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COMMERCIAL SCALE EXPANDED BED HYDROPROCESSING OF SOLVENT REFINED COAL (SRC) EXTRACT

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ABSTRACT

The base case catalyst screening run on unmodified American Cyanamid 1442B cobalt-molybdenum catalyst has been completed. Two hydrogenated Koppers Heavy Residue Creosote Oil solvents were employed in the 50/50 SRC/solvent feed blends - a 400°F and a 500°F IBP solvent with the 400°F solvent being run first. No significant differences in conversion and denitrogenation were noted for the two solvents.

Following an initial high conversion of 77 weight percent of 850°F+ material, the conversion remained approximately constant at 65 weight percent from Period 5 through Period 12 (a change in solvent occurring at Period 7/8). The hydrogen content of the heavy oil through the same periods was approximately 7.5 weight percent (6.35 weight percent in the two SRC/solvent feed blends). When processing the 400°F IBP solvent, the denitrogenation activity of the catalyst declined steadily from 61.3 to 50.4 percent. With the 500°F IBP solvent, the denitrogenation activity declined from 55.8 to 39.5 percent.

SUBTASK I

TESTING DENITROGENATION CATALYSTS
WORK ACCOMPLISHED

The hydrogenated KC-Oil solvent used for the catalyst screening study was prepared in the Lummus HDS unit. A heavy oil and a light oil are produced by a vacuum flash with the IBP of the heavy oil being approximately 500°F. In order to prepare the two different solvents for Run LCF-29 - a nominal 400°F and a 500°F IBP solvent - the heavy oil was used as-is and the light oil was distilled. The light oil was topped to 400°F minus and the 400°F plus material was added to the as-is heavy oil to produce the nominal 400°F IBP solvent. A second portion of the light oil was topped to 500°F minus and the 500°F plus material was added to the as-is heavy oil to produce the nominal 500°F IBP solvent.

Table 1 presents the inspection data for the two solvents - LCF-29/1-7 is the 400°F solvent and LCF-29/8-13 is the 500°F solvent. The solvent represented by LCF-30 in Table 1 is a sample of the as-is heavy oil from the HDS unit (obtained from a blend of seven drums of heavy oil). Variations in the operation of the product recovery section of the HDS unit contribute to the relatively large amount of IBP-500°F fraction (11.8 volume percent) found in the nominally 500°F heavy oil (LCF-30).

Table 2 presents the feed blend properties obtained from blending the three solvents described previously with approximately 50% SRC. The feed blend for LCF-29/1-7 is lighter than LCF-29/8-13, has a lower viscosity and softening point, and a larger IBP-650°F distillate fraction - all of which reflect the addition of the 400-500°F light oil material from the light oil distillation into the hydrogenated heavy oil solvent. The elemental analyses of the two feed blends are virtually identical.

The chronology for Run LCF-29 is presented in Table 3. Table 4 presents the yield of heavy oil liquid products from Run LCF-29 and the gravity for each fraction. A light oil product gravity is also shown.

A summary of the weight ratio conversion of 850°F+ material, gravity change, and nitrogen, hydrogen, and sulfur contents of the heavy oil liquid product for Run LCF-29 is presented in Table 5. The conversion, denitrogenation, and hydrogen content of the heavy oil liquid product are shown in Figure 1. The nominal 400°F IBP solvent feed blend was processed first. The conversion and denitrogenation function were initially at a very satisfactory high level (77 weight percent conversion and 61.3 percent denitrogenation), but very quickly declined. Based on previous experience in the original contract, the conversion is best represented by a stabilizing plateau at approximately 65 weight percent irrespective of the solvent employed. However, the denitrogenation function continually showed a definite decrease with both solvents. It will be noted that the denitrogenation function also experienced a small increase when the solvent in the feed blend was changed from 400°F to 500°F IBP which only slightly perturbed the declining trend.

The data obtained for Period 13 are indicative of a further decrease in conversion, denitrogenation function, and heavy oil hydrogen content. The effect of the data from Period 13 was not included in the data interpretation previously described as there was no way of determining whether or not the Period 13 data were representative of a trend or merely an artifact of the operation.

Table 6 summarizes completed and projected work for 1977 and 1978 on the contract extension.

SUBTASK I

TESTING DENITROGENATION CATALYSTS
WORK FORECAST

The catalyst screening study will continue with the testing of several other different catalyst candidates (each run maximum 10-day duration). The best nitrogen removal catalyst and related operating conditions will be used for all the subsequent subtasks.

The following catalyst program has been adopted for the near future:

a) Nickel-molybdenum
   Shell S-324

b) Nickel-tungsten
   Shell S-354

c) Cobalt-molybdenum
   American Cyanamid Modified 1442B

d) Nickel-molybdenum
   Ketjen Fine 153S-0.8E

Additional catalyst which are available encompass the following:

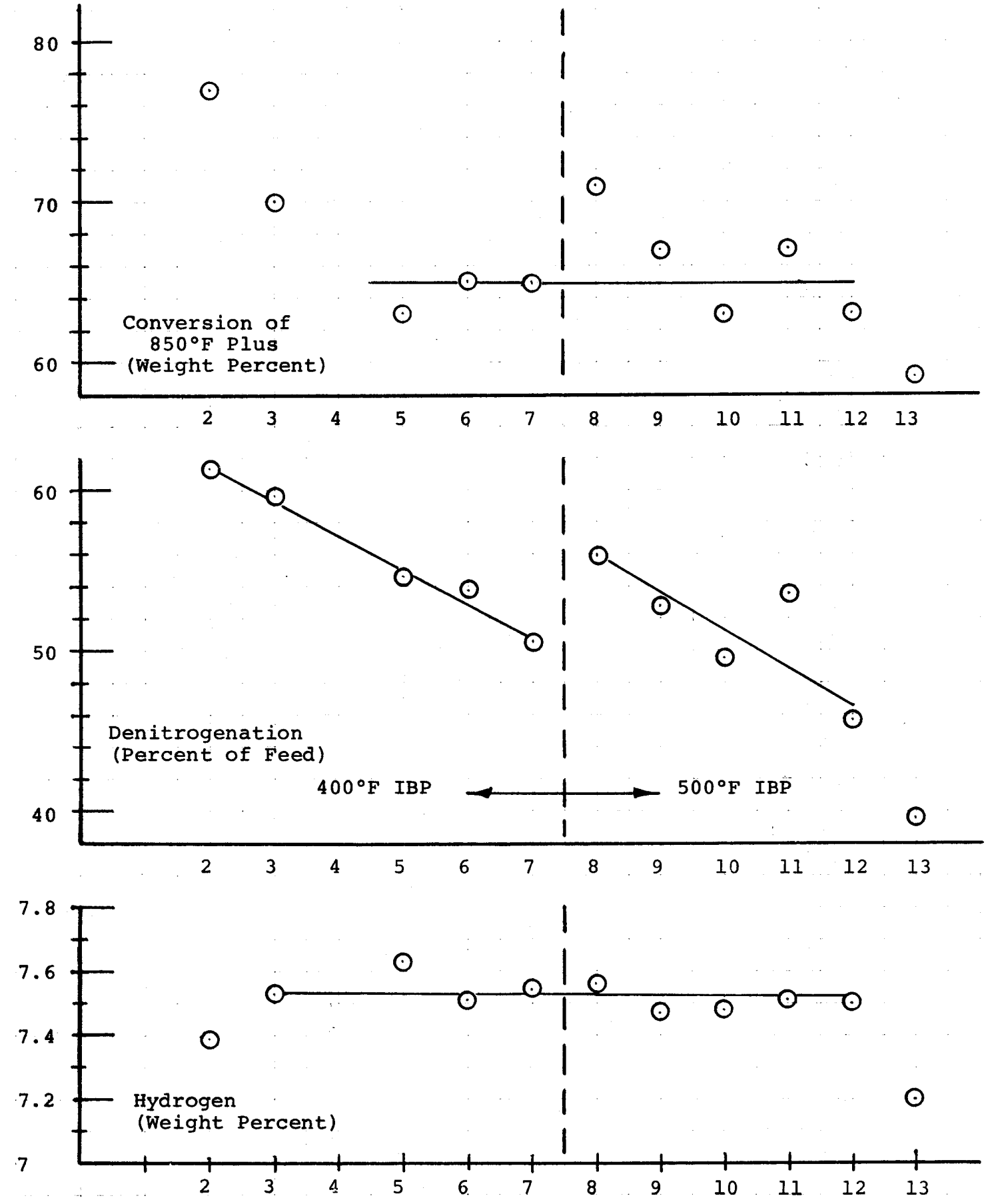
a) Ketjenfine
   Cobalt-molybdenum 124S-0.8E
   124S-0.8E HD
   124S-0.8E LD

b) American Cyanamid
   Nickel-molybdenum 1443B

c) Nalco
   Nickel-molybdenum NM-504
   Nickel-tungsten NM-550

FIGURE 1

RUN LCF-29



JDP 9/21/77

TABLE 1

LC-FINING PILOT PLANT OPERATION
FOREIGN SOLVENT PROPERTIES
HYDROGENATED KOPPERS HEAVY RESIDUE CREOSOTE OIL

Run No. (LCF-)	29	29	30
Period	1-7	8-13	
Gravity, Sp 60/60°F	1.080	1.103	1.1062
Pour Point, °F	<-10°	-7°	-5°
Viscosity, Kin. CS @ 100°F	11.76	15.72	17.87
Kin. CS @ 210°F	2.36	2.64	2.79
Elemental Content, Wt%			
Carbon	91.05	92.18	92.17
Hydrogen	7.33	6.73	6.70
Oxygen	0.48	0.67	0.59
Nitrogen	0.27	0.69	0.41
Sulfur	<0.06	0.15	0.09
Ash, Wt%	TR	TR	TR
Distillation, Vapor Temp, °F	(b)	(b)	(b)
IBP	369	323	337
5 Vol%	466	490	460
10	498	530	495
20	537	565	540
30	575	580	570
40	600	612	589
50	630	645	600
60	658	654	639
70	692	677	672
80	730	730	710
90	790	808	789
95	840	-	-
Final Temperature, °F	850	850	850
Distillate Recovered, Vol%	95.6	95.6	92.4
Residue, Vol%	4.6	4.9	6.5(c)
Loss (-),Gain (+), Vol%	+0.2	+0.5	-1.1
Distillate Fractions			
IBP-500°F, Vol%	9.7	(3.4)(a)	11.8
Gravity, Sp 60/60°F	0.9672	-(a)	1.0063
Sulfur, Wt%	TR	TR	<0.06
500-650°F, Vol%	47.7	49.9	49.8
Gravity, Sp 60/60°F	1.0497	1.0591	1.090
Sulfur, Wt%	<0.06	0.11	0.08
650-850°F, Vol%	38.2	41.8	30.8
Gravity, Sp 60/60°F	1.1243	1.1388	1.1527
Sulfur, Wt%	<0.06	0.16	0.10
850°F+ Residue, Vol%	4.6	4.9	6.5(c)
Gravity, Sp 60/60°F	1.234	1.232	-(d)
Sulfur, Wt%	<0.06	0.21	0.07

(a) Insufficient Sample
(b) Lummus Standard 250ml Vacuum Distillation
(c) Based on assumed specific gravity of residue
(d) Residue was semi-solid and therefore unable to determine specific gravity by ASTM-D71-MODIFIED.

TABLE 2

LC-FINING PILOT PLANT OPERATION
FEED BLEND PROPERTIES
SRC-PREHYDROGENATED KOPPERS HEAVY RESIDUE CREOSOTE OIL

Run No. (LCF-)	29	29	30
Period	(1-7)	(8-13)	
Composition			
Solvent, Wt% (ex drum)	46.4	46.9	47.0
SRC, Wt% (ex drum)	53.6	53.1	53.0
850°F+, Vol% (by distilln)	47.8	51.6	50.7
850°F+, Wt% (by distilln)	50.1	53.7	52.3
Gravity, °API	-11.9	-13.3	-14.1
, Sp 60/60°F	1.1836	1.1967	1.2048
Softening Point, °F	107	133	118
Viscosity, Kin. CS @ 350°F	9.73	16.67	10.88
, Kin. CS @ 400°F	5.03	9.84	5.95
Elemental Content, Wt%			
Carbon	88.76	88.85	89.37
Hydrogen	6.34	6.36	6.32
Oxygen	2.45	2.94	2.52
Nitrogen	1.19	1.29	1.23
Sulfur	0.43	0.44	0.41
Ash, Wt%	0.08	0.18	0.11
Distillation, Vapor Temp.,°F			
IBP	430	428	420
5 Vol%	515	534	500
10	556	568	549
20	610	615	610
30	654	665	653
40	705	740	720
50	810	850	826
Final Temperature, °F	850	850	850
Distillate Recovered, Vol%	54.3	49.8	52.0
Residue, Vol%	47.8	51.6	50.7
Loss (-), Gain (+), Vol%	+2.1	+1.4	+2.7
Distillate Fractions			
IBP-650°F, Vol%	29.6	27.5	30.0
Gravity, °API	4.7	2.0	2.9
, Sp 60/60°F	1.0389	1.0599	1.0528
Sulfur, Wt%	0.10	0.11	0.06
Nitrogen, Wt%	0.36	0.36	0.27
650-850°F, Vol%	24.6	22.2	22.0
Gravity, °API	-6.5	-7.0	-6.9
, Sp 60/60°F	1.1322	1.1366	1.1356
Sulfur, Wt%	0.22	0.21	0.14
Nitrogen, Wt%	0.76	0.66	0.64
850°F+, Vol%	47.8	51.6	50.7
Gravity, °API	-17.6	-17.8	-17.7
, Sp 60/60°F	1.2420	1.2440	1.2430
Sulfur, Wt%	0.65	0.63	0.67
Nitrogen, Wt%	2.28	2.03	2.00

TABLE 3

LC-FINING PILOT PLANT OPERATIONS

SRC-PREHYDROGENATED HEAVY CREOSOTE OIL BLEND
RUN LCF-29
CHRONOLOGY

July 9 to July 11, 1977
Periods 1 & 2

The feedstock was a blend of SRC with heavy creosote oil that was prehydrogenated in the Lummus HDS Pilot Plant. The solvent was prepared to contain material nominally boiling above 400°F.

Operations were satisfactory.

July 11 to July 12, 1977
Period 3

A feed interruption occurred as a result of a "vapor lock" or gas in the feed pump checks. Solvent replaced the feed for about an hour and some solvent was pumped to the second reactor recycle pump for short periods because of upsets.

July 12 to July 13, 1977
Period 4

Operations were still upset and the feed pump was operated at higher than the desired rate to re-establish normal conditions.

July 13 to July 16, 1977
Periods 5 to 7

Some short feed interruptions which were corrected as they arose occurred in each period. The temperature of the heated line to the feed pump was reduced to minimize any vapor formation and "vapor lock" in the pump.

July 16 to July 22, 1977
Periods 8 to 13

The feedstock was replaced with a new blend of SRC and prehydrogenated heavy creosote oil as solvent. This solvent, however, was prepared to be material nominally boiling above 500°F.

Operations were satisfactory. A short feed interruption and reactor upset occurred in each of the last two periods, 12 and 13. The feed suction line temperature was reduced further.

The operation was shutdown with the completion of Period 13 as scheduled.

TABLE 4

LC-FINING PILOT PLANT OPERATION
SUMMARY OF LIGHT & HEAVY OIL RECOVERED
SRC-PREHYDROGENATED KOPPERS HEAVY RESIDUE CREOSOTE OIL

Run LCF-29 Period	Light Oil		Heavy Oil Fractions									
			IBP-500°F		500-650°F		650-850°F		850°F+		Total	
	Vol%	°API	Vol%(a)	°API	Vol%(a)	°API	Vol%(a)	°API	Vol%(a)	°API	Vol%	°API
	Nominal Solvent BP - 400°F											
1 (b)	-	-	-	-	-	-	-	-	-	-	-	-
2	-	15.2	11.0	19.8	45.5	7.7	31.9	-2.5	10.8	-18.3	-	1.6
3	-	16.4	13.6	18.5	45.6	5.9	25.8	-3.0	14.3	-16.3	-	1.2
4 (c)	-	-	-	-	-	-	-	-	-	-	-	-
5	-	14.5	11.4	18.2	44.7	5.7	25.7	-2.6	17.9	-14.5	-	-0.3
6	-	15.3	10.6	17.9	44.8	5.7	26.8	-2.3	16.9	-15.8	-	-0.2
7	-	15.3	7.9	16.3	38.5	6.4	33.4	-2.7	17.1	-16.7	-	-0.8
	Nominal Solvent BP - 500°F											
8	-	15.0	8.9	19.1	43.6	6.1	32.2	-2.6	15.0	-16.4	-	-0.1
9	-	14.2	11.1	18.0	42.3	5.4	27.5	-3.2	18.0	-16.4	-	-0.9
10	-	14.2	8.0	20.1	42.4	6.3	31.3	-2.7	19.1	-16.5	-	-0.6
11	-	14.1	8.0	20.3	41.6	6.5	33.7	-2.8	17.2	-16.7	-	-0.6
12	-	13.8	8.5	18.7	41.7	5.4	30.2	-3.4	19.5	-16.6	-	-1.8
13	-	13.4	9.2	17.0	43.4	4.4	25.6	-4.0	21.4	-16.5	-	-2.2

(a) Volume percent yield based on heavy oil recovered.
(b) Initial product not representative, inadequate purge of start-up material.
(c) Product not analyzed due to operational upset.

Catalyst - American Cyanamid 1442B Cobalt-Molybdenum Unmodified

TABLE 5

LC-FINING PILOT PLANT OPERATION
HEAVY OIL PRODUCT ANALYSES
SRC-PREHYDROGENATED KOPPERS HEAVY RESIDUE CREOSOTE OIL

Period LCF-29	Reactor Temperature °F	Nitrogen Content Wt%	Hydrogen Content Wt%	Sulfur Content Wt%	Wt. Ratio of 850°F+ (Feed-Prod / Feed)	Gravity Rise °API(d)
	Nominal Solvent BP - 400°F+					
1 (a)	810	- (c)	-	-	-	-
2	↓	0.46 (61.3)	7.39		0.77	10.0
3		0.48 (59.7)	7.53		0.70	13.2
4 (b)		-	-	-	-	-
5		0.54 (54.6)	7.63		0.63	11.7
6		0.55 (53.8)	7.51		0.65	12.0
7		0.59 (50.4)	7.54	<0.06	0.65	11.7
	Nominal Solvent BP - 500°F+					
8	810	0.57 (55.8)	7.56	<0.06	0.71	14.2
9	↓	0.61 (52.7)	7.47		0.67	13.1
10		0.65 (49.6)	7.48	<0.06	0.63	13.4
11		0.60 (53.5)	7.51		0.67	13.4
12		0.70 (45.7)	7.50		0.63	12.0
13		0.78 (39.5)	7.20	<0.06	0.59	11.6

(a) Initial product not representative, inadequate purge of start-up material.
(b) Product not analyzed due to operational upset.
(c) Numbers in parentheses refer to percent denitrogenation.
(d) Gravity rise is the difference in the TLP gravity and the feed gravity.

Catalyst - American Cyanamid 1442B Cobalt-Molybdenum Unmodified

TABLE 6

EXPANDED BED HYDROPROCESSING OF SOLVENT REFINED COAL
EXTENSION RUNS
WORK SCHEDULE