RECENT ADVANCES IN COAL/HEAVY OIL CO-PROCESSING

R.H. STALZER, L.K. (THEO) LEE, J.L. HU
HYDROCARBON TECHNOLOGIES, INC.
1501 NEW YORK AVENUE
LAWRENCEVILLE, NEW JERSEY 08648

ABSTRACT

The first half of a 36 month U.S. DOE Bench Scale Co-Processing Program (Contract No. DE-AC22-94PC91036) with combined processing of coal and petroleum resid at Hydrocarbon Technologies, Inc. has been completed. This program is jointly funded by the U.S. Department of Energy, Mitsui SRC and Hydrocarbon Technologies, Inc. Experimental activities undertaken include three tests with HTI's two-stage continuous stirred tanks reactor system and two tests with HTI's two-stage bench scale ebullated-bed reactor system. The parameters investigated during these tests include: the addition of an aromatic solvent, the replacement of the first stage supported catalyst with a dispersed catalyst, an increase in space velocity, and low/high temperature staging of the reactors.

Two aromatic oils were used in this program, a coal derived oil (CDL) and FCC decanted oil, both show a similar small negative impact on residuum conversion and overall distillate yield and no impact on coal conversion. The hybrid catalyst system of dispersed and supported catalysts was very effective for co-processing of coal and oil. The use of a dispersed catalyst in the first stage and supported catalyst in the second stage exhibited many advantages over two-stage supported catalyst operation, due to the first stage having a larger thermal volume due to the absence of supported catalyst. This resulted in improved coal conversion, residuum conversion, and distillate yield as well as lower sulfur and nitrogen removal. The best results with this hybrid catalyst system were achieved using a combination of HTI's $FeOOH/SO_4$ dispersed catalyst with Molyvan-A (5000 ppm of Fe and 100 ppm of Mo). Low/high temperature staging, as opposed to operating the reactors at equal temperatures, results in an improvement in coal conversion, resid conversion and total distillate yield.

Introduction

Co-Processing refers to the combined processing of coal and petroleum-derived heavy oil feedstocks. The coal feedstocks used are those typically utilized in direct coal liquefaction: bituminous, subbituminous, and lignites. Petroleum-derived oil is typically a petroleum residuum, containing at least 70 W% material boiling above 525 ^{o}C. The combined coal and oil feedstocks are processed simultaneously with the dual objective of liquefying the coal and upgrading the petroleum-derived residuum to lower boiling (< 525 ^{o}C) premium products. HTI's investigation of the co-processing technology has included work performed in laboratory, bench and PDU scale operations.

The concept of co-processing technology is quite simple and a natural outgrowth of the work done with direct coal liquefaction. In direct coal liquefaction, a feed coal slurry is produced by mixing pulverized coal with a process-derived recycle oil. This slurry allows the coal feedstock to be pumped and preheated to reaction conditions. The concept of co-processing is to replace the process-derived recycle oil with an external, petroleum-derived residue which also needs to be upgraded. This eliminates costs and equipments associated with preparation and handling of the recycle slurry oil and should, therefore, reduce the cost of liquid fuels from coal.

Process Description
The continuous tests for this program were performed in two similar continuous reactor systems present at HTI. The smaller unit is a continuous stirred tank reactor system (CSTR) with specialized internals that increase this units approximation to a fully ebullated bed. The second unit is a bench scale unit (BSU) which utilizes fully ebullated reactors. Both units are essentially similar in terms of their process flow with some additions to the BSU due to the ebullation of the reactors. Since these two units have different thermal volume / catalytic volume ratio's, comparison of conditions will be made only between the same units. *Figure 1* shows the flow diagram for the Bench Scale Unit.

The coal/oil slurry is premixed offline and charged to a feed tank on a periodic basis. The slurry feed is pumped through both reactors with no interstage separation. The effluent from the second reactor is separated in a hot separator. The overhead from the hot separator is sent to a cold separator and separated into a vent gas stream and a separator overhead stream (SOH). The vent gases are metered, sampled, and sent to flare. For the CSTR the bottoms from the hot separator are collected and separated off-line by pressure filtrations into a pressure filter liquid (PFL) and a pressure filter cake (PFC). For the BSU the bottoms are sent to a continuous atmospheric still. The overhead from the atmospheric still (ASOH) and the SOH are combined and analyzed. The bottoms from the atmospheric still are separated offline in a batch vacuum distillation into a vacuum still overhead stream (VSOH) and a vacuum still bottoms stream (VSB). These streams are then analyzed. Part of the VSOH is used as a process oil in the buffer pumps for the first and second stage reactors. No other recycle of products was performed during these test.

Addition of an Aromatic Solvent
Two aromatic solvents were tested in this program for their impact on the co-processing of coal and oil. The first was a coal derived liquid (CDL) composited from the products of previous coal liquefaction test. The second was an FCC decant oil. These two oils replaced 25 W% of the feed oil for their tests. These oils have a much lower $524+^{o}C$ resid content than the Hondo oil does, 20.08 W% for the FCC oil and 17.01 W% for the CDL as compared to 81.42 W% for the Hondo oil.

The operating conditions for these two test compare very well with the operating conditions for the BSU baseline test. Relative space velocity (actual space velocity / reference space velocity), relative reactor temperatures (actual temperature - reference temperature) and overall relative

reactor severity (actual severity / reference severity) are virtually identical. The only real difference among these three conditions is the age of the catalyst, and even this is similar enough to allow conclusions to be drawn. Both the CDL and the FCC oil show a slight shift in the oil fractions yields from the naphtha fraction, C_4-177 $^{\circ}$C, to the heavy distillate fraction, 343-524 $^{\circ}$C. The impact of these aromatic oils on coal conversion is slightly positive, increasing from 93.4 W% to 93.7 W% for the CDL and 94.3 W% for the FCC oil; however, their impact on the 524+ $^{\circ}$C resid conversion is slightly negative, from 88.6 W% to 87.1 W% for the CDL and 87.4 W% for the FCC oil. The C_4-524 $^{\circ}$C distillate yield is essentially the same with or without either of the supplementary aromatic oils. Desulfurization shows no significant effect from the aromatic oils. Denitrogenation shows an improvement with the the aromatic oils, increasing from 51.8 W% to 57.1 W% for the CDL and to 58.1 W% for the FCC oil.

Replacement of the First Stage Supported Catalyst with a Dispersed Catalyst
The use of a dispersed catalyst was tested in the CSTR unit. For the baseline condition both reactors were charged with an equal quantity of catalyst. For the dispersed condition the second reactor was charged with a normal quantity of catalyst while the first reactor was left empty. A combination of dispered catalysts, HTI's sulfated iron catalyst at 5000 wppm iron and Molyvan-A at 100 wppm Mo, were then fed to the first stage along with the coal/oil slurry. As shown in *Table 1* these two conditions were performed at similar space velocity and catalyst age. The reactor temperatures were slightly higher for the baseline test and this results in a slightly higher overall severity.

The disperesed condition resulted in a much higher coal conversion, 94.42 W% compared to 87.0 W%, due to Reactor 1 having a larger thermal volume from the absence of a supported catalyst. The resid conversion was also slightly higher for the dispersed condition, 81.5 W% compared to 80.4 W%. This resulted in the dispersed condition having a higher distillate yield, 75.4 W% compared to 72.2 W%, and a higher hydrogen consumption, 6.56 W% compared to 5.89 W%. The supported catalyst test had a higher level of both sulfur removal, 82.7 W% compared to 81.7 W%, and nitrogen removal, 39.0 W% compared to 9.4 W%. The oil fraction yields for these two conditions shows that the supported catalyst has the better selectivity towards the lighter fractions. While the larger thermal volume in the first stage of the dispersed catalyst condition gives better conversion and total yields, these yields are shifted more towards the heavy fractions.

Low/High Temperature Staging
The use of low/high temperature staging was tested in the BSU. In typical coal/oil co-proceesing both reactors are maintained at the same temperature. For this condition the first stage temperature was lowered by 16.1 $^{\circ}$C and the second stage temperature was raised by 17.2 $^{\circ}$C, as compared to the baseline condition. The space velocity was maintained the same and the reltive severity was also the same. The catalyst age for the low/high temperature staging conditions was less than for the baseline condition, 441 gm feed / gm catalyst as compared to 672 gm feed / gm catalyst.

The oil fraction yields show a shift of the naphtha and heavy distillate fractions towards the middle distillate fraction for the low/high temperature condition. Temperature staging also results in better overall process performance as the coal conversion increases from 93.4 to 95.0 W%, resid conversion increases from 88.6 to 90.6 W% and C_4-524 ^{o}C distillate yield increases slightly from 79.1 to 79.9 W%. Heteratom removal is the same for both conditions. Hydrogen consumption also remains unchanged.

Conclusions
The two aromatic oils tested, a coal derived liquid and the FCC decanted oil, show no substantial impact on the process peformance and a slight negative impact on the oil fractions yield structure. These results are despite both of these conditions having a slightly lower catalyst age than the baseline condition.

Use of a dispersed catalyst to replace the first stage supported catalyst results in a larger thermal volume for the first stage reactor. This increase in thermal volume increases coal conversion, resid conversion, and distillate yield while the absence of a supported catalyst decreases heteroatom removal. The distillate yield is also shifted more towards the heavy fractions for the dispersed catalyst as compared to using supported catalyst in both stages.

Low high temperature staging results in an improvement in coal conversion, resid conversion, and distillate yield with no impact on heteroatom removal. It also shift the distribution of oil fractions from the naphtha and heavy distillate fractions towards the middle distillate fraction.

Plans for Future Work
Future continuous tests for this program will explore alternate supported catalysts and dispersed catalysts in either a two stage catalytic/catalytic process or in a thermal/catalytic process using the dispersed catalyst in the first stage. Other test being planned involve the use of an interstage separator to recover the gas and part of the light liquid products produced in the first stage and only feed the heavier products to the second stage. This concentrates the heavier fractions in the second stage and also allows for a higher hydrogen partial pressure. Finally the effect of on-line hydrotreating of the products will be examined.

TABLE 1: COMPARISON OF CONDITIONS

Test Type	Baseline	Baseline	Aromatic CDL	Aromatic FCC Oil	Dispersed Catalyst	Low/High Temp.
Unit	CSTR	BSU	BSU	BSU	CSTR	BSU
CONDITION PARAMETERS						
Catalyst Age (wt/wt)	812	672	439	551	856	441
Relative Space Vel.	1.46	1.43	1.46	1.44	1.58	1.51
Relative Temp K-1,^{o}C	5.5	-3.33	-2.22	-3.33	0.2	-19.4
Relative Temp K-2,^{o}C	2.6	-2.78	-2.50	-1.94	0.9	+14.4
Relative Severity	1.26	0.90	0.91	0.91	0.97	0.88
NORMALIZED YIELDS, W% MAF FRESH FEED						
C_1-C_3	7.83	6.28	6.86	7.00	6.68	6.43
C_4-177 ^{o}C (Naphtha)	15.3	17.84	14.69	12.93	13.81	15.53
177-343 ^{o}C (Mid Dist.)	29.28	32.31	33.27	34.01	30.54	37.81
343-524 ^{o}C (Heavy Dist.)	27.6	28.92	31.04	31.72	31.09	26.56
524+ ^{o}C	13.34	7.79	7.82	7.84	14.69	6.54
Unconverted Coal	3.71	2.16	2.04	1.85	1.43	1.62
Water	4.96	5.14	5.14	5.15	5.01	5.91
CO_x	0.82	0.19	0.26	0.25	0.82	0.22
NH_3	0.36	0.67	0.64	0.66	0.09	0.66
H_2S	2.68	3.21	2.77	3.23	2.39	3.18
PROCESS PERFORMANCE, W% MAF FRESH FEED						
H_2 Consumption	5.89	4.45	4.47	4.59	6.56	4.46
Coal Conversion	87.0	93.4	93.7	94.3	94.4	95.0
524+ ^{o}C Conversion	80.4	88.6	87.1	87.4	81.5	90.6
C_4-524 ^{o}C Distillate Yld	72.2	79.1	79.0	78.7	75.4	79.9
Desulfurization	82.7	95.9	96.0	95.7	81.7	95.1
Denitrogenation	39.0	51.8	57.1	58.1	9.4	51.9