

A STUDY OF DISPERSED IRON-BASED ADDITIVES IN COAL LIQUEFACTION

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INTRODUCTION

Iron-based additives have been extensively (1-5) evaluated for their catalytic behavior in direct coal liquefaction. The catalytic activity of these iron-based additives depends not only on their chemical composition but also on their effective contact area with the coal/solvent mixture. Various preparation techniques have been investigated (6) to produce nanoscale iron-based catalyst precursors to enhance its activities.

The activity of two different iron-based additives for liquefying a Wyoming sub-bituminous coal, Black Thunder mine coal, was evaluated in a two-stage, bench scale continuous flow unit. One of these additives, iron oxide, was introduced in form of a powder to the slurry feeding system, while the second additive was impregnated on the coal matrix using an incipient wetness technique developed at the Pittsburgh Energy Technology Center.

This paper describes the findings of the bench scale evaluations (Runs CC-7 and CC-15) which were intended to examine the relative effects of catalyst type and reactor configuration (e.g. Catalytic/Thermal or Thermal/Catalyst).

EXPERIMENTAL

Coal Preparation

Black Thunder mine coal was used as feed. Analyses of the feed coals are shown in *Table 1*. The feed coals (HRI-5630 and 5828) were screened to -70 mesh and dried under nitrogen to obtain moisture content between 5-10 W% for tests when the iron additive was added in form of a powder. The impregnated coal feed (L-780) was dried to 5 to 12 W% moisture content.

The PETC incipient wetness technique involves the contact of coal with a solution of iron salt followed by precipitation (impregnation) of hydrated iron oxide on accessible coal surfaces.

The iron content of the untreated coal was 0.2 W% (dry basis), while that of the impregnated coal feed contained 0.57 to 0.65 W% of iron.

Start-up/Make-up Solvent

Each run was start-up with coal derived distillates. The start-up oil used in CC-7 was HRI-5648 and was derived from Wilsonville using Illinois coal as feed. This oil was also used as make-up oil in the early part of the run to supplement the process-derived oil for the recycle oil requirements. In the later part of the run, the make-up oil, if required, was made up from the accumulated process-derived oil. Run CC-15 employed filtered process derived liquids stored in Tank 4 from a recent HRI PDU run (Run 260-03) as start-up and make-up oils. Analyses of these solvents are summarized in *Table 2*.

Additives

In Run CC-7 the iron-based additive was in an oxide form. This additive was labelled as magnetic pigment and was purchased from Wright Industries (Brooklyn, New York). Analyses of the iron additive are shown in *Table 3*. In Run CC-15, iron was added as hydrated oxide and was impregnated on the coal matrix.

Liquefaction Tests

The liquefaction tests were carried out in a 20 Kg/day continuous flow unit employing two backmixed reactors, as shown *Figure 1*. An additional pretreater was added to the system in Run CC-15 for activating the iron catalyst precursor prior to the thermal stage (first stage).

Each run usually starts with coal derived distillates from Wilsonville or HRI's PDU. The unit is then brought to equilibrium by the recycling of pressure filter liquids to the coal slurry preparation section on a bi-hourly basis. Mass balance is performed every 8 or 12 hours and a daily average is then reported. Each of the conditions tested is of minimum 3 days duration to ensure the validity of the data point.

Due to the low inherent sulfur content of Black Thunder mine coal, sulfur was added in form of liquefied hydrogen sulfide to ensure proper sulfidation of the catalyst precursor as well as maintaining the supported catalyst in a sulfided state.

RESULTS AND DISCUSSION

Coal conversion is normally calculated from the ash-to-solid (quinoline insoluble) ratio of product and comparing it with the feed coal. This assumes that non-ash portion of the product is organic unconverted coal. This is not entirely true as asking transforms mineral matter into other inorganic form. In dealing with sub-bituminous coal, HRI usually considers ash on a SO₂-free basis to discount the sulfur capture by lime that might occur during asking. When additives are introduced, calculation of true coal conversion can be uncertain and imprecise. If additive contains iron as in this case, it captures sulfur from coal or coal-derived liquid or from hydrogen sulfide.

If the liquefaction product containing this sulfided iron species is ashed, the inorganic material undergoes transformation. For example, if the product contains FeS, it could be oxidized to Fe₂O₃ or some other oxide. If it is converted to Fe₂O₃, it would lose weight during asking. As a result, the amount of the mineral matter in the product would be underestimated and that of the organic matter overestimated. Calculated coal conversion would then be lower than the real conversion.

A true or more accurate value of coal conversion could be arrived at if the chemical nature of the iron species in the product and in the ashed form is known. Since this information was lacking, it was assumed here that the iron species in the liquefaction product was present as pyrrhotite Fe_(1-x)S with x of 0.15 and that it was converted to Fe₂O₃ during asking.

Dispersed Iron Oxide

Run CC-7 was conducted to study the effect of reactor configuration in two-stage liquefaction: catalytic/thermal vs thermal/catalytic modes of operation.

The supported catalyst charged to the unit was a blend of fresh Shell 317 catalyst (12.5 W%) and the recovered catalyst (87.5 W%) from an earlier run (CC-5). The latter was obtained from the first stage of a run which also used Black Thunder mine coal. Table 4 summarizes the run plan and results. The catalytic stage temperature was maintained at 399°C. The temperature of the thermal stage was varied from 440-448°C and space velocity varied from 44-67 lb/h/ft³ cat. The additive used in this run was iron oxide, the magnetic pigment supplied by Wright Industries. The rates of the additive and hydrogen sulfide were about 5.5 and 3.8 W%.

Figure 2 and 3 compares the performance of different reactor configurations. In catalytic/thermal mode of operation, increasing the thermal stage temperature from 440°C (Condition 1) to 448°C (Condition 2) increased C₁-524°C distillate yield (2.0 W% maf coal) as increased coal and residuum conversions outpaced increase in gas yield. With the thermal stage at 448°C, catalytic/thermal configuration gave higher coal and residuum conversions relative to thermal/catalytic configuration (Condition 3). However, the product quality was superior in the latter case.

Compared to catalytic/catalytic mode (Run CC-4 Condition 2), thermal/catalytic and catalytic/thermal configurations gave slightly higher coal conversion, as shown in Table 4. Typically, conversion of sub-bituminous coals is quite sensitive to residence time which was less in the catalytic/catalytic mode of operation due to catalyst hold-up in the reactor. However, residuum conversion and distillate yield were higher in catalytic/catalytic configuration. The process performance in this configuration was superior with less gas yield, lighter distillate slate. Hydrogen consumption was higher, however, it was used efficiently to produce a better quality product.

Iron Impregnated Coal (CC-15)

The performance of iron impregnated (about 5000 ppm Fe) Black Thunder mine coal was measured in a thermal/catalytic mode of operation. The second stage contained

a fresh charge of Criterion 317 Ni/Mo catalyst. The catalyst was presulfided in situ by holding the catalyst at various temperature levels during the start-up period under a continuous stream of hydrogen sulfide and start-up oil.

The iron catalyst precursor(FeOOH) was activated with H₂S at 275°C (Condition 1) and 290°C (Conditions 2 to 4). The test was conducted using constant conditions of space velocity of about 42.5 lb coal/h/ft³ (supported catalyst), and temperatures of 427°C and 413°C for the thermal and the catalytic reactors, respectively. The run plan and results are given in *Table 5*.

The yield of C₁-C₃ gas remained constant around 10.5 W% maf coal reflecting the relatively stable operation. Although the results were masked by the continuous deactivation of the supported catalyst throughout the course of the run, the process performance in term of coal conversion, 524°C conversion, and C₄-524°C distillate yield were higher in tests with iron impregnated coal as compared with the untreated coal (Condition 3).

In the presence of iron additive, coal conversions varied slightly between 92.7 and 93.1 W% maf coal (Conditions 1, 2 and 4). In Condition 3, no dispersed catalyst was used. The coal conversion dropped by 2.7 W% to 90.0 W%. The decrease in residuum conversion (3.7 W%) and distillate yield (7.7 W%) were more noticeable because these performances were more sensitive to catalyst activity. Iron additive was reintroduced in Condition 4, repeat of Condition 2. The coal conversion increased back up to 92.7 W%, while the residuum conversion and distillate yield rebound to a level as projected assuming linear deactivation in catalyst activity. Interstage samples show that all coal conversion occurred in the thermal stage (at 427°C). Similar trend was observed on the effect of iron additive on coal conversion in the interstage sample, i.e. 3.7 to 4.1 W% lower when no additive was used.

The iron impregnated coal contained substantially higher nitrogen content (L-780, 2.64 W%) than the untreated coal (HRI-5828, 0.95 W%). This was probably due to the sorption of ammonium nitrate on the coal matrix during the precipitation procedure. As a result, both the interstage and the two-stage product liquids exhibited higher nitrogen content when iron impregnated coal was used, as shown in *Table 4*.

CONCLUSION

Black Thunder mine coal was liquefied in thermal/catalytic and catalytic/thermal modes of operation to study effect of iron additive on process performance. With the limited data and variations in catalyst age, in the thermal/catalytic mode of operation, it seems that the distillate yield with 5000 ppm of finely dispersed iron (on the coal matrix) was 66.0 W% and was equivalent to, if not slight more higher, than that with 5.7 W% of magnetic pigment (Run CC-7 Condition 5). However, the selectivity toward lighter product was higher in the case of magnetic pigment reflecting the higher overall reaction severity used in the test.

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REFERENCE

Gary D. and Given, E.N., "Pyrite Catalysis in Coal Liquefaction", *Ind. Eng. Chem. Process Des. Dev.*, Vol 21, pp. 113-117, 1982.

Stohl, F.V. :The Effect of Iron Sulfide Surface Area Variations on Coal Liquefaction", *Fuel*, Vol. 62, pp. 69-72, 1983.

Southern Electric International, Inc., Technical Progress Report, "Run 258 with Subbituminous Coal", DOE Contract No. DE-AC22-82PC50041.

Southern Electric International, Inc., Technical Progress Report, "Run 260 with Black Thunder Mine Subbituminous Coal", DOE Contract No. DE-AC22-90PC90033, January 1992.

Hydrocarbon Research, Inc., Quarterly Reports No. 5, 6 and 11, DOE Contract No. DE-AC22-88PC-88818.

Cugini, A.V., Utz, R.G., Krastman, D. and Hickey, R.F. "Effect of Activation Conditions on Dispersed Iron Catalysts in Coal Liquefaction.", *Preprints, Fuel Chemistry Division, ACS Vol. 36, No. 1, pp. 91-102, 1991.*

TABLE 1
FEED COAL ANALYSES

HRI No.	<u>5630</u>	<u>5828</u>	<u>L-780</u>
Moisture Content, W%	6-9	8.41	8.81
Ash Content, W% (mf)	6.69	6.95	7.15
SO ₃ -free, W% (mf)	5.74	5.71	6.03
Ultimate Analysis, W% (maf)			
Carbon	71.90	72.51	72.38
Hydrogen	4.91	4.08	4.31
Sulfur	0.38	0.51	0.49
Nitrogen	1.04	0.95	2.64
Oxygen (by diff.)	21.77	21.95	20.18
Iron Content, W% (mf)	n/a	0.20	0.57-0.65

TABLE 2
ANALYSES OF START-UP SOLVENT

HRI No.	5648	L-769
API Gravity	n/a	10.1
Elemental Analysis, W%		
Carbon	90.14	88.95
Hydrogen	9.85	10.08
Sulfur	0.13	0.06
Nitrogen	0.37	0.34
ASTM D-1160 Distillation,		
IBP	391	318
5 V%	413	339
10 V%	426	345
20 V%	432	358
30 V%	443	366
40 V%	450	376
50 V%	459	385
60 V%	469	398
70 V%	476	416
80 V%	483	449
90 V%	499	479
95 V%	511	517
FBP	542	524*

- Boiling point at 96 V%

TABLE 3
ANALYSES OF IRON ADDITIVES

<u>Magnetic Pigment</u>	
Moisture, W%	0.02
Sulfur, W%	0.003
Iron, W%	61.22
Forms of Iron, W%	
Fe	0.05
FeO	25.14
Fe ₂ O ₃	70.42

TABLE 4
Evaluation of Dispersed Iron Oxide (CC-7)
Catalyst: Shell 317 Ni/Mo Coal: Black Thunder Mine

Run No.	7	7	7	7	7	4
Condition	1	2	3	4	5	2
Mode						
1st Stage	Cat.	Cat.	Therm.	Therm.	Therm.	Cat.
2nd Stage	Therm.	Therm.	Cat.	Cat.	Cat.	Cat.
Temperature, °C						
1st Stage	398	399	448	448	441	399
2nd Stage	441	448	399	399	399	441
Catalyst Age, lb coal/lb cat.						
1st Stage	658	801	—	—	—	717
2nd Stage	—	—	974	1101	1107	1088
Space Velocity						
lb coal/h/ft ₃ cat.	66.9	65.6	68.3	45.7	43.8	68.9
Additive Rate, W% mf coal	5.5	5.3	5.5	5.4	5.7	5.2
H ₂ S Rate, W% mf coal	4.5	4.7	4.3	6.3	5.4	1.8
Performance, W% maf coal						
C ₁ -C ₃	9.96	12.01	4.81	17.41	14.10	8.81
H ₂ Used	6.73	7.43	8.07	8.31	8.28	8.60
C ₄ -524 °C	58.5	60.5	59.4	55.8	59.0	64.6
Coal Conversion	90.4	93.3	91.3	92.4	90.8	88.1
524 °C* Conv.	85.5	89.0	89.1	87.7	87.4	87.5
HDN	57.4	55.1	71.2	69.0	53.9	76.9

TABLE 5
Evaluation of FeOOH Impregnated Coal (CC-15)
Catalyst: Shell 317 Ni/Mo Coal: Black Thunder Mine

Condition	1	2	3	4
Mode				
1st Stage	Therm.	Therm.	Therm.	Therm.
2nd Stage	Cat.	Cat.	Cat.	Cat.
Temperature, °C				
Pretreating	275	298	297	297
1st Stage	426	429	427	427
2nd Stage	413	412	413	412
Catalyst Age, lb coal/lb cat.				
2nd Stage	143	227	314	403
Space Velocity				
lb coal/h/ft ³ cat.	42.3	41.7	43.7	42.7
Additive Rate, W% mf coal	0.4	0.4	None	0.4
H ₂ S Rate, W% mf coal	3.5	3.6	3.2	3.0
<u>Performance, W% maf coal</u>				
C ₁ -C ₃	10.55	10.78	10.35	10.49
H ₂ Used	9.26	9.0	8.14	8.34
C ₄ -524 °C	66.1	64.1	56.4	60.2
Coal Conversion				
1st Stage	91.1	91.1	87.0	90.7
2nd Stage	93.1	92.7	90.0	92.7
524 °C ⁺ Conv.	89.1	87.7	84.0	85.3
HDN	90.0	87.1	66.6	82.6

FIGURE 1 - HRI TWO STAGE EBULLATED BED BENCH SCALE UNIT

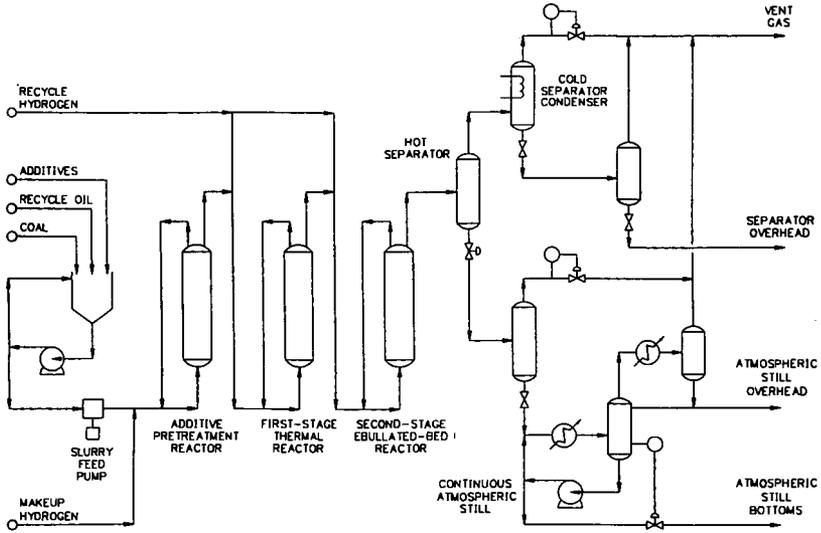
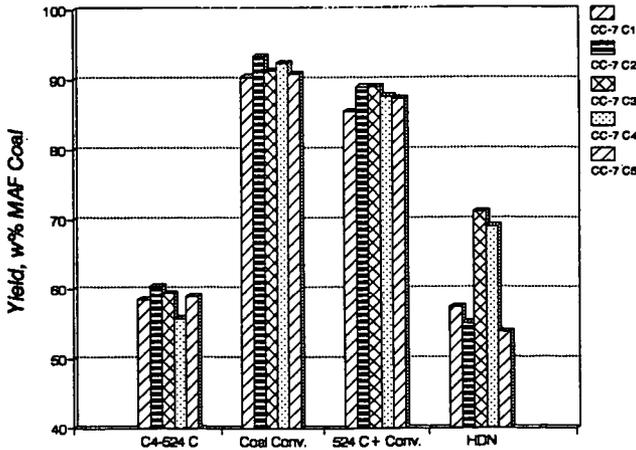


FIGURE 2 - PROCESS PERFORMANCE OF IRON OXIDE AS ADDITIVE: CATALYTIC/THERMAL vs THERMAL/CATALYTIC



**FIGURE 3 - PROCESS PERFORMANCE OF IRON OXIDE AS ADDITIVE:
GAS YIELD AND HYDROGEN CONSUMPTION**

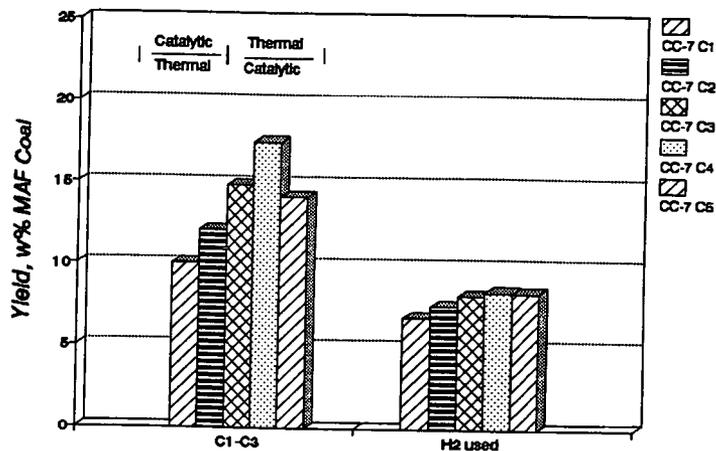


FIGURE 4 - NITROGEN CONTENT OF SELECTED INTERSTAGE SAMPLES

