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DOE/PC/79818--T10

BENCH-SCALE CO-PROCESSING
Contract No. DE-AC22-87PC79818

Technical Progress Report No. 17 (07/1/92-09/30/92)
Technical Progress Report No. 18 (10/1/92-12/31/92)
Technical Progress Report No. 19 (01/1/93-03/31/93)
Technical Progress Report No. 20 (04/1/93-06/30/93)

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UOP's second co-processing contract, DE-AC22-87PC79818, began in April 1988. The major objective of this contract is to establish a database for the optimization of the co-processing concept by improving the effectiveness of the co-processing catalyst system. Two major mechanisms for improving the catalyst system are to be investigated: employment of more effective catalysts and utilization of improved catalytic environments. These two mechanisms are defined in the contract Statement of Work under Task 3.2 as Subtask 3.2.1 and 3.2.2, respectively.

This report covers a span of four quarters, starting from July 1, 1992 to June 30, 1993. During this period the project was in a hold. As explained below, a request was made to add more funds to the contract to investigate catalytic environment improvements. Most of the time during this four quarters was spent in preparation of the proposal, review of the proposal by PETC, and getting additional funding approved for the contract. No experimental work was carried out on any of the tasks of the contract during these four quarters.

Prior to the period covered by this report, UOP had successfully completed Subtask 3.2.1 and identified a molybdenum-based catalyst that is highly active and effective in achieving improved co-processing performance at significantly lower metal concentrations (0.05% - 0.1% by weight of Mo) in the catalyst. The new catalyst was developed in slurry autoclave tests and demonstrated in the continuous bench-scale pilot plant. A long-term operability study, Run 37,

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was successfully completed in the 1st quarter of FY 1992 (see Technical Progress Report No. 14 for the reporting period 10/1/91 to 12/31/91). For this run (Run 37), the reference feedstocks, Lloydminster vacuum resid and Illinois No. 6 coal were used. The operating conditions for this run were reaction temperatures of 455°C and 465°C, reactor pressure of 3000 psig, base space velocity, and a liquid recycle to fresh feed ratio of 7.5:1. For this run, a catalyst concentration of 0.1 wt-% Mo was used. The average conversion and yield for the 455°C operation were 90.5 wt-% coal conversion, 74.5 wt-% heptane insoluble conversion, 78.9 wt-% nondistillable conversion, and 63.7 wt-% C₅-510°C liquid yield. The average conversion and yield for the 465°C operation were 92.6 wt-% coal conversion, 84.8 wt-% heptane insoluble conversion, 85.0 wt-% nondistillable conversion, and 65.6 wt-% C₅-510°C liquid yield.

Although significant progress was made in meeting the objectives of Subtask 3.2.2, Improvement in Catalytic Environment, this task was not fully completed because of funding limitations. Two new catalytic environments were to be investigated to improve the co-processing concept. These two environments are liquid recycle and new generation reactor systems. The first environment, liquid recycle, has been demonstrated in bench-scale pilot plant Run 21 (see Quarterly Progress Report No. 5 for the period 4/1/89 to 6/30/89 for this contract), and it does significantly improve the operability of the bench-scale unit by giving it more inertia against feed upsets. The improved back-mixing and higher superficial velocities in the reactor helped to decrease coking at the reactor walls. As a result, improved co-processing performance as evidenced by higher conversions and better desulfurization, was achieved. For example, at a 2.5:1 ratio of liquid recycle to fresh feed, asphaltene and nondistillable conversions increased by about 5 wt-% over reference performance with no recycle. The successful implementation of the liquid recycle operation is now incorporated in the co-processing baseline operation.

However, as a result of operational and maintenance problems occurring in the early stages of the liquid recycle evaluation, the resource requirements for this task were much greater than initially planned. For example, Run 27 was carried out with 0.05 wt-% Mo catalyst for a period of 339 hours-on-stream (HOS). The reactor pressure was at 3000 psig and reactor

temperature was varied from 426°C to 461°C. The liquid recycle to fresh feed ratio was estimated to be between 5.2 at 426°C to 8.4 at 461°C. Several problems were encountered in subsequent efforts to duplicate Run 27 conditions. Though all the reasons for the unsuccessful trials are not clear yet, a successful long-term operation (Run 37) was carried out only when the Mo concentration in the catalyst was relaxed to 0.1 wt-%. One of the uncertainty in Run 27 was the liquid recycle to fresh feed ratio. This ratio may have been much higher than that estimated and may have helped in the successful operations at the lower Mo (0.05 wt-%) concentration. UOP gained valuable operating lessons during the unsuccessful trials, but in the process, also used much higher resources than originally planned. As a result, the second concept, namely, the evaluation of the new generation reactor system, has not been investigated yet.

To evaluate all of the possible ways of improving catalyst effectiveness, and hence, to develop a broader database for the optimization of the co-processing concept and to arrive at a more logical contract endpoint, UOP had requested additional funding under the current contract to complete an evaluation of the new generation reactor systems. Activities during these four quarters of the subject contract concentrated on developing a plan and detailed program outline for the evaluation of the new reactor concepts. UOP's program outline and resource requirements were reviewed by DOE, and additional funding was allocated to the contract. The contract modification incorporating these changes was executed at the end of June 1993.

The final task (Task 4.0) of contract DE-AC22-87PC79818 involves the assessment of the new co-processing performance. This task was scheduled to be completed in the first quarter of 1993; however, UOP, in concurrence with DOE's project manager, postponed the assessment until the new reactor concepts can be evaluated in the continuous pilot plant.

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