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CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL
FOURTH QUARTERLY REPORT FOR THE PERIOD

1 JULY 1993 - 30 SEPTEMBER 1993

A.G. Comolli
E.S. Johanson
L.K. Lee
V.R. Pradhan
R.H. Stalzer

FINAL

WORK PERFORMED UNDER CONTRACT

DE-AC22-93PC92147

HYDROCARBON RESEARCH, INC.
100 OVERLOOK CENTER, SUITE 400
PRINCETON, NJ 08540

OCTOBER 1993

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ABSTRACT

This quarterly report covers the activities of Catalytic Multi-Stage Liquefaction of Coal during the Period July 1 - September 30, 1993, at Hydrocarbon Research, Inc. in Lawrenceville and Princeton, New Jersey. This DOE Contract Period is from December 8, 1992 to December 7, 1994.

The overall objective of this program is to produce liquid fuels from coal by direct liquefaction at a cost that is competitive with conventional fuels. Specifically, this continuous bench-scale program contains provisions to examine new ideas in areas such as: low temperature pretreatments, more effective catalysts, on-line hydrotreating, new coal feedstocks, other hydrogen sources, more concentrated coal feeds and other highly responsive process improvements while assessing the design and economics of the bench-scale results.

This quarterly report covers work on Laboratory Scale Studies, Continuous Bench-Scale Operations, Technical Assessment and Project Management.

SUMMARY

This report describes preliminary results obtained from the residual oil microautoclave reactivity tests and the third bench-scale operations (CMSL-03).

The main objective of Bench Run CMSL-03 was to evaluate the impact of using synthesis gas as reducing gas in the first stage of a two-stage liquefaction scheme. In combination with water, synthesis gas is known to be effective in dissolution of coal and removal of oxygen at relatively low thermal severity conditions. The use of synthesis gas, rather than high purity hydrogen, may lead to potential savings in both capital and operating costs through possible elimination of the external water-gas shift reactor and a smaller first stage reactor.

Using a mixture of syngas containing 25 V% of H_2 in CO, promoted by ammonium heptamolybdate and dimethyl disulfide, the overall process performance on liquefaction of Wyoming Black Thunder Mine coal was better than that of hydrogen alone. The coal conversion, 524°C⁺ residuum conversion and distillate yield was 2.5, 2.7 and 3.0 W% (maf coal) higher, respectively. Due to both the use of lower thermal severity and interstage separation of low boiling liquids, the overall hydrogen consumption was less than 7.5 W% vs 9 to 11 W% for previous bench runs with the same coal, but at higher process severity conditions.

Economic studies will be conducted to evaluate the impact of process improvement concepts demonstrated in the first three bench runs under this contract. These concepts include the use of bi-metal dispersed catalyst, higher coal loading (lower recycle solvent/coal ratio) and synthesis gas as reducing gas.

TASK 2 - LABORATORY SCALE STUDIES

RESIDUAL OIL ACTIVITY EVALUATION

The scoping Runs RE-01 to RE-06 of the Residual Oil Activity Program have been completed. The analyses of the products indicates that the presulfided catalyst prepared for the program was of characteristic activity for such catalyst, and that there is a close relation of residual oil conversion to reaction severity. Also, blending of the residual oil component with the coal liquefaction distillate to be used in the balance of the program was complete, and the blended mixture had residual oil conversion behavior very near that of the residual oil in the native liquid from which the residuum was obtained. The attached graph compares the residual conversion in the blend with that of the native liquid.

Catalyst

The catalyst used in these tests was Criterion C-317 catalyst that had been presulfided in a fixed bed using a TNPS/Tetralin mixture at temperature increasing from 230°C to 370°C over a 14 hour period. The resulting catalyst had the following composition:

Sulfur	6.15 W%
Carbon	8.24 W%
Hydrogen	1.65 W%
Nitrogen	0.03 W%
Molybdenum	7.54 W%
Nickel	1.64 W%

The sulfur content corresponds to 104% of that required for the formation of MoS_2 and NiS .

Blending

The 227-55-23A PFL used in these tests, and from which the 524°C⁺ (975°F⁺) component was obtained, was the product of CTSL Bench Unit operations on Black Thunder Mine coal, and has been used in a number of earlier Microautoclave Tests. It contains 32.0 W% 524°C⁺ (975°F⁺) by D-1160 distillation, and analyzed 29.64% residuum by TGA analysis.

The 524°C⁺ Residuum was blended at 177°C (350°F) with HRI 5868 Heavy coal liquefaction distillate derived from Illinois No. 6 coal obtained from Wilsonville, in the following proportions:

524°C ⁺ Residuum	9.0 Grams
HRI 5868	21.0 Grams
Blend Recovery	28.8 Grams

which should result in 30 W% residuum in the blend, without allowance for any residuum in the distillate blend. The TGA analysis of the resulting blend indicated 34.8 W% residuum. TGA analyses of the HRI 5868, which was also used in CC-14 under the last CTSI program, indicated 1.3 W% residuum. It is considered that results indicate essentially complete dissolution of the residuum component in the HRI 5868 solvent.

Results of Microautoclave Tests

Table 1 summarizes the results of four tests, at varying catalytic severities, with the native 227-55-23A PFL, and of two tests with the blend at two levels of catalytic severity. The attached figure plots (*Figure 1*) the degree of residual conversion against catalytic severity for the two feeds.

The residual oil conversion in the tests with the native PFL increased directly with increasing catalyst severity, although not exactly following a simple first order kinetic pattern in which the ratio of product and feed concentration would be linear on such a semi-log plot. Earlier work with the PFL had a similar relation and it has been concluded that the best kinetic fit of the data would be with a first order mechanism involving two species of different reactivity. This appears to be rational for the current data.

With the 30% blend, the results in terms, as presented in *Figure 1*, are very close to those obtained with the native PFL. At a common catalytic severity, 30 min*gm/gm, the apparent conversion was 49% with the PFL, and 46% with the blend. At this point it is considered that this deviation is possibly in the range of the experimental error.

TASK 3 - BENCH-SCALE STUDIES

RUN CMSL-03 (227-79) IMPACT OF SYNGAS ON LIQUEFACTION

Objectives and Background

The objective for this run was to evaluate the impact of using a syngas mixture (CO/H_2) as a first-stage reducing gas in a two-stage liquefaction of Black Thunder Mine coal.

The production of hydrogen constitutes one of the major operating cost components of a coal liquefaction process. Alternative sources of hydrogen such as synthesis gas, a mixture of carbon monoxide and hydrogen coming directly out of a gasifier or reformer, can potentially reduce the operating cost by 10-15%. It is known¹⁻³ that in the presence of an alkali salt, a mixture of CO/H_2 and water is very effective in solubilizing high oxygen-containing low rank coals at relatively mild severity conditions, usually below 400°C.

Scope of Work

The dissolution of Black Thunder Mine coal was evaluated using two different reducing gases (H_2 or CO/H_2) in a thermal-catalytic two-stage operations. The impact of syngas on liquefaction was evaluated in terms of first-stage product quality and overall process performance.

Summary

Under relatively mild liquefaction conditions, first and second stage temperature of 388 and 427°C respectively, the performance of using syngas vs hydrogen as reducing gas was compared. A mixture of syngas and water as reducing gas for the coal solubilization step (1st stage) of a two-stage operation resulted in an improved process performance in terms of coal and resid conversions, hydrogen utilization and distillate yields. In the presence of syngas and water, both the coal and resid conversions increased by 2.5 W%, while the distillate yield was 3 W% higher. The distillate yield of 64.6 W% maf coal is only 2.5 W% less than that previously obtained on the same coal but under catalytic-catalytic two-stage operations, with hydrogen as reducing gas in both stages, and carried out at higher reaction severity conditions.

The use of ammonium molybdate (1500 ppm Mo) and 1 W% dry coal of H_2S was proven to be effective in promoting the conversion of CO and H_2O to H_2 and CO_2 , the Water-Gas Shift reaction. The CO conversion was as high as 93% of the estimated equilibrium value.

Run Plan

This Bench unit run is a two-stage operation employing a first-stage fully backmixed slurry reactor, followed by a second-stage catalytic ebullated bed reactor. A simplified process flow diagram is shown in *Figure 2*. The volume of both reactors was equal. Coal was dissolved in the first-stage in the presence of syngas and water, while the primary coal liquids were further upgraded in the second-stage under typical hydroprocessing conditions. An interstage separator was installed to remove gases and light distillates generated from the first-stage and to recover any unreacted CO/H₂O. Fresh hydrogen was fed to the second hydroprocessing stage. Products from the second stage reactor were recovered using a hot separator (as separator overhead) and a continuous atmospheric still (CAS) which have Atmospheric Still Overheads (ASOH) and CAS Bottoms. The CAS Bottoms were pressure filtered in a batch mode into pressure filter liquid (PFL) and pressure filter cake (PFC). PFL was used as recycle solvent and as buffer liquids for the ebullating pump operations.

The run plan is given in *Table 2*. Four process conditions were achieved in this 15-day run. The actual operating conditions are shown in *Table 3*. Condition 1 extended from Periods 1 to 5 using pure hydrogen as reducing gas for both reaction stages. This condition served as a Base Case for comparing with the other three run conditions in which a mixture of synthesis gas containing 75 V% carbon monoxide was used in the first stage, while hydrogen was injected into the second stage reactor. With the exception of the first stage reducing gas, process conditions for Conditions 1 and 2 were similar: coal space velocity of 680 Kg dry/hr/M³ catalyst, first stage temperature of 388°C, and second stage temperature of 427°C. In Conditions 2 to 4, water was injected to the upstream of the preheater to obtain an overall water content of 40 W% of dry coal in the feed slurry. Condition 3 evaluated the impact of increasing the first stage temperature from 388 to 399°C, while Condition 4 explored the effect of higher coal space velocity (1.5 times higher than that during Conditions 1 through 3).

Tri-nonyl polysulfide (TNPS) and hydrogen sulfide was added to the first and second stage, respectively. The target sulfur addition rate to the first stage was 1 W% of dry coal and 3 W% to the second stage.

Coal

A Wyoming sub-bituminous coal, Black Thunder Mine, was used as the feedstock. The coal analyses of the feed (HRI-5828) are given in *Table 4*. This batch of coal was previously evaluated in CC-13, CC-15 and CMSL-01. This coal had about 25 W% moisture and was pulverized without further drying.

Start-up/Make-up Oil

The start-up/make-up oil composited of coal derived liquids generated from previous bench runs (Runs 227-76 and 227-78) using Illinois No. 6 coal. These liquids were pressure filter liquids from the shut down periods and recovered oils extracted from the

filter cake generated throughout these runs. The elemental analysis and boiling point distribution of the blended (L-794) is shown in *Table 5*.

Catalyst

Based on microautoclave studies reported in the last quarterly report, ammonium heptamolybdate was used to promote the conversion of CO in the presence of water to CO₂ and hydrogen (water-gas shift reaction) in the coal solubilization stage (first -stage). Ammonium heptamolybdate was added in the form of an aqueous solution to the slurry mix tank and was equivalent to 1500 ppm of Mo based on the dry coal rate.

The second-stage ebullated bed reactor was charged with fresh Shell 317 1/32" extrudate catalyst, presulfided during the start-up procedure.

PERFORMANCE AND RESULTS

The daily material balance varied between 95 and 99 W% with the most variation at the end of the run, as illustrated in *Figure 3*. The liquefaction performance during Run CMSL-03 is summarized in *Table 6*, while the qualities of SOH, ASOH, PFL and PFC are given in *Tables 7 through 12*.

Coal Conversion

When hydrogen was used in the first stage, Condition 1, coal conversion varied from 88.3 to 91.0 W%, as shown in *Figure 4*. Coal conversions in all other conditions, when syngas was used, were higher than that of Condition 1 suggesting syngas was more effective in breaking down the coal structure. Under similar thermal reaction severity coal conversion in Condition 2 was 1 to 2.5 W% higher than Condition 1. The highest coal conversion (92.4 W%) was observed in Condition 3, which was carried at the highest reaction severity, higher first temperature at the lower coal space velocity. Increasing the space velocity by 40 W% as in Condition 4 resulted in lower coal conversion (2 W% lower).

524°C Residuum Conversion

The residuum conversion, calculated by dividing the 524°C residuum yield by the value of maf coal feed, is a strong function of catalyst age. Due to the batchwise catalyst operations, residuum conversion value is expected to decline gradually as the run progresses. Residuum conversions varied between 85 to 90 W% maf coal, as shown in *Figure 5*. Despite the catalyst aging effect, the conversion levels increased from 87.2 to 89.9 W% when the first stage reducing gas was changed from hydrogen to syngas. The increase in first stage temperature (Condition 3) resulted in 3 W% decrease in residuum conversion, while the increase in coal space velocity in Condition 4 had a much lesser effect.

C₁-C₃ Gas Make

There was no significant difference in C₁-C₃ gas make with the type of reducing gas used and within the narrow range of reaction severity tested, as given in *Table 6*. Conditions 1 and 2 gave similar levels of gas make of 6.52-6.56 W% maf coal. These values are definitely much lower than previously obtained values (9 to 12 W%) with Black Thunder coal, primarily because of the lower first and second stage temperatures used in CMSL-03. This reduction in gas make will positively effect the hydrogen utilization factor as less hydrogen will be consumed to form light hydrocarbon gases. Also, the gas make varied according to the thermal reaction severity in Conditions 3 and 4. The increase in first stage temperature by 10°C caused the gas make to increase slightly by 0.2 W%, while 40 W% increase in coal space velocity resulted in a decline of 0.92 W%.

C₁-524°C Distillate Yield

Using the hydrogen in both stages (Condition 1) yielded 61.6 W% maf coal of distillates (refer to *Table 5*). Under similar conditions, the use of syngas (Condition 2) improved distillate yield by 3 W% to 64.6 W% maf coal. Although higher first stage temperature had a positive impact on coal conversion, the distillate yield was indeed 3 W% lower. The net result was a significant increase in residuum yield, as illustrated in *Figure 6*. Since the WGS reaction is slightly exothermic, and therefore should not be strongly affected by small variations in temperature (10°C), the negative impact in distillate yield suggesting retrogressive reactions may have taken place. It is possible that the residence time in the first reactor may be unnecessarily high for reactions between coal and CO and/or the nascent hydrogen. The distributions of distillable products confirmed the degrading of distillates going from Conditions 2 to 3, shown in *Figure 7*.

Inspections of Product

Analyses of gaseous, liquid and solid products are listed in *Tables 7 through 12*.

Gas analysis, shown in *Table 7*, revealed that the CO and CO₂ concentration in the first stage off-gas rose from 2.9 V% in Condition 1 to approximately 58.5 V% in Conditions 2 through 4 when the reducing gas was changed from hydrogen to synthesis gas.

Contrarily, the carbon oxides content of the second stage off-gas was less than 0.4 Vol% reflecting the high degree of separation in the interstage separator.

Tables 8 through 10 summarize analyses of the first and second Stage Separator Overheads, and Atmospheric Still Bottoms.

Except in Condition 4, the ratio of the first to second stage overheads was about 50/50. This ratio increased to 69/31 while the coal and gas space velocity were increased by 40% in Condition 4. Since the second stage overheads had been further hydrogenated

in the catalytic ebullated bed reactor, in all conditions, it had better overall properties than the first stage separator product. Its API gravity was generally lower (35.7-37.3 vs 18.9-26.9) and it contained less sulfur (0.011-0.018 W% vs 0.064-0.079 W%) and nitrogen (0.049-0.16 vs 0.059-0.34 W%), and more hydrogen (12.52-12.84 W% vs 10.76-11.74 W%).

Due to the better defined cut point with the atmospheric distillation column, atmospheric Still Overheads contained much lesser 343°C⁺ materials (less than 1 W%) than that of the Separator Overhead products (ranging from 24.0 to 45.7 W% in the first stage SOH and 9.9 to 12.4 W% in the second stage). The overall properties of ASOH did not vary much from condition to condition. The API gravity was around 30, while H/C ratio was around 1.68. The heteroatoms (sulfur and nitrogen) contents were slightly higher in ASOH than that of the second stage Separator Overheads, as illustrated in *Figures 8 and 9*.

Comparing the nitrogen content of the first and second stage products from Condition 1 with that of Conditions 2 and 3, the latter products contained 3 to 4 times less nitrogen suggesting that CO is more effective in cleavage of carbon-nitrogen bonds. This result provides additional incentive of substituting hydrogen with CO as reducing gas for coal dissolution in the first stage of a two stage liquefaction process.

The properties of pressure filter liquid (recycle solvent) for each operating condition are tabulated in *Table 11*. As the catalyst became aged through the course of the run, the content of 524°C⁺ resid and asphaltenic compounds in PFL increased, as illustrated in *Figures 10 and 11*, respectively. The 524°C⁺ content increased from 2.5 W% in Period 1 to 38.0 W% in Period 15. The concentration of the asphaltenic compounds (cyclohexane insolubles) rose about 5.5 times through the same period. The H/C ratio of PFL decreased correspondingly as the run progressed.

The ASTM ash and quinoline insoluble contents, as well as elemental analysis of the pressure filter cakes, are given in *Table 12*.

Inspections of TBP fractions, interstage reactor samples and recovered catalysts will be presented in the next quarterly report.

CO Conversion

CO interacts with coal either directly or indirectly via nascent hydrogen formed from the water-gas shift reaction. The WGS reaction:

is slightly exothermic, hence low temperature tends to shift the reaction towards the right.

The equilibrium CO conversion, defined as,

$$100 * \frac{\text{Wt. of CO in feed} - \text{Wt. of CO in off-gas}}{\text{Wt. of CO in feed}}$$

for a syngas feed containing 25 Vol% of H₂ is estimated to be 45.3% under process conditions prevailed in the first stage reactor. In calculating the amount of CO in the off-gas, a small correction was made to account for the amount of CO which may have been produced when hydrogen was used as reducing gas. The correction was based on the average CO production from Period 5.

Table 13 provides a summary of the amount of CO, CO₂ and H₂ that were entering and leaving the first and second stage reactors. CO conversions varied between 42 W% in Conditions 2 and 3, and 28 W% in Condition 4. The high range of the CO conversion is corresponding to 93.6% of the equilibrium value of 45.3 W%, while the low range value is 62.4%, suggesting ammonium heptamolydate/hydrogen sulfide catalytic system is very effective in promoting the WGS reaction.

Although it is impossible to separate the direct CO-coal interaction from that via the WGS reaction, a hydrogen equivalent utilization value is defined as the net disappearance of hydrogen and CO from the feed mixture. Conditions 2 and 3 had the highest equivalent hydrogen consumption as compared with Condition 1 (H₂ in both stages) and Condition 4, in which the coal space velocity was increased by 40 W%. With the exception of Condition 4, these values were in general higher than the H₂ consumption values obtained from the elemental balance. These differences give some indication of the direct interaction of CO with coal.

TASK 4 - TECHNICAL ASSESSMENT

Studies on economic impact of (1) substituting synthesis gas for hydrogen in coal liquefaction, (2) using dispersed catalyst instead of supported catalyst and (3) increasing coal concentration in reactor feed are being evaluated.

TASK 5 - PROJECT MANAGEMENT

Due to delays in the POC program, schedule for the next bench run is planned to be in January, 1994. The objectives of CMSL-04 are to determine the relative performance of CO/H₂O vs hydrogen in a fully-ebullated two-stage system and to determine the effect of an interstage separation on CTSL process performance.

The expected results are:

1. Equivalent yields with syngas or hydrogen but with better hydrogen efficiency for syngas operations,
2. A direct comparison of syngas/H₂O vs all hydrogen feed,
3. A more accurate cost comparison of syngas vs hydrogen and direct coupled vs interstage separation,
4. Hydrogenating data with interstage separation,
5. Possible data on the influence of feeding wet sub-bituminous coal.

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Table 1

Microautoclave Tests Evaluating Residual Oil Activities

Scoping Phase - Evaluation of Blend Preparation Technique

Catalyst - HRI 5902P, Criterion S-317, Presulfided with TNPS/Tetralin in Fixed Bed

Pressure - 2000 Psig H₂

Run RE-	Feed	Time, Min	Cat/Oil	Residuum, W% Charge	W% Product	Min*Cat/Oil	Cprod/Cfeed
1	227-55-23-PFL	30	1.00	29.64	15.17	30.0	0.512
2	227-55-23-PFL	30	0.25	29.64	22.90	7.5	0.773
3	227-55-23-PFL	60	1.00	29.64	11.74	60.0	0.396
4	227-55-23-PFL	60	0.25	29.64	20.96	15.0	0.707
5	30% 55-23 RES*	30	1.00	34.82	18.90	30.0	0.543
6	30% 55-23 RES*	30	0.25	34.82	28.06	7.5	0.806

* 30% 975°F* from 227-55-23 PFL Blended with 70% HRI 5868 Coal Liquefaction Distillate

TABLE 2

RUN PLAN FOR THE BENCH RUN CMSL-3 (227-79)

BLACK THUNDER COAL (25W% moisture)

1ST STAGE ADDITIVE: Ammonium Heptamolybdate, 1500 ppm Mo per dry coal feed.

2ND STAGE CATALYST: SHELL-317 Ni/Mo 1/32" Extrudates

Back Pressure: 2500 psig.

Condition	1	2	3	4
Periods	1-5	6-9	10-12	13-15
Reducing Gas (CO/H ₂)				
1st Stage	0/100	75/25	75/25	75/25
2nd Stage	0/100	0/100	0/100	0/100
Sulfur Additive				
TNPS (1st Stage)	1 S W% of dry coal.....			
H ₂ S (2nd Stage)	3 S W% of dry coal.....			
Space Velocity, (2nd stage)				
lb dry coal/hr/ft ³ cat.	44	44	44	67
Temperature, °C (°F)				
1st Stage	388 (730)	388 (730)	399 (750)	399 (750)
Interstage Separator	388 (730)	388 (730)	388 (730)	388 (730)
2nd Stage	427 (800)	427 (800)	427 (800)	427 (800)
Hot Separator	315 (600)	315 (600)	315 (600)	315 (600)
Atmospheric Still	288 (550)	288 (550)	288 (550)	288 (550)
Recycle Solvent/Coal Ratio	1.2	1.2	1.2	1.2

TABLE 3
OPERATING CONDITIONS FOR RUN CMSL-03 (227-79)

Condition	1	2	3	4
Period No.	7/11/93	7/15/93	7/18/93	7/21/93
Date (Start of Period)				
Reducing Gas (CO/H ₂)				
1st Stage	0/100	75/25	75/25	75/25
2nd Stage	0/100	0/100	0/100	0/100
2nd Stage Catalyst Age (kg Dry Coal/Kg cat.)	123	234	316	419
2nd Stage Space Velocity (lb dry coal/h/ft ³ catalyst)	42.0	43.1	42.4	59.0
(kg dry coal/h/M ³ catalyst)	674	692	680	947
System Pressure (MPa)	17.3	17.5	17.3	17.3
(Psig)	2490	2520	2500	2500
Temperature, °C				
1st Stage Reactor	388	388	399	399
2nd Stage Reactor	427	427	427	427
Recycle Solvent/dry Coal Ratio	1.20	1.20	1.09	1.30
Makeup oil/dry Coal Ratio	0	0	0.12	0.03
Additive, W% dry coal				
1st stage Sulfur	1.0	1.0	1.0	1.0
2nd stage Sulfur	2.8	2.7	1.7	0.4
1st stage Molybdenum	0.15	0.15	0.15	0.15

TABLE 4
ANALYSIS OF FEED COAL FOR CMSL-3

HRI No.	5828
Moisture Content	25.4
Proximate Analysis, W% Dry Basis	
Volatile Matter	43.37
Fixed Carbon	50.36
Ash	6.27
Ultimate Analysis, W% Dry Basis	
Carbon	70.4
Hydrogen	3.88
Sulfur	0.44
Nitrogen	0.87
Ash	6.27
Oxygen (by diff.)	18.14
H/C Ratio	0.66
SO ₃ -free Ash	5.59

TABLE 5**ANALYSIS OF START-UP SOLVENT FOR CMSL-3**

HRI No.	L-794
API Gravity	14
Elemental Analysis, W%	
Carbon	88.16
Hydrogen	10.48
Sulfur	0.144
Nitrogen	0.35
ASTM D-1160 Distillation, °F	
IBP	491
5 V%	569
10 V%	601
20 V%	641
30 V%	668
40 V%	700
50 V%	726
60 V%	755
70 V%	802
80 V%	880
90 V%	975
WEIGHT PERCENTS	
IBP-650°F	22.51
650-850°F	51.28
850-975°F	9.97
975°F+	15.42
LOSS	0.82
TOLUENE INSOLUBLES, W%	1.31

Table 6

PROCESS PERFORMANCE OF CMSL-3 (227-79)				
Condition	1	2	3	4
Period Number	5	9	12	15
Date (start of Period)	07/11/93	07/15/93	07/18/93	07/21/93
Hours of Run (end of Period)	112	208	280	344
II Stage Cat. Age, Kg Coal/Kg Cat	123	234	316	419
Stage 2 Coal Space Velocity				
Kg coal/hr/m3 catalyst	674	692	680	947
Total Material Recovery % (Gross)	98.75	97.22	99.14	95.04
First-Stage CO Conversion, % of Equi	N/A	93.6	93.6	62.4
PROCESS PERFORMANCE, W% maf Coal				
Coal Conversion	89.5	92	92.4	90.1
975 F+ Conversion	87.2	89.9	86.9	85.8
C4-975 F Distillate Yield	61.6	64.6	61.6	62
Hydrogen Consumption	7.82	7.73	7.14	6.97
Hydrodenitrogenation, W%	75.9	84.8	80.7	72.4
Hydrogen Efficiency, Kg Dist./Kg H2	7.88	8.35	8.63	8.89
ESTIMATED NORMALIZED YIELDS*,				
W% MAF COAL				
C1-C3 in Gases	6.52	6.56	6.76	5.84
C4-C7 in Gases	4.15	4.51	3.43	2.90
IBP-390 deg F	11.91	15.34	10.30	10.70
390-500 deg F	11.47	11.06	9.16	8.48
500-650 deg F	21.30	19.55	18.19	17.81
650-850 deg F	11.80	12.76	18.42	20.54
850-975 deg F	0.99	1.29	2.15	1.58
975 deg F+	2.31	2.07	5.48	4.29
Unconverted Coal	10.49	8.00	7.65	9.95
Water	17.09	16.14	14.47	14.12
CO	0.57	0.67	0.73	0.75
CO2	8.21	8.63	9.35	9.14
NH3	0.85	0.95	0.90	0.80
H2S	0.16	0.12	0.17	0.07
Hydrogen Consumption	7.82	7.73	7.14	6.97
* The Normalized Product Yields for Periods 9, 12, and 15 were Estimated by Isolating the Effects of the WGS Reaction from the CTSL Yield Structure (W% maf Coal)				

TABLE 7

Run Number	227-79	227-79	227-79	227-79
Condition	1	2	3	4
Period Number	5	9	12	15
Date (Start of Period)	07/11/93	07/15/93	07/18/93	07/21/93
Hours of Run (End of Period)	112.	208.	280.	352.
STAGE I VENT GAS, V%				
H2	94.03	37.93	37.95	37.78
CH4	0.44	0.00	0.00	0.00
C2H4	0.00	0.00	0.00	0.00
C2H6	0.23	0.19	0.27	0.26
C3H6	0.03	0.02	0.02	0.04
C3H8	0.14	0.14	0.19	0.18
C4H8	0.02	0.01	0.01	0.03
N-C4H10	0.05	0.04	0.07	0.09
I-C4H10	0.01	0.01	0.01	0.02
C5H10	0.00	0.00	0.00	0.00
N-C5H12	0.07	0.01	0.09	0.03
I-C5H12	0.01	0.01	0.03	0.02
METHYL-CYCLOPENTANE	0.00	0.00	0.00	0.00
CYCLOHEXANE	0.01	0.00	0.00	0.01
N-C6H14	0.00	0.00	0.01	0.01
2 + 3-METHYLPENTANE	0.00	0.00	0.00	0.00
C6-C7	0.02	0.01	0.01	0.01
CO	0.26	37.03	33.28	46.44
CO2	2.64	22.25	25.58	11.97
H2S	0.42	0.35	0.43	0.79
NITROGEN	1.24	1.68	1.72	2.23
OXYGEN	0.38	0.32	0.33	0.09
STAGE II VENT GAS, V%				
H2	79.43	72.01	80.19	85.06
CH4	1.67	2.57	2.67	2.47
C2H4	0.00	0.00	0.00	0.00
C2H6	0.78	0.73	0.75	0.61
C3H6	0.01	0.01	0.01	0.01
C3H8	0.70	0.67	0.66	0.46
C4H8	0.00	0.00	0.00	0.00
N-C4H10	0.31	0.33	0.30	0.21
I-C4H10	0.05	0.06	0.05	0.03
C5H10	0.00	0.00	0.00	0.00
N-C5H12	0.13	0.15	0.13	0.10
I-C5H12	0.05	0.09	0.05	0.06
METHYL-CYCLOPENTANE	0.00	0.00	0.00	0.00
CYCLOHEXANE	0.11	0.15	0.08	0.07
N-C6H14	0.06	0.06	0.03	0.02
2 + 3-METHYLPENTANE	0.01	0.01	0.00	0.00
C6-C7	0.04	0.09	0.03	0.03
CO	0.04	0.10	0.11	0.13
CO2	0.07	0.20	0.10	0.07
H2S	1.69	0.96	0.58	0.19
NITROGEN	14.39	21.40	13.94	10.34
OXYGEN	0.46	0.41	0.32	0.14

Table 8

COMPARISON OF FIRST AND SECOND STAGE SOH DURING CMSL-3				
Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
First Stage/Second Stage				
Weight/Weight Ratio	50/50	49.6/50.4	49.6/50.4	68.6/31.4
Gravity, API	26.9/37.0	22.9/37.2	21.4/37.3	18.9/35.7
IBP, deg F	185/141	182/119	171/120	187/148
FBP, deg F	778/734	791/745	821/743	821/763
ASTM D-86 Distillation, Composition				
W % IBP-350 deg F	14.0/41.3	11.9/45.6	11.5/45.9	9.6/44.0
W% 350-500 deg F	10.3/18.3	10.5/17.3	10.4/17.5	9.1/18.3
W% 500-650 deg F	51.6/29.8	45.6/25.6	41.0/25.3	35.2/24.8
W% 650 deg F+	24.0/9.9	31.5/10.7	36.6/10.7	45.7/12.4
W% Loss	0.1/0.7	0.5/0.8	0.5/0.6	0.4/0.5
Elemental Analysis				
Carbon, W%	85.56/85.96	86.0/87.25	86.08/86.96	86.33/86.97
Hydrogen, W%	11.74/12.52	11.37/12.84	11.11/12.74	10.76/12.67
Sulfur, W%	0.079/0.011	0.086/0.012	0.064/0.018	0.064/0.012
Nitrogen (Antek), W%	0.22/0.15	0.057/0.049	0.15/0.072	0.34/0.16
H/C RATIO	1.65/1.75	1.59/1.77	1.55/1.76	1.50/1.75

Table 9

CMSL-3: SEPARATOR OVERHEAD (SOH) INSPECTION				
Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
Gravity, API	32	30.7	26.7	24
IBP, deg F	141	119	120	148
FBP, deg F	778	791	821	821
ASTM D-86 Distillation, Composition				
W % IBP-350 deg F	27.6	30.1	23	19.9
W% 350-500 deg F	14.3	14.2	12.8	11.9
W% 500-650 deg F	40.7	34.8	35.8	32.1
W% 650 deg F+	17	20.3	28	35.7
W% Loss	0.4	0.6	0.6	0.4
Elemental Analysis				
Carbon, W%	85.76	86.63	86.52	86.46
Hydrogen, W%	12.13	12.11	11.93	11.33
Sulfur, W%	0.05	0.05	0.04	0.05
Nitrogen (Antek), W%	0.19	0.05	0.07	0.29
H/C RATIO	1.70	1.68	1.65	1.57

Table 10

CMSL-3: ATMOSPHERIC STILL OVERHEAD (ASOH) PROPERTIES				
Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
Gravity, API	31	30.3	29.4	29.5
IBP, deg F	266	246	247	247
FBP, deg F	585	580	575	589
ASTM D-86 Distillation, Composition				
W % IBP-350 deg F	15.3	20.3	19.5	20.9
W% 350-500 deg F	48	46.5	48.1	46.7
W% 500-650 deg F	36.7	31.9	32.1	32.4
W% 650 deg F+	0	0.9	0	0
W% Loss	0	0.4	0.3	0
Elemental Analysis				
Carbon, W%	86.29	86.99	86.35	87.42
Hydrogen, W%	12.1	12.21	12.14	12.24
Sulfur, W%	0.009	0.02	0.02	0.01
Nitrogen (Antek), W%	0.17	0.051	0.07	0.2
H/C RATIO	1.68	1.68	1.69	1.68

Table 11

CMSL-3: PROPERTIES OF THE PRESSURE FILTER LIQUID				
Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
Gravity, API	12.5	7.5	5.3	1.7
IBP, deg F	513	508	540	531
ASTM D-1160 Distillation, Composition				
W % IBP-650 deg F	18.07	12.87	12.28	8.57
W% 650-850 deg F	52.11	46.37	45.84	37.66
W% 850-975 deg F	8.8	15.42	11.7	14.31
W% 975 deg F+	20.61	24.56	29.79	39.17
W% Loss	0.41	0.78	0.39	0.29
Elemental Analysis				
Carbon, W%	89.22	89.35	89.7	89.14
Hydrogen, W%	10.45	9.6	9.34	8.75
Sulfur, W%	0.02	0.02	0.03	0.04
Nitrogen (Antek), W%	0.1	0.17	0.44	0.58
H/C RATIO	1.41	1.29	1.25	1.18
CCR, W% PFL	5.97	10.18	12.35	17.13
CYCLOHEXANE INSOLUBLES, W%	1.88	3.68	6.16	11.49
TOLUENE INSOLBLES, W%	0.18	0.38	0.66	1.17

Table 12

CMSL-3: INSPECTION OF THE PRESSURE FILTER CAKE				
Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
Elemental Analysis				
Carbon, W%	65.74	63.22	61.98	68.25
Hydrogen, W%	5.63	5.17	4.8	5.39
Sulfur, W%	1.54	1.56	1.24	1.12
Nitrogen (Antek), W%	0.63	0.52	0.59	0.74
H/C RATIO	1.03	0.98	0.93	0.95
Composition, W%				
Ash (Quinoline Filtration)	24.05	27.87	27.91	21.57
ASTM Ash, W%	23.13	26.49	27.61	20.91
S in Ash, W%	4.45	4.46	4.14	4.05
Unconverted Coal (Adj.)	36.42	31.81	31.99	30.36

Table 13

Carbon Oxides and Hydrogen Balance
(Values are in gmole)

Condition	Feed Gas				Product Gas				Difference (Product - Feed)			
	1	2	3	4	1	2	3	4	1	2	3	4
First Stage												
CO	0	630	630	983	2.3	365	365	707	2	-265	-265	-276
CO2	0	0	0	0	23.6	214	274	178	24	214	274	178
H2	1057	418	416	502	840	366	408	564	-217	-52	-8	62
Equivalent H2									-215	-317	-273	-214
Second Stage												
CO	0	0	0	0	0.32	0.74	0.8	1.35	0.32	0.74	0.80	1.35
CO2	0	0	0	0	0.56	1.48	0.73	0.73	0.56	1.48	0.73	0.73
H2	910	906	907	1278	632	535	587	877	-278	-371	-320	-401
Equivalent H2									-278	-370	-319	-400
Two Stage												
CO	0	630	630	983	2.64	365.7	365.8	707.1	3	-264	-264	-276
CO2	0	0	0	0	23.9	215.5	274.7	178.7	24	216	275	179
H2	1967	1324	1323	1780	1472	901	995	1441	-495	-423	-328	-339
Equivalent H2									-492	-687	-592	-615
(W% dry coal)									6.59	9.20	8.07	5.93
H2 Consumed*									7.39	7.30	6.74	6.19
(W% dry coal)												

* Based on elementally balance normalized yield calculations.

FIGURE 1

FIGURE 2

HRI SYNGAS - H₂ TWO-STAGE COAL LIQUEFACTION SCHEME

CMSL-3 : Average Daily Material Balance

FIGURE 3

FIGURE 4

CMSL-3 : 975 F+ RESID CONVERSIONS FOR WORK-UP PERIODS

FIGURE 5

CMSL-3 : 975 F+ RESIDUAL OIL YIELD FOR WORK-UP PERIODS

FIGURE 6

CMSL-03 Distillate Distribution

FIGURE 7

FIGURE 8

CMSL-03 Nitrogen Content

FIGURE 9

CMSL-03: Properties of Recycle Oil

API and 524C+

FIGURE 10

CMSL-3 : Asphaltene & Preasphaltene Contents of the Recycle Oil

FIGURE 11

END

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