TITLE : REFINING AND END USE STUDY OF COAL LIQUIDS I — PILOT PLANT STUDIES

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1. Abstract

The Office of Fossil Energy, Pittsburgh Energy Technology Center is examining the ways in which coal liquids may best be integrated into the refinery of the 2000 - 2015 time frame and what performance and emission properties will prevail among the slate of fuels produced. The study consists of a Basic Program administered by Bechtel Group, Inc. to build a linear programming refinery model and provide processing and fuel properties data through subcontractors Southwest Research Institute, Amoco Oil R&D, and M.W. Kellogg Company. The model will be used in an Option 1 to devise a slate of test fuels meeting advanced specifications, which will be produced and tested for physical ASTM-type properties, engine performance, and vehicle emissions. Three coal liquids will be included: a direct liquid from bituminous coal, another from subbituminous, and a Fischer-Tropsch indirect liquefaction product. This paper reports the work to date on fractions of the first direct liquid including naphtha hydrotreating, heavy distillate hydrotreating, FCC of the heavy distillate hydrotreater products. Also reported are the first stages of work on the indirect liquefaction wax including feed preparation and FCC tests of blends with petroleum FCC feed.

2. Project Overview and Objective

What is the best way to integrate coal liquids into the refining industry of the future (2000 - 2017 time frame)? The answer to this question, the supporting data, and related fuel utilization issues are the subject of *Refining and End Use Study of Coal Liquids*. In sequence with the companion paper, " - II, Linear Programming Analysis", this paper will review the work to date in the project. With Bechtel Group as prime contractor managing the project and performing the refinery modeling, Southwest Research Institute, Amoco Oil R & D, and M.W. Kellogg Company are studying the unit operations uniquely affected by introducing a yet-to-be-determined optimum concentration of coal liquids in the crude stream of a modern refinery. Further project overview is provided in Paper II.

Both direct and indirect liquids are being studied. Feed and product properties, processing requirements & behavior, refining economics, and fuel performance and emissions are objectives of the project. An overview of the work is given in Figure 1. The arrows represent the flow of materials and information through the stages of the work. The optimization of concentrations and product recipes is discussed in Paper II, while the individual unit operations studied to date under the heading of "processing" in Figure 1 are discussed here.

3. Refining Scheme

The coal liquids, direct or indirect, are produced outside the petroleum refinery. The approach adopted in the *End Use Study* is to make the least perturbation of the existing refining process by mixing the coal feedstocks with the crude oil entering the refinery; except that for indirect liquids, maximum benefit of their paraffinic nature would be made by distilling them separately and sending appropriate boiling range cuts to individual refinery units most suited for them.

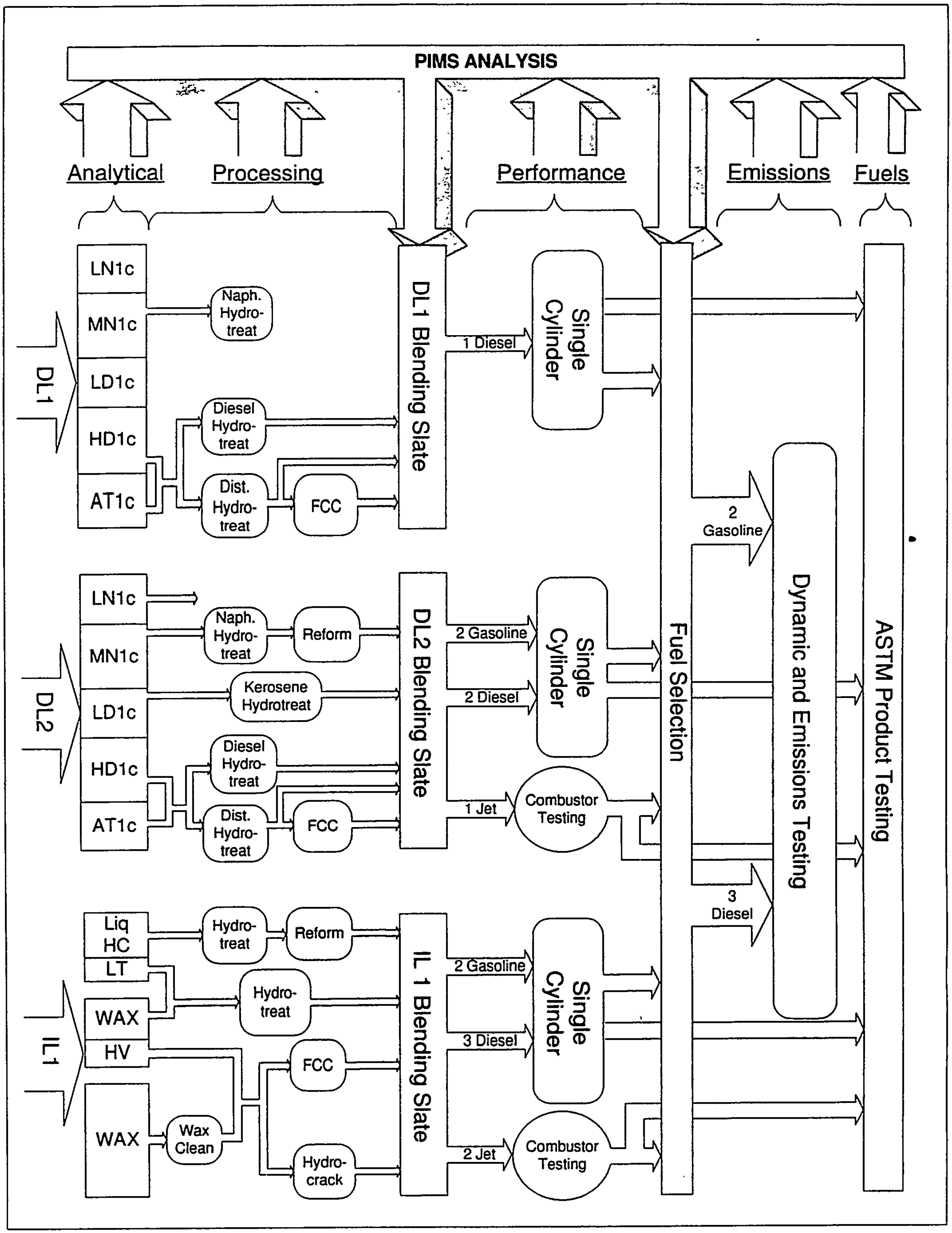

Figure 1. Overview of End-Use Study

Figure 2 shows the refining scheme selected for the study. Only proven technologies were considered for inclusion in the Bechtel refinery model and then only units needed for the slate of fuels being considered in the future time frame: two grades of conventional and reformulated gasolines, three grades of diesel (& low aromatics diesel for the IL1), jet A. Other refinery products (fuel oil, asphalt, gases, etc.) are considered in the computer modeling to satisfy the mass balance.

In the sections below, the hydrogenation of the naphtha stream for reforming, hydrogenation of the heavy distillate for FCC feed and product blending, fluid catalytic cracking of the heavy distillate, and indirect wax processing to date will be discussed. The work thus far concerns coal feeds DL1 and IL1 described below.

4. Direct Liquid Feedstock

The coal liquid feedstock, DL1, was produced by HRI, Inc. in the DOE Close Coupled, Two-Stage PDU plant during Proof of Concept Run 1 from Illinois #6 coal, a bituminous feed. Operations were arranged to recycle 750°F$^+$ material to extinction and to omit the in-line hydrotreating. At Southwest Research Institute, the full-boiling material was distilled into four fractions: light naphtha, medium naphtha, light distillate and heavy distillate according to the atmospheric split shown on Figure 2. The 7% atmospheric bottoms was allowed to remain with the heavy distillate as a matter of practicality. In the future, a subbituminous feed will liquefied for study in the program as DL2.

5. Naphtha Hydrotreating

Naphtha hydrotreating is an integral part of the preparation of the refinery streams blended into gasoline. The objectives of the test of DL1 naphtha were to:

- reduce the sulfur content to less than 0.5 ppm by weight to protect the reforming catalyst
- reduce the nitrogen content to less than 0.5 ppm by weight
- increase the hydrogen content of the naphtha
- obtain process data and operating efficiency data at various operating conditions.

The pilot plant of the DOE Alternative Fuel Center at Southwest Research Institute was configured for hydrogenation: feedstock is pumped from a weighing tank, heated to 400°F in a feed preheater, and passed to the reactor. On the way to the feed heater, make-up and recycle streams of high pressure (770 - 1400 psig) hydrogen join the feedstock. The make-up hydrogen flowrate was set at 10 SCFH and the recycle was held constant at 20 SCFH. The aggregate hydrogen flows constituted a gas contacting rate of 2208 - 4258 SCFB. The reactor is composed of two stages- a 3.5 liter guard bed, followed by a 4.0 liter reactor. The reactor is packed with an equilibrium nickel-molybdenum catalyst, Criterion HDN-60. The processed feedstock is cooled and depressurized after leaving the reactor first in a high, then a low, pressure separator. Hydrogen gas is recovered in the high pressure separator, scrubbed, and returned to the reactor. For the coal liquid naphtha, which was in short supply, a smaller (one-eighth scale) reactor was used for the test matrix.

During the course of the experiment, pressures, temperatures, and flow rates were varied over a matrix of conditions selected to achieve the experimental objectives of the naphtha hydrogenation while still considering typical refinery conditions. The matrix of conditions is shown in Figure 3. System conditions were monitored, and when sufficiently stabilized, a sample was drawn from the low pressure separator outlet. The specific gravity was measured with a density meter and hydrogen content was determined by ASTM D 3701, broadband NMR method. A stripper column was not used during the run in order to conserve DL1 feedstock, instead, the samples were caustic washed to remove H_2S and submitted for nitrogen (by

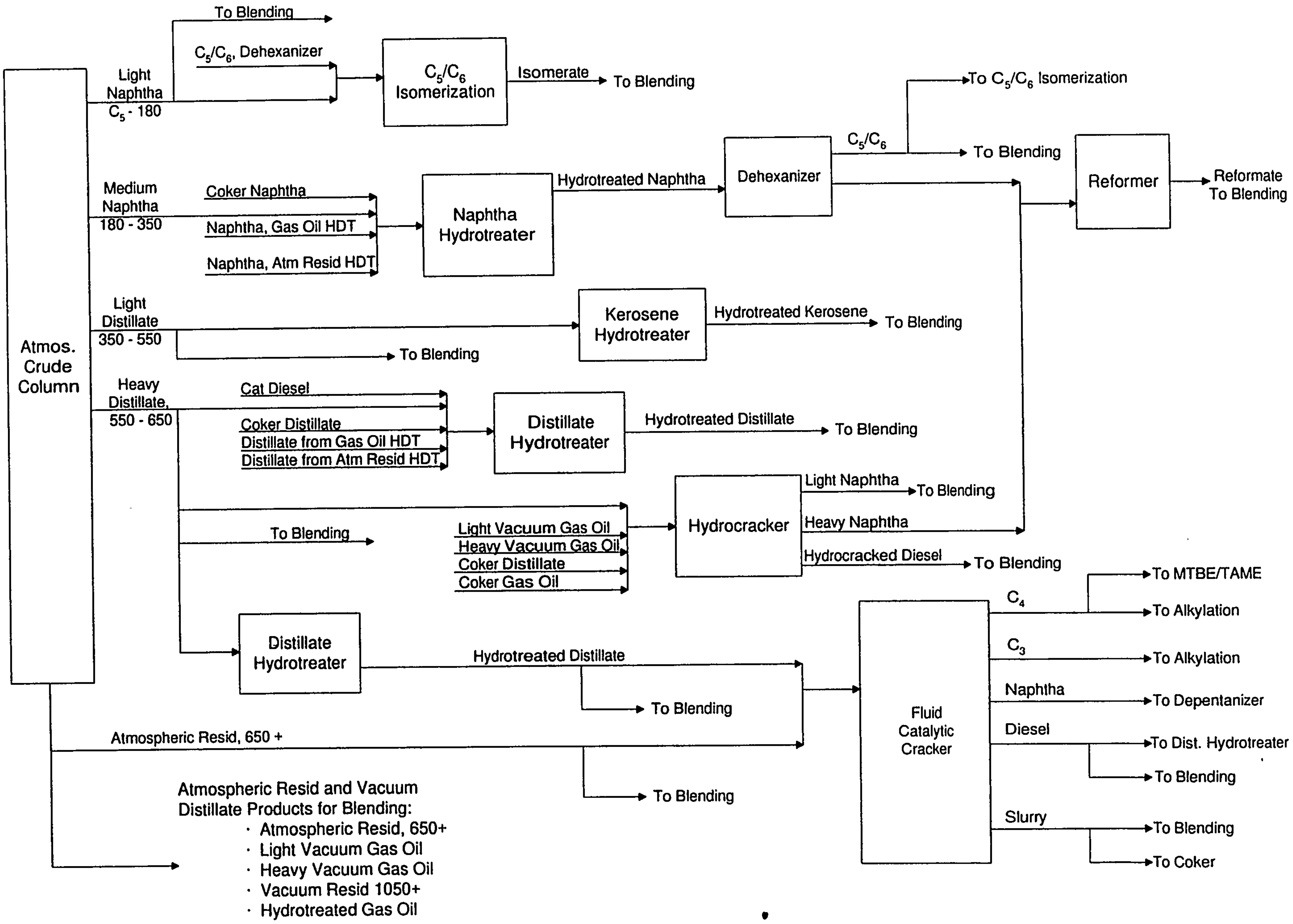

Figure 2. PIMS Refinery Model

chemiluminescence, Antek) and hydrogen content (D 3701) analyses. This sampling method precluded measuring sulfur content of the product. Gas samples were also taken from the vent sample port for gas chromatographic analyses.

Three feedstocks were used in the naphtha hydrotreating. The first was a petroleum feedstock which was selected in consultation with Amoco as a typical refinery naphtha normally used as hydrotreater feedstock. The second experimental feed was the neat DL1 naphtha fraction. The third feedstock was a blend of 67% petroleum naphtha/33% coal naphtha (by volume).

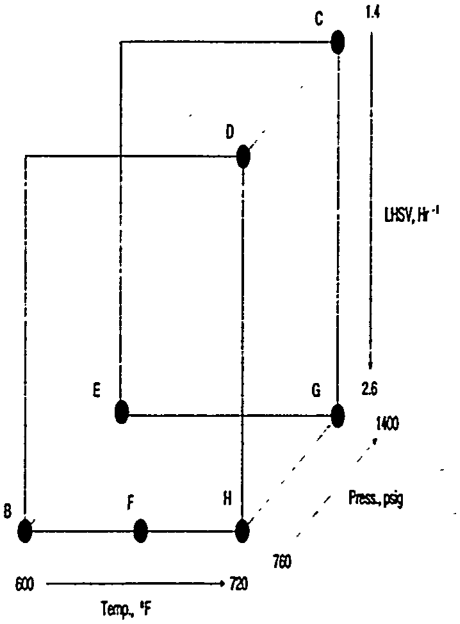

Figure 3. Experimental Matrix for DL1 Naphtha Hydrotreating

The test sequence began with the petroleum feedstock at the low severity condition A. At steady state (determined by reaching constant density and hydrogen contents), a product sample was drawn at this and each subsequent condition. The petroleum feed was tested first to provide a benchmark for the PIMS library data and to perform startup on a more abundant feed to conserve DL1 naphtha. The neat coal liquid was then introduced at the low severity condition B. The temperature, pressure, and residence time were increased to the high severity level C, and a sample was drawn and tested to assure that the nitrogen was below 0.5 PPM. Once this had been established, the neat coal liquid was tested at five additional conditions with varying pressure, temperature, and flow rate at severities between the two extremes, B and C. The petroleum/coal liquid blend was then tested at three conditions (I, J, and K) and the petroleum feedstock was reintroduced as the process was brought back to its initial, low severity condition L. Comparison of this last test condition to the first shows whether there has been significant catalyst de-activation.

Experimental Results: The test conditions and measurements are summarized in Table 1. There is a narrow range of product properties; e.g., for the neat coal naphtha, the density differs by only 0.008 gm/ml and the hydrogen content differs by 0.37 wt% between the extremes of process severity. The hydrotreating produced good hydrodenitrogenation, with product nitrogen values at or below the target (values marked <1).

The wire frame representation of the experimental matrix in Figure 3 illustrates which direct comparisons may be made between sample points sharing common values of two test parameters, but differing in the third. Table 2 compares points differing in only one parameter, and presents the effects of increasing pressure, temperature, and flow rate. Pressure influenced the hydrogenation more strongly than temperature or flowrate in the ranges studied. The hydrogen content increased by an average of 0.22% wt when the

Table 1. Naphtha Hydrotreating Summary

SAMPLE#	Feed Type	Avgerage Processing			Density g/mL	H2 Wt% NMR	Nitrogen
		Deg F	Psig	LHSV			PPMW
Coal	Feed DL1 Naphtha				0.794	13.62	219
Petrol	Feed Petr				0.767	13.95	<1
A	Petr	599	770	2.6	0.765	14.06	<1
B	DL1	596	770	2.7	0.787	13.89	3
C	DL1	723	1397	1.4	0.780	14.21	<1
D	DL1	722	762	1.4	0.784	13.84	2
E	DL1	602	1397	2.7	0.786	13.98	<1
F	DL1	656	762	2.7	0.786	13.97	<1
G	DL1	720	1396	2.7	0.782	14.13	3
H	DL1	718	762	2.8	0.788	13.94	3
I	Blend	722	764	1.5	0.768	14.25	10
J	Blend	722	1400	1.3	0.761	14.80	<1
K	Blend	603	766	2.6	0.771	14.12	<1
L	Petr	607	768	2.7	0.771	13.34	<1
M	Petr	721	772	1.5	0.760	14.39	<1

pressure was increased from 770 to 1400 psig. The pressure also had the greatest effect on density, decreasing the density by an average of -0.0037 gm/ml when the pressure was increased from 770 to 1400 psig. The changes in specific gravity generally confirmed the change in hydrogen content. Increasing the temperature from 600° to 720°F consistently increased the hydrogen content, but reducing the LHSV from 2.7 to 1.4 hr^{-1} increased the hydrogen content only at high pressure (1400 psi). At low pressure (770 psi) the hydrogen content decreased.

Table 2. Naphtha Hydrotreating Main Effects

Effect	Sample Points	Effect on H_2	Effect on SG	Average Effect on H_2	Avgerage Effect on SG
Temperature (600 to 720°F)	B to H E to G	+0.05% +0.15%	+0.001 -0.004	+0.010%	-0.0015
Pressure (770 to 1400 psig)	B to E H to G D to C	+0.09 +0.19 +0.37	-0.001 -0.006 -0.004	+0.22%	-0.0037
LHSV (1.4 to 2.7 hr-1)	C to G D to H	-0.08 +0.10	+0.002 +0.004	+0.01%	+0.003

There is a three step progression in temperature between points B, F, and H. The points share a common pressure (770 psig) and LHSV (2.7 hr^{-1}). In this case, the consumption of hydrogen is greater and the specific gravity is lower at the intermediate temperature, point F. This would suggest that there may be a critical temperature between 600 and 720°F where the processing efficiency is maximum. The higher temperatures favor the reverse or dehydrogenation reactions arriving at the hydrogen concentration dictated by thermodynamic equilibrium. The effect of high naphthenes concentration in the feed probably caused some dehydrogenation, locally, at hot spots within the reactor during operation in the low hydrogen pressure and high temperature part of the matrix.

The experimental results show that the catalyst lost activity during the sequence of experiments. Aromatics hydrogenation and heteroatom removal in a petroleum feed were observed before and after the sequence to indicate whether a major activity loss, which could complicate the modeling effort, had occurred. Activity reduction can come from the high temperature levels of the most severe points of the present matrix without regard to the specific feedstocks. The usual measure of catalyst deactivation (the change in temperature required to restore product quality) was simulated with points L and M by raising the temperature on the petroleum feedstock, and indeed, an increase in conversion was observed.

The selection of the experimental matrix was influenced by the expected increase in processing severity over current refinery practice that would be expected in the time frame of interest to the current study. The naphtha results indicate that the increase in severity went too far, and caused little improvement in product quality and may have contributed to catalyst deactivation. Considering that the matrix was developed with guidance from the literature of earlier coal liquid processing experiments, the current coal liquid was much more readily upgraded than was expected.

6. Distillate Hydrotreating

Hydrogenation of heavier fractions is practiced to increase hydrogen content and thereby improve the yield of valuable components, as well as to remove impurities that are unacceptable in fuels and which are damaging to downstream processing. The objectives of the test of DL1 heavy distillate were to:

- reduce the sulfur content to less than 380 ppmw
- reduce the nitrogen content to less than 380 ppmw
- increase the hydrogen content to 12 wt% or higher for FCC pretreatment
- reduce aromatics content, improving ignition quality
- obtain process data and operating efficiency data at various operating conditions.

The pilot plant hydrotreating configuration was identical to the one used in the naphtha processing. The hydrogen was circulated at a slightly greater flow rate than in the naphtha processing: make-up hydrogen was set at 12 SCFH and the recycle hydrogen was set at 24 SCFH. The make-up hydrogen varied from 1084 to 2981 SCFB, and the recycle hydrogen was added at between 2167 and 5961 SCFB. Pressures, temperatures, and flow rates were adjusted to attain 17 different conditions, A through Q in Figure 4. The operating conditions were varied between a low severity condition, set to match current refinery practice, and a high severity condition sufficient to reduce the sulfur and nitrogen contents of the treated distillate well below 380 ppmw to obtain storage stability. Pressures were varied between 700 psig and 1350 psig. Temperatures were varied from 620 to 688°F. The LHSV was also varied between 0.8 and 2.2 hr^{-1}.

Three feedstocks were used in the distillate hydrotreating. The first was a petroleum gas oil with properties to match the DL1 heavy distillate (within practical availability). The second was the DL1 heavy distillate fraction. The third was a blend of the two: 67% petroleum distillate/ 33% coal heavy distillate (by volume). The hydrotreating was done according to the test sequence depicted in the wire frame drawing of Figure 4.

The test sequence began with the petroleum feedstock at the low severity condition A. A sample was drawn at this and each subsequent condition. The neat coal liquid was then introduced at the low severity condition B. The temperature, pressure, and residence time were then increased to the high severity Condition C, and a sample was drawn and tested to assure the nitrogen was below 380 PPM. After several adjustments, this was established. The neat coal liquid was tested at nine additional conditions with varying pressure, temperature, and flow rate at severities between the two extremes of Conditions B and C. The petroleum/coal liquid blend was then tested at three conditions (M, N, and O), and the petroleum feedstock was reintroduced as the process was brought back to its initial, low severity condition P. Comparison of this last test condition to the first showed whether there had been significant catalyst deactivation, and this was checked by increasing the severity on the petroleum feedstock to Condition Q.

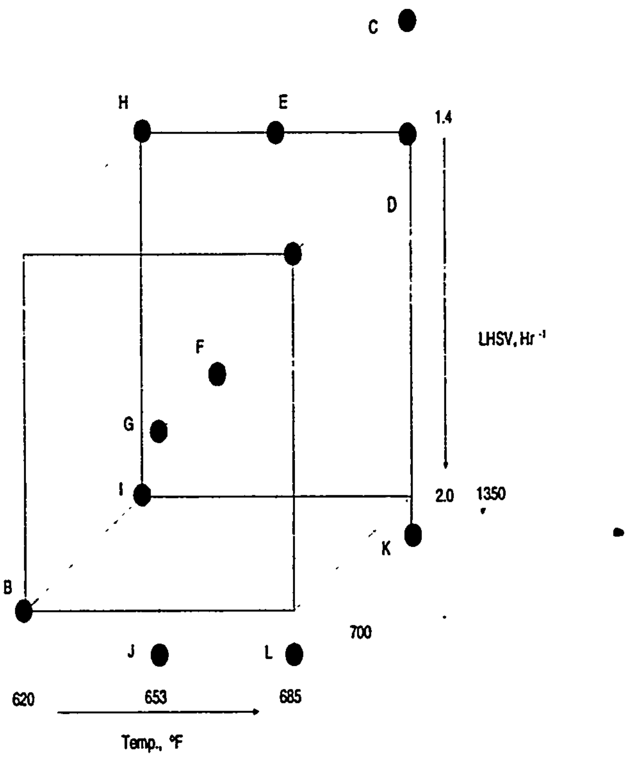

Figure 4. Experimental Matrix for DL1 Heavy Distillate Hydrotreating

Experimental Results: The test set points and the data collected are summarized in Table 3. The hydrogen content of the processed DL1 distillate consistently fell above 12 wt%, satisfying the test objective. The exception was Condition L, whose high flow rate made the condition effectively less severe than point B. Multiple tests of the hydrogen content showed an *average* hydrogen content of the product of 11.98 wt%. The range of product properties for the coal distillate was narrower than it was in the naphtha processing. The density differed by only 0.006 gm/ml and the hydrogen content differed by 0.24% wt between the extremes of process severity.

The hydrotreating step reduced sulfur and nitrogen in the DL1 heavy distillate below the 380 ppmw criterion required for product stability. Table 4 compares points differing in only one parameter, and presents the main, average effects of increasing pressure, temperature, and flow rate from the low to the high value of each parameter. As with the naphtha hydrotreating, the most influential control parameter was an increase in pressure from 700 to 1350 psig, which resulted in the predominant effect of increasing the hydrogen content by 0.105 wt%. An increase in hydrogen content was usually, but not always, accompanied by a

Table 3. Distillate Hydrotreating Summary

SAMPLE #	Feed Type	Avgerage Processing			Density	H2 Wt%	Nitrogen
		Deg F	Psig	LHSV	g/mL	NMR	PPMW
Coal Dist	DL1Feed				0.919	11.87	590
Petrol	Petr Feed				0.868	12.22	109
A	Petr	619	700	1.9	0.851	13.20	<1
B	DL1	624	700	2.0	0.914	12.06	351
C	DL1	687	1350	0.8	0.909	12.23	2
D	DL1	688	1350	1.3	0.913	12.14	44
E	DL1	649	1345	1.4	0.913	12.14	115
F	DL1	654	1025	1.4	0.914	12.09	218
G	DL1	650	700	1.4	0.915	12.07	300
H	DL1	620	1345	1.4	0.913	12.17	238
I	DL1	622	1351	2.0	0.914	12.20	303
J	DL1	653	700	2.2	0.914	12.13	355
K	DL1	684	1351	2.1	0.911	12.10	129
L	DL1	685	700	2.2	0.915	11.98	321
M	Blend	686	699	2.0	0.875	12.57	53
N	Blend	685	1351	0.7	0.859	13.08	<1
O	Blend	618	700	1.9	0.876	12.55	119
P	Petr	620	699	1.9	0.854	12.87	53
Q	Petr	652	700	1.4	0.847	12.80	11

decrease in density, but over the narrow range of the data, no inference about resulting hydrocarbon composition should be made. There is an occasional inconsistency between these two effects. Increasing either the temperature (from 620 to 688°F) or LHSV (from 1.4 to 2.7 hr^{-1}) changed the hydrogen content and specific gravity by lesser amounts, and in inconsistent ways. A decrease in the LHSV should not decrease the hydrogen content. This information suggests that the variation within the data (analytical precision and randomness) is obscuring the effects caused by varying the process conditions over a limited range of severity.

7. Discussion of Hydrogenation Experiments

Regression analyses were performed on the data from both the naphtha and the distillate hydrotreater experiments. Predictive linear models of the specific gravity and hydrogen fraction were generated in a form relating these product properties linearly to the three operating parameters. This permitted a simplified model using a single plotting parameter, an index of hydrogenation severity. The severity term, S, is the

Table 4. Distillate Hydrotreating Main Effects

Effect	Points	Effect on H_2	Effect on SG	Average Effect on H_2	Average Effect on SG
Temperature (620 to 688°F)	H to D I to K	-0.03% -0.10%	0 -0.003	-0.0125%	-0.0015
Pressure (700 to 1350 psig)	B to I G to E	+0.14% +0.07%	0 -0.002	+0.105%	-0.001
LHSV (1.4 to 2 hr-1)	H to I D to K	+0.03% -0.04%	-0.001 -0.002	-0.005%	-0.0015

combination of the controllable operating parameters: S = P·T/LHSV. In general, as the pressure, temperature, or processing duration (1/LHSV) increases, the products are processed more fully, whether for desulfurization, denitrogenation, or hydrogenation. Consequently, as the severity term increases, the hydrogen content should increase and the specific gravity decrease. Figure 5 shows the increase in hydrogen content (relative to the feedstock) for the naphtha and distillate hydrotreater runs. The figure shows a linear relationship between the hydrogen content and the severity term, considering the uncertainty in the data. The scatter in the data does not obscure the strong correlation. The same holds true for the specific gravity vs. severity.

The correlation coefficient, r^2, which is one measure of the goodness of fit of a model to data, was calculated for the severity model and a linear polynomial (e.g. $SG = a_0 + a_1 T + a_2 P + a_3 LHSV$) with terms comprised of the individual operating parameters as shown in Table 5. The numbers show that the severity model has a slightly stronger correlation to the data than the linear model.

Table 5. Comparison of Correlation Coefficients for Distillate Hydrotreating

Property	R^2 (P,T,LHSV)	R^2 (Severity)
H_2 Wt%	0.37	0.52
Specific Gravity	0.59	0.59

8. Distillate FCC

Fluid catalytic cracking (FCC) of higher-boiling fractions of crude oil increases the value of heavy feedstocks and balances the product blending pool by providing gasoline blending components. In this unit process, feedstock is preheated before injection into the bottom of a vertical, fluidized bed reactor containing the finely divided, zeolite cracking catalyst. Steam and reactor gases transport the vaporized feed and catalyst up the riser and out to another vessel, the regenerator, where product gases are separated from the catalyst. The catalyst is valved into a lower vessel freed of deposited coke by combustion air before being recycled to the riser. The most significant operating parameters are catalyst to oil ratio and operating temperatures, while measured variables of interest include gasoline yield, gasoline octanes, and "coke make".

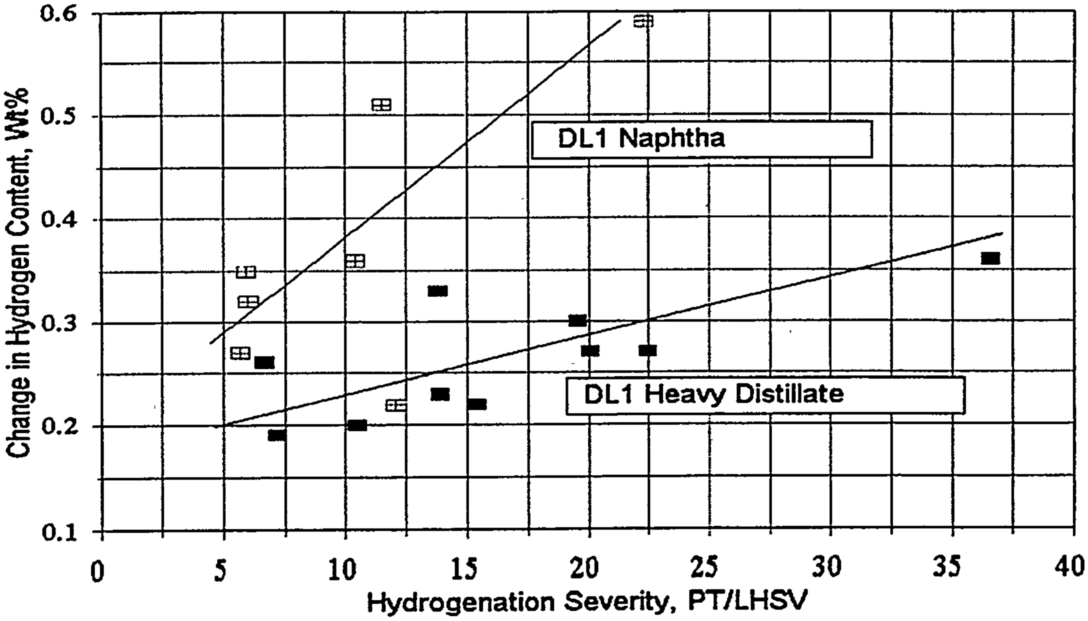

Figure 5. Hydrotreating Severity

The experiments performed at M.W. Kellogg Company were in two parts:

- Microactivity Tests (MAT) similar to ASTM D 3907 on the following:

IDENTITY	DESCRIPTION
DL1 Neat Heavy Distillate	550°F$^+$ fraction of DL1
HTR Dist Product J	Slightly hydrotreated heavy distillate
HTR Dist Product R	Highest severity heavy distillate
HTR Dist Product C	Severely hydrotreated heavy distillate
Petroleum Gas oil	Matched boiling range
Blend	50:50 (vol) DL1 Dist & Petr Gas Oil

- Pilot plant FCC tests on:

IDENTITY	DESCRIPTION
Petroleum Gas Oil	Matched boiling range
DL1 HTR Dist Product C	Severly hydrotreated 550°F$^+$ fraction of DL1
Blend	33:67 (vol) DL1 Dist & Petr Gas Oil

A MAT test apparatus consists of a glass reaction tube containing 3 to 7 grams of prepared FCC catalyst in a two-zone furnace (970°F) and syringe injector delivering 1 ml over a 30-second time span.

The procedure includes a nitrogen flush after injection then GC analysis of the product gases. The liquid product is also analyzed by GC to determine conversion to gasoline (yield) and to estimate octane number. The carbon on the catalyst is determined by measuring CO_2 production upon burnoff. A mass balance accounting for >95% of the material is required for a successful run. The MAT test runs provided:

- Yield over a range of conversions for each liquid
- Gasoline composition of one product of each feed
- Octane numbers of selected products showing effect of hydrotreating.

The results of the MAT testing are interpreted through plots of conversion to gasoline and coke yield such as in Figure 6, which shows both parameters as a function of catalyst to oil ratio. For three materials of varied hydrotreating severity, the overall effect of hydrogen content on gasoline yield is shown in Figure 7. The line for "potential gasoline" also takes into account C3 and C4 olefins plus butane, which are used in alkylation and ether production to the benefit of gasoline. This desireable effect is directly from the molecular structure of the coal-derived component. The range of hydrotreating severity increased the gasoline yield from 52 to 65 Wt% as a linear function of hydrogen concentration.

The pilot plant runs are summarized in Table 6 for the three liquids tested. The catalyst rates averaged 48.2 pounds per hour of Vektor-50 FCC catalyst from Conoco while oil rates were ~0.47 pounds per hour. Riser outlet pressure was 35 psig. Other data appear in the table. All three feedstocks ran well with little filter plugging propensities, which bodes well for the test fuel production run in Option 1.

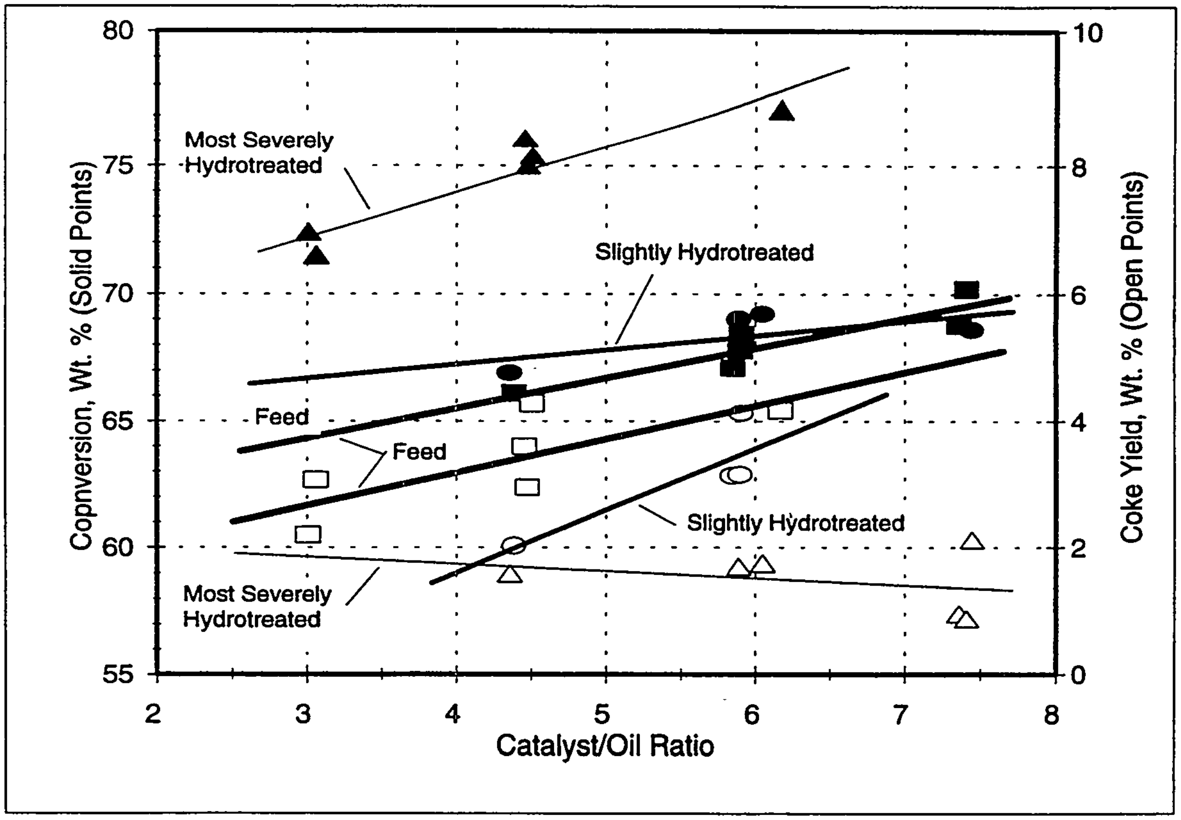

Figure 6.. FCC Performance of Hydrotreated DL1 Heavy Distillate

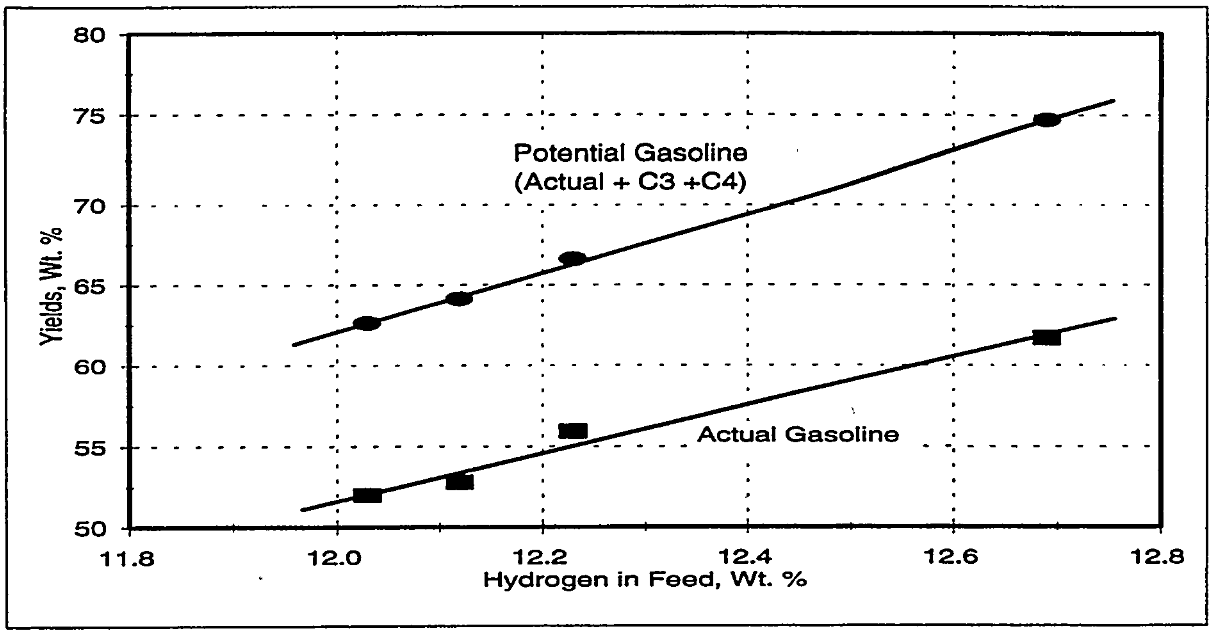

Figure 7. Effect of Distillate Hydrogen Content on Gasoline Yield

Table 6. DL1 Heavy Distillate FCC Pilot Plant Operations Summary			
Run Number	1	2	3
Feed	Gas Oil	DL1 Dist	Blend
Catalyst/Oil Ratio	12.2	12.2	12.0
Temperatures			
Feed Preheat	212	212	214
Catalyst Inlet	1265	1253	1252
Riser Average	984	987	983
Material Balance			
Closure, Wt%	98.50	98.49	98.46
Conversion, Wt%	74.13	74.20	73.18
C2 & Lighter	3.34	2.03	2.83
C3 & C4	15.37	13.73	15.02
C5 - 430°F	50.52	55.17	51.01
430°F$^+$	25.87	25.80	26.82
Coke	4.90	3.27	4.32
Octanes			
Engine RON/MON	91.0/80.3	91.0/80.0	90.7/80.2
GC RON/MON	93.2/81.1	92.8/81.0	90.7/80.7

Compared to the petroleum stock, the coal liquid made much less coke and nongasoline products. The lower coke make would require far more conversion than would yield the optimum product distribution (maximum gasoline). In practice this indicates the need for an auxiliary fuel to supply adequate energy in the regenerator to keep the FCC unit in heat balance at the required temperatures. The required heat inputs at optimum yields were calculated for each material for use in optimizing the LP refinery model.

9. Indirect Wax Processing

As shown in Figure 1, the sequence of steps applied to the upgrading and integration of Indirect Liquid 1 (IL1) differs from the sequence for the DLs, because of the nature of the Fischer-Tropsch product. Air Products and Chemicals produced the IL1 feedstock in the DOE Alternative Fuels Process Development Unit (PDU) at LaPorte, Texas during tests to check the hydrodynamics of the unit. In the PDU an artificial coal gasification syngas is conducted through a slurry of high activity iron oxide catalyst, which polymerizes the methane and the paraffin products of polymerization. The overflow from the slurry reactor enters several stages of separation to return catalyst and low molecular weight paraffins to the reactor. Product paraffins leave the process as a stream of hydrocarbons liquid at room temperature, a light wax slurry, and a heavy wax, which is solid at room temperature. There are traces of olefins and oxygenates made during the reaction. There is also an aqueous effluent.

Feed Preparation: The first step in the investigation was reconstituting the fractions of interest for processing experiments. As a test of hydrodynamics, it was not a concern to preclude incidental catalyst release with the heavy wax. Catalyst cannot leave with light wax and hydrocarbon liquid, because they are condensed from vapor when they are discharged. Since the iron-based catalyst would interfere with downstream processing experiments and would not be present in a commercial production wax, a clean up step was added in which the 5 Wt% iron was reduced below 500 ppmw.

After lab-scale experimentation, a technique was implemented at Southwest Research Institute to remove nearly 99.9 Wt % of the catalyst while not skewing the hydrocarbon distribution of the heavy wax. Approximately 20 V% catalyst containing wax was dissolved in Isopar M™ solvent at 250°F and sent through 1.5 micron cellulose filter paper in a plate and frame filter press. The Isopar M solvent was removed by two-pass distillation in a wiped film pilot plant under vacuum. The next step was removing the 20 Wt% 650°F$^+$ material contained in the light wax for recombination with the clean heavy wax. Each portion of this heavy fraction of the light wax was mixed with four parts clean heavy wax to reconstitute the as-produced 650°F$^+$ portion of the PDU product for further experiments.

Fluid Catalytic Cracking Experiments: At Amoco Oil R&D, FCC pilot plant runs were made at 20 and 40 Wt% wax concentration in conventional petroleum FCC feed from the Amoco Whiting, IN refinery. The catalyst (also used at M.W. Kellogg) was fed at ~2 pounds per hour. Liquid feed was about 0.22 pounds per hour. Other operating data as well as pilot plant results appear in Table 7.

Table 7. IL1 FCC Pilot Plant Operations Summary

Run Number	1	2	3
Feed	FCC Petr.	20 Wt%	40 Wt%
Catalyst/Oil Ratio	9.43	9.57	8.88
Temperatures			
Feed Preheat	394	393	394
Riser Average	953	953	952
Material Balance			
Closure, Wt%	100.04	100.00	100.01
Conversion, V%	71.52	75.44	79.98
C2 & Lighter	2.14	2.04	1.79
C3 & C4	14.05	15.84	17.43
C5 - 430°F	51.37	53.32	56.36
430°F$^+$	28.78	25.05	20.69
Coke	3.68	3.76	3.75
Octanes			
	88.2/79.6	86.6/78.8	86.7/79.2

Initial runs with the wax blends exhibited injector nozzle plugging from coke buildup. The plugging was determined to come from composition, rather than catalyst fines. Boring out the injector nozzle from 0.02" to 0.04" allowed the pilot plant to run successfully on both blends. Analysis of the data show that the incremental naphtha yields were 82 V% for the 40% blend and 75 V% for the 20% blend *versus* 62 V% for the petroleum FCC feed. The incremental C4+ olefins yield was 18 Wt% for both wax blends compared to 10 Wt% for the petroleum. The results indicate that the cycle oil produced is very light and that very little of the more troublesome decant oil is produced.

Incremental product values, using a 1994 price structure, show the LaPorte FT wax/gas oil blend products to be worth three dollars per barrel more than the gas oil cracked products alone. This is principally because of the greater naphtha yield and because of the valuable light olefins. Compared to previous work on fixed bed FT wax cracked products, there was only a one octane number debit compared to the petroleum-only case, while there was a 4 octane number debit for similar fixed bed products. Also the coke make was 75% higher with IL1 than fixed bed FT wax processing.

10. Summary and Future Work

The *End Use Study* is nearing the completion of its pilot plant analysis of DL1 fractions and will soon begin work on DL2. In fact, the DL2 feedstock, POC-2 from subbituminous coal, is being fractionated now. The unexpectedly superior properties of DL1 resulted in hugher than necessary processing severities, which resulted in narrow ranges of product properties from naphtha and heavy distillate hydrotreating. Operating conditions in subsequent experimental matrices will be broadened accordingly.

The naphtha hydrotreating showed good denitrogenation and readily met the specification of ½ ppmw needed to protect modern reforming catalysts. Similar results were observed in special testing for sulfur. Good agreement between hydrogen concentration increase and density decrease (except at two experimental points) indicated that the feed resisted dehydrogenation by reverse reactions which tend toward the concentration of aromatics favored by in thermodynamic equilibrium.

The heavy distillate hydrotreating achieved 90 - 97 Wt% hydrodenitrogenation, well below the target production concentration of 380 ppmw. Limited tests showed similar results for sulfur. Hydrogen addition was readily achieved. Observed catalyst deactivation probably arose from temperature excursions as shown by increased treatment of the petroleum stock upon increasing reactor temperature. Byproduct hydrogen sulfide can be removed by stripping with nitrogen gas to obtain a stable product.

FCC pilot plant and MAT tests showed that gasoline yields increase from 52 to 62 Wt% when the DL1 distillate is severely hydrotreated. Coke production was low indicating that extra heat would be needed to balance cracking operations at the optimum conditions for gasoline production. The indications were that all the products were good gasoline producers and would be unlikely to foul catalysts. Octane numbers produced were comparable to petroleum and the effect of hydrotreating was to make a small increase with increasing hydrogen content. The prospects for the production run of blend components from cracking of DL1 heavy distillate is favorable.

Work on IL1 is at an early stage. Reconstitution of the heavy wax fraction by cleaning and distillation is complete. FCC pilot plant testing of 20 and 40 Wt% blends of the resulting heavy wax showed better performance in cracking than comparable fixed bed FT wax feeds. A 75 Wt% higher coke production was observed for IL1 over a similar fixed bed FT feed. Calculations showed a three dollar per barrel premium of IL1 heavy wax blends over the matched petroleum feed from increased naphtha production and the higher proportion of valuable light olefins. This value was attained with only a small reduction in octane numbers of the FT blend's naphtha *versus* the petroleum naphtha. In all the IL1 would make a valuable FCC feed.

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