to duplicate the test conditions that were used during the first co-processing run with 0.05 wt-% Mo catalyst (Run 27).² The purpose of this approach was to reference the plant at 425°C, 445°C, and 455°C before the temperature

was increased to 465°C. However, the plant operations at 425°C were poor. The flowmeter plugged several times, and the liquid recycle operation was sluggish. The new automatic bypass to the recycle flowmeter worked as designed, and so the operations were maintained. The stripper column and vacuum column also experienced upsets that resulted in plugging problems.

The reactor temperature was increased to 443°C to try to improve the conversions and plant operability. The operations of the reactor and recycle sections improved, but the back end of the plant continued to operate poorly. After 144 HOS, a leak developed in the reactor outlet. Upon tightening the top head of the reactor, the reactor outlet line ruptured, and the plant was forced to shut down. Although the plant operations were never completely lined out, two periods of operation were analyzed anyway to investigate the cause of the operational problems.

Table 2 compares the data from Periods 8 and 9 with two periods at a similar temperature from Run 27, the original 0.05 wt-% Mo run. The conversions and product yields of Periods 8 and 9 are low compared with Run 27. The average heptane-insoluble conversion was only 60.8 wt-% as compared to an average of 79.8 wt-% for Run 27. This significantly lower heptane-insoluble conversion probably indicates the presence of retrograde reactions. Based on this limited non-steady-state data, the expected conversions and yields were not achieved in this run.

Table 2
Run 36 and Run 27 Results at Approximately 445°C

	Run			
	36*	36*	27	27
Period	8	9	12	13
Temperature	443	443	446	446
Normalized Conversion, wt-%				
Coal	78.0	85.5	88.8	89.2
C ₇ Insolubles	56.1	65.6	80.6	78.9
Nondist. (510°C+)	50.7	62.0	70.2	74.1
Yield, wt-%				
C ₅ -510°C+	44.3	51.8	60.3	67.3
510°C+	36.1	28.6	25.9	22.2

* The results do not represent lined-out plant operations.

Future Work

Because the cause of the poor plant performance is not completely understood, the current plan is to modify the approach of the long-term operability test. The catalyst concentration will be increased to 0.1 wt-% Mo instead of the 0.05 wt-% Mo. A catalyst concentration of 0.12 wt-% Mo was successfully demonstrated in the bench-scale unit in the first Mo-catalyzed bench-scale run. In addition, the target operating temperature will be reduced from 465°C to 455°C, and the minimum liquid recycle ratio will be increased from 5:1 to 7.5:1 recycle to fresh feed. These modifications should help reduce the possibility of retrograde reactions. Enough product sample will be obtained to complete the detailed product analysis required for an economic analysis.

References

1. C. A. Piasecki, et. al., Bench-Scale Co-Processing Quarterly Report No. 12, prepared for the United States Department of Energy under Contract No. DE-AC22-87PC79818, October 9, 1991.
2. D. A. Nafis, et. al., Bench-Scale Co-Processing Quarterly Report No. 7, prepared for the United States Department of Energy under Contract No. DE-AC22-87PC79818, Mar. 27, 1990.

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.