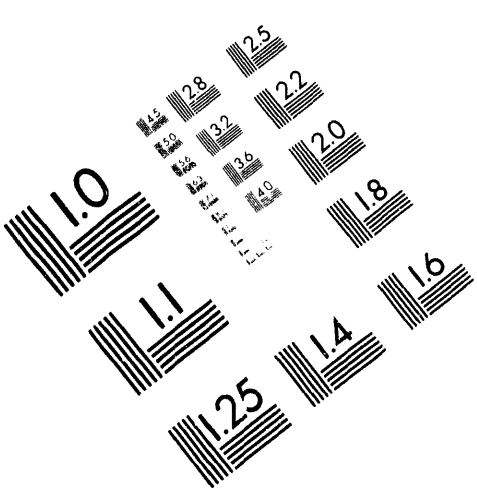

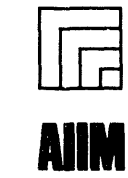

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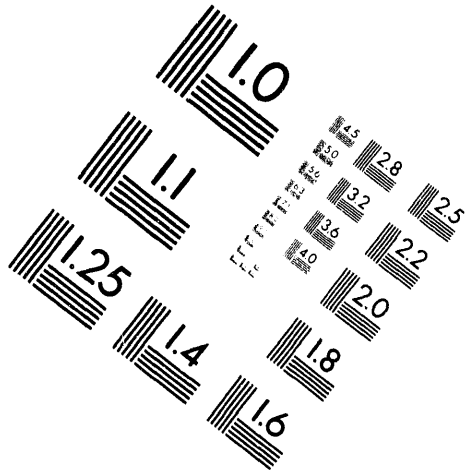

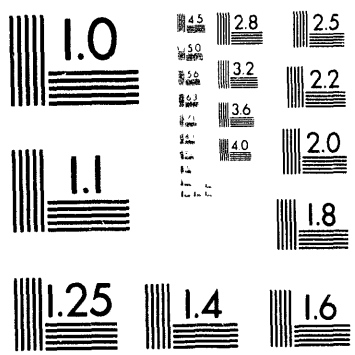

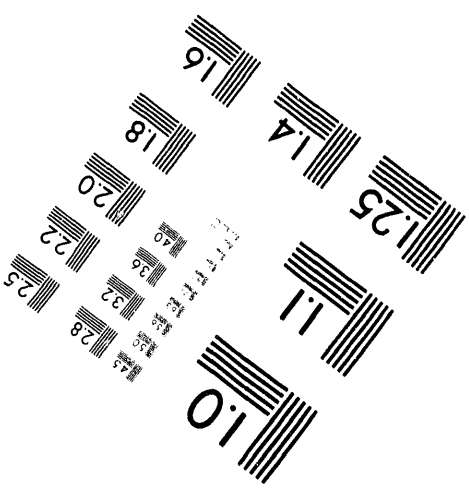

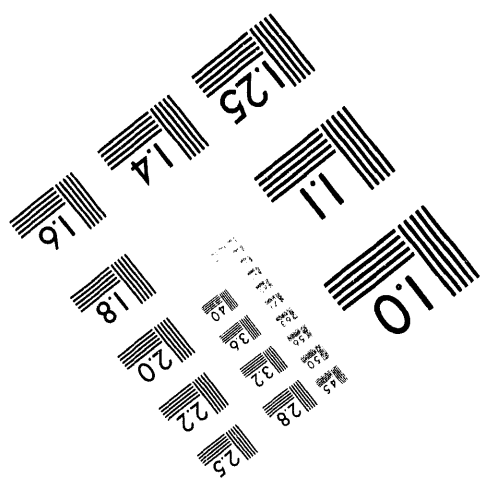

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DOE/PC/79818--T11

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

Technical Progress Report No. 22 (10/01/93-12/31/93)

by

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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 the period of October 1, 1993 to December 31, 1993. During this period work on Subtask 3.2.2, Improvement in Catalytic Environment, was carried out and the bench-scale co-processing pilot plant was operated in the co-current mode with product recycle and increased catalyst concentration. The project objective was to achieve 90+ % conversion of the 510°C+ non-distillables at 2800 psig. Currently work is on-going in a stirred autoclave at the same catalyst concentration as that in the runs reported here, and the results of these autoclave runs will be summarized in Technical Progress Report No. 23.

EXPERIMENTAL

Feedstock

Lloydminster vacuum resid (R10, UOP 58-1625) was used as the feed for Pilot Plant 558 co-current Aurabon runs. For the two runs discussed in this report, no coal was added to the feed. The vacuum resid was obtained from Husky Oil Lloydminster Refinery in May, 1988. The properties of the feedstock are presented in Table 1. The feed has an API of 6.6 with 82 wt% of the feed boiling above 510°C. The feed contains 4.8 wt% sulfur, 0.6 wt% nitrogen, 13.6 wt% heptane insoluble and 17.4 wt% microcarbon residue.

Pilot Plant Testing

Two runs, Run 42 and 43, were conducted in Pilot Plant 558, a schematic diagram of which is shown in Figure 1. In both runs, Lloydminster vacuum resid spiked with 0.5 wt% Mo present as a slurry-phase catalyst was processed. Operating conditions for Runs 42 and 43 can be viewed in Tables 2 and 3, respectively. Plant outlet pressure was maintained at 2800 psig except during plant upsets. The target

fresh feed rate was 0.5 liquid hourly space velocity (LHSV), where LHSV was defined as (cc fresh feed per hour) / (cc reactor volume). The reactor temperature ranged from 350°C to 470°C.

The feed was pumped upflow into the reactor. A slip stream was taken off the high pressure separator (HPS) bottoms to maintain a constant level in the HPS which was held at 125°C and 2500 psig. The rest of the HPS bottoms was recycled back to the reactor unless indicated otherwise. The recycle to feed ratio varied between 0 and 12:1. The slip stream was taken into a low pressure stripper (LPS) where the light ends were stripped off at 135°C and 50 psig by an upflow N_2 stream. The HPS off-gas was taken into a three-phase separator where it was contacted with water, removing any salts which were contained in the partially condensed HPS off-gas. The hydrocarbon from the three-phase separator was sent to the debutanizer column.

The three-phase off-gas was recycled back to the reactor. It was mixed with fresh H_2 and fed upflow into the reactor. Some of the three-phase off-gas was bled off to maintain a hydrogen purity of approximately 90 mol%. The LPS bottoms product was collected in a container kept in a hot box. The debutanizer column bottoms were collected while the overhead gas was measured and vented.

Operations

Run 42

Run 42 was started up in the once-through mode with a fresh feed rate of 0.5 LHSV. Plant pressure was 2800 psig and the reactor block temperatures were set to obtain an internal average bed temperature (ABT) of 420°C. The gas recycle rates were set to obtain 9000 SCFB (6.9 SCFH) H_2 to the reactor and 6000 SCFB (4.6 SCFH) H_2 to feed. A summary of the run operating conditions for period 1 is given in Table 2.

After 8 hours on stream (HOS), an exotherm was detected in the reactor bed. The temperatures rose to 440°C at 13" above the reactor inlet. The reactor temperature was lowered in an attempt to eliminate this exotherm. While the magnitude of the maximum bed temperature decreased, the exotherm remained. The run was aborted at 26 HOS when a plug developed in the reactor. This plug caused a 200 psia pressure differential to appear across the reactor which could not be cleared.

Run 43

Run 43 was also started up in the once-through mode with plans to establish HPS recycle to feed once levels were established. Plant pressure, fresh feed rate and gas recycle rates were set at 2800 psig, 0.5 LHSV, and 9000 SCFB (6.9 SCFH) H_2 to the reactor/6000 SCFB (4.6 SCFH) H_2 to feed, respectively, as in Run 42. On account of exotherms observed in Run 42, an initial average bed temperature (ABT) of 400°C was targeted. Summary of the run operating conditions and pilot plant log sheets beginning with period 4 (48 to 60 HOS) are given in Tables 3 and 4, respectively. During the line-out period (7 HOS), a 100 psia pressure differential appeared across the reactor. This was cleared by increasing the gas recycle rates and cutting out the make-up H_2. A second plug developed at 10.5 HOS and was also cleared with increased gas recycle rates.

Recycle was established at 15.5 HOS (period 1). The HPS level and recycle to feed were lost at 16 HOS. The reactor temperatures were lowered to avoid coking in the reactor. A pressure differential appeared across the reactor which cleared itself when it reached 700 psia. At 22 HOS (period 1), the plant

pressure fell to 2650 psig.

Recycle was re-established during period 2, at which point the temperature of one of the furnace blocks controlling the preheater was increased by 5°C. A plug began to develop at 39.5 HOS (period 3) and was cleared by increasing the recycle rate and cutting out the fresh feed.

The plant operations stabilized and the ABT was increased to 410°C at 49.5 HOS (period 4). The ABT did not become steady but instead cycled between 405 and 415°C.

Another 700 psia pressure differential developed across the reactor at 70 HOS (period 5) which cleared itself within 5 minutes. After the plug cleared, the HPS level decreased and recycle was lost. At 72 HOS (period 5), the recycle line to the reactor and the reactor itself plugged. Both were cleared by 73 HOS (period 5). The recycle rate was increased to a recycle to fresh feed ratio of 20:1 to make sure that the reactor and recycle line plugs were cleared. The ABT continued to cycle during periods 6 and 7.

At 100.5 HOS, the ABT was increased to 425°C. Thirty minutes later (101 HOS, period 8), a 50 psia pressure differential appeared across the reactor. The recycle gas rates were tripled in an attempt to clear the plug before it became too large. This caused the plant pressure to increase to 3100 psig. When the plug cleared at 113 HOS (period 9), the plant and reactor pressures equilibrated at 2900 psig. The excess recycle gas (ERG) drag was increased to bring the pressure down to 2800 psig. The pressure upset caused the HPS level to fall to 13 ma (*i.e.*, near empty) and recycle was momentarily lost.

At 126 HOS (period 10), the reactor temperature suddenly increased to 420°C and was cycling during periods 10 and 11. At 154 HOS (period 12), the reactor temperature rose again and recycle was lost. All reactor temperatures were decreased to 420°C and recycle gas rates were increased. A small plug developed at 157 HOS (period 13) which was easily cleared. Recycle was re-established at 161 HOS (period 13) at a recycle to fresh feed ratio of 10:1 and recycle gas rates were decreased to original specifications. Reactor temperatures were increased during period 14 once operations were stabilized.

The plant was producing only 15% overhead (material to the debutanizer column) at 182 HOS; the furnace block temperatures were therefore increased by 5°C. This caused an immediate exotherm to develop. To reduce the exotherm, the recycle rate was increased. At this point, it was decided that having preheater furnace block temperatures exceeding 500°C in order to achieve an isothermal bed temperature profile was not desirable. Reactor temperatures would be adjusted to maintain a constant maximum bed temperature and the temperature differential across the reactor would be monitored. The maximum temperature targeted was 440°C.

At 204 HOS (period 17), the maximum bed temperature rose to 450°C. It was decided that as long as the temperature remained near or below 450°C, no adjustments would be made. At 215 HOS (period 17), a plug began developing across the reactor. The pressure differential was approximately 70 psia. As the pressure differential increased (period 18), the preheater temperature was decreased by 5°C and the recycle rate was increased. At 229.5 HOS (period 19), the maximum bed temperature dropped to 434°C.

The pressure differential across the reactor was 100 psia at 265 HOS (period 22) and the maximum bed temperature was 450°C. Preheater temperatures were lowered to try to lower the bed temperature. At 290 HOS, the pressure differential increased to 400 psia and the run was terminated.

Figures 2 and 3 plot temperature profiles at different hours on stream. The legends indicate the furnace

block temperatures. Two furnace blocks controlled the preheater, and the reactor portion was controlled by two separate blocks. The block controlling the inlet portion of the reactor is designated as "In" and that controlling the outlet portion of the reactor is designated as "Out" in the figures. As Figure 2 illustrates, for virtually constant furnace block temperatures, the reactor temperature profile varied by as much as 15°C above 2" from the inlet, and nearly 40°C at the inlet. Figure 3 shows that increasing all the furnace block temperature settings by 5°C raised the reactor temperature by 30 to 60°C. Lowering the preheater block temperatures to 475°C resulted in a 80°C gradient across the reactor.

RESULTS AND DISCUSSION

No analysis was taken of the product from Run 42. The run was aborted before the plant was lined out. The restriction in the reactor was approximately 4.5" long and started 16" above the preheater (10" from the top of the reactor). The plug was solid and could not be dissolved in toluene. The restriction had to be drilled out. The exotherm observed at the beginning of the run is consistent with having 0.5 wt% Mo in the feed. It is well known that Mo is one of the most active catalysts for heavy resid conversion (RBearden and CLAldridge, AIChE 90th National Meeting, 1981).

In spite of starting Run 43 with an ABT of 400°C, it was not possible to eliminate exotherms. Moreover, throughout Run 43 development of hot spots was observed. This suggests that the catalyst distribution in the reactor might not have been uniform. Pockets of catalyst starvation and development of hot spots are likely to lead to plugging, which occurred frequently in Run 43. It was extremely difficult to control the reactor temperature in this run. Aside from exotherms and development of hot spots, reactor temperatures varied erratically when the furnace block temperatures, feed rate and gas rates were held essentially constant.

Product samples from periods 15 and 20 in Run 43 were analyzed and the results are summarized in Table 5. The conversion levels were comparable in the two periods and were low. While the ABT in period 15 was 427°C, because of the size of the inventory in the plant, the product collected in period 15 was more likely produced in earlier periods, where the ABT was much lower (399°C in period 13 and 412°C in period 14). Similarly the product produced in period 20 was most likely produced in periods 18 and 19 when the ABT was 417 and 401°C, respectively. Clearly, overall conversion is a larger function of temperature than catalyst concentration. As a result of carrying out resid conversion at low reactor temperatures, gas make and coke make were also low. Asphaltene (heptane insoluble) conversion was considerably higher than the 510°C+ conversion, and this suggests that asphaltene conversion is more readily effected in the presence of catalyst, whereas overall resid conversion is primarily governed by temperature.

Run 43 was aborted at 290 HOS. Upon unloading the reactor a restriction was found, deposited approximately 1" above the preheater and 1.5" in length. The solid deposits were found to consist of 76.9 wt% C, 3.5% H, 8.0% S and 7.3% Mo, suggesting that there was some catalyst accumulation in the reactor, and further that there was considerable coking. Product recycle could in part account for plugging, as no attempt was made to remove coke pre-cursors from the recycle stream and they were recycled together with unconverted feed.

Difficulties encountered in controlling the reactor temperature suggest that the liquid flow characteristics in the reactor were such that there was little back-mixing. The superficial gas velocity at 15000 SCFB of H_2 is 0.27 cm/s, while the superficial liquid velocity at a recycle ratio of 10:1 is 0.08 cm/s. Commercially, the superficial gas velocity is expected to fall in the range 3 - 8 cm/s, where much greater back-mixing is likely to be achieved, but where foaming becomes a serious problem. At the flow rates

employed in Run 43, it is most unlikely that there was any foaming. At the same time, it appears that there was not nearly as much back-mixing as needed, particularly in the presence of a very active catalyst where hot spots can easily develop unless the catalyst is very uniformly distributed in an isothermal reactor.

Table 1

Feed Analysis

Analysis of Lloydminster Vacuum Redid
UOP 58-1625

API Gravity	6.6
Specific Gravity	1.0246
Distillation, °C	
IBP	379
5	455
10	473
20	509
EP	512
% EP	22
% 510°C	82
C wt%	83.6
H wt%	10.3
S wt%	4.8
N wt%	0.6
MCRT wt%	17.4
C_7 Insol wt%	13.6
Ni ppm	82
V ppm	183
Pour Point, °C	54

Table 2 : Run 42 Operating Conditions

Period	FF Rate LHSV	Rec to FF Ratio	H_2 Drag cf/hr	H_2 to Rx SCFH	H_2 to Feed SCFH	Plant Press psig	Rx Internal ABT (°C)
1	0.48	0	2.0	8.2	5.0	2800	421

Table 3 : Run 43 Operating Conditions

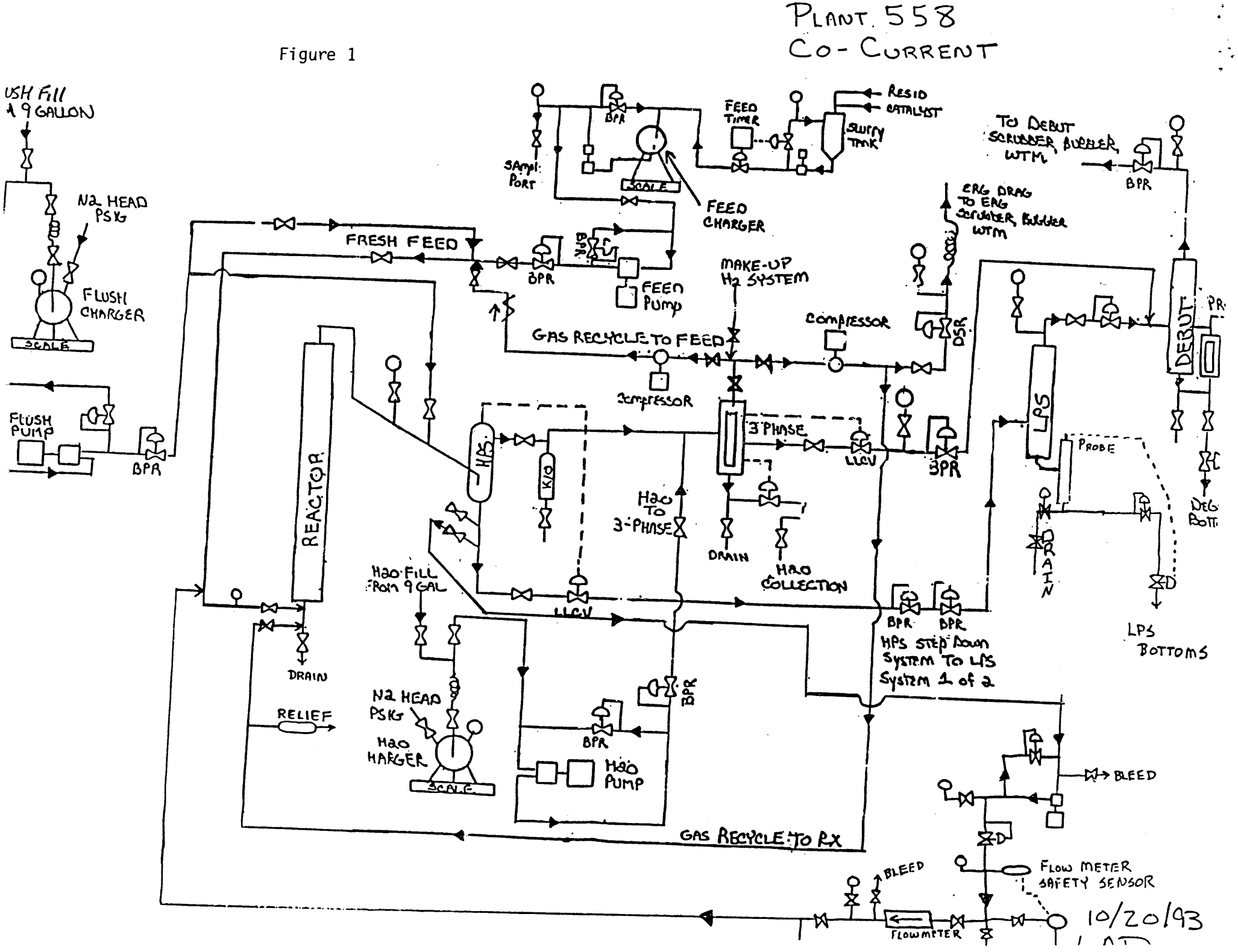
Period	FF Rate LHSV	Rec to FF Ratio	H_2 Drag cf/hr	H_2 to Feed SCFH	H_2 to Rx SCFH	Plant Press psig	Rx Internal ABT °C	Max Temp °C
4	0.59	3.5	0.63	8.6	11.7	2800	409	414
5	0.46	4.0	0.56	8.7	13.5	2800	411	418
6	0.46	8.5	0.48	9.9	13.4	2800	397	416
7	0.51	6.6	0.63	9.8	12.1	2800	408	423
8	0.52	6.6	0.59	11.1	14.9	2800	415	429
9	0.48	7.3	0.52	9.8	12.8	2800	416	421
10	0.51	6.7	0.58	9.3	12.2	2800	409	417
11	0.50	6.8	0.50	9.4	12.5	2800	412	425
12	0.54	5.9	0.59	9.6	13.8	2800	416	430
13	0.74	1.7	0.50	21.5	38.9	2800	399	411
14	0.54	10.0	0.56	9.3	15.9	2800	412	434
15	0.49	10.8	0.54	9.2	15.3	2800	427	460
16	0.50	10.2	0.48	9.6	14.5	2800	410	439
17	0.50	10.2	0.50	9.1	14.9	2800	422	444
18	0.53	9.7	0.54	12.1	22.6	2800	417	441
19	0.46	10.9	0.55	9.2	15.1	2800	401	441
20	0.48	10.5	0.58	9.6	16.0	2800	411	442
21	0.43	11.5	0.59	9.7	16.6	2800	410	442
22	0.56	8.7	0.79	9.2	16.0	2800	424	443
23	0.46	10.7	0.79	9.5	15.2	2800	426	451

Table 5

Plant 558 Run 43

Period	15	20
ABT (°C)	427	411
510°C+ conversion	34%	35%
Heptane insoluble conversion	57%	56%
Microcarbon residue conversion	30%	29%
Sulfur removal	57%	58%
Nitrogen removal	59%	59%
Wt% coke yield	0.7%	0.9%
Wt% C_1-C_4 yield	2.3%	3.3%

Figure 1


PLANT 558
CO-CURRENT
USH Fill
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N2 HEAD PSIG
FLUSH CHARGER
SCALE
FLUSH PUMP
BPR
FRESH FEED
SAMPL PORT
BPR
SCALE
FEED CHARGER
FEED TIMER
RESID
CATALYST
SLURRY TANK
FEED Pump
BPR
MAKE-UP H2 SYSTEM
GAS RECYCLE TO FEED
Compressor
Compressor
TO DEBUT SCRUBBER, BUBBLER, WTM
BPR
ERG DRAG TO ERG SCRUBBER, BUBBLER WTM
DSR
DEBUT
PR
LPS
PROBE
DRAIN
LPS BOTTOMS
DEG BOTT
REACTOR
HPS
KO
3 PHASE
LLCV
BPR
H2O TO 3-PHASE
DRAIN
H2O COLLECTION
H2O FILL FROM 9 GAL
LLCV
BPR
BPR
HPS STEP DOWN SYSTEM TO LPS System 1 of 2
DRAIN
RELIEF
N2 HEAD PSIG
H2O HARGER
SCALE
BPR
H2O PUMP
BPR
BLEED
GAS RECYCLE TO RX
BLEED
FLOW METER SAFETY SENSOR
FLOWMETER
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