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3.1 Linear Programming Model - Task 3

The development of the linear programming model for an all petroleum feed refinery has been completed and a topical report summarizing the design basis for this model was issued on March 20, 1995.

In this section of the quarterly report, the following three topics will be discussed:

- Refinery expansion scenario
- Initial coal liquid pilot plant data
- Preliminary coal liquid evaluation studies

3.1.1 Refinery expansion scenario

As was mentioned in the topical report, a refinery expansion scenario was adopted to determine product pricing. This scenario was also chosen as a basis for evaluating the three coal liquids that are being examined in this study. The refinery expansion scenario is a reasonable assumption because:

- No grass roots refineries will be built in the future for economic, environmental, and political reasons.
- As small or uneconomical refineries shutdown, larger and more complex refineries will expand to fill the void.
- Coal liquids will have the highest value when credit is given for capital cost avoidance. In an expansion, the use of higher quality coal liquids will allow for lower capital expenditures.

The effect of adopting a refinery expansion scenario is discussed in section 3.1.3.4.

3.1.2 Initial coal liquid pilot plant data

The Direct coal liquid 1 (DL1) heavy distillate hydrotreating pilot plant tests conducted by SwRI provided treated samples produced under a number of conditions. Three of these samples (treated under mild, medium and high severity conditions) and an untreated sample were sent to M.W. Kellogg for catalytic cracking tests. This section of the report describes how the results from the SwRI and Kellogg tests were used in the LP model.

The goal of this work task was to take the raw test data and develop yields, consumptions, and properties for hydrotreating and catalytic cracking the DL1 heavy distillate. These yields, consumptions, and properties were then inputted into the model so that the coal liquid would be processed in the model in accordance with the Task 4 pilot plant work.

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Heavy Distillate Hydrotreating

Input to the model for the three heavy distillate samples that were sent to Kellogg was developed as follows:

- Hydrogen consumptions were estimated for the three heavy distillate samples based on hydrogen uptake and heteroatom removal.
- Volumetric yields were adjusted to achieve a weight balance for each condition.
- Distinct liquid product streams were created for each severity level. Key blending properties were estimated for each heavy distillate product.
- Capital costs and utilities (per barrel) were assumed to be the same for each severity level.

The last item is a simplifying assumption which is discussed in section 3.1.3.1.

Catalytic Cracking

Input to the model for the three treated and one untreated heavy distillate samples was developed as follows:

- Volumetric yields were calculated for the four coal liquid heavy distillates based on Kellogg weight based yield data.
- For each product cut range (naphtha, diesel, etc.) the properties were assumed to be the same regardless of the feed type.
- Fuel usage was adjusted for each feed type to achieve a heat balance condition.

The results from the above work is summarized in the table below. It shows that, as expected, as hydrotreated severity increases, the hydrogen consumption and distillate yield increases, and the specific gravity decreases. For catalytic cracking, the gasoline yields increase as the hydrogen content of the feed material increases.

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Distillate Hydrotreating

SwRI run number	49J-46	49C-23	49R
Severity	Low	Medium	High
Hydrogen Consumption, SCF/bbl	212	286	565
Distillate yield, volume %	100.15	100.49	101.69
Product specific gravity	0.914	0.909	0.887

Catalytic Cracking

Feed type	Neat	Low	Medium	High
C5-430, volume % of feed	63.6	63.8	66.9	73.7
Fuel usage, MMBtu/bbl	0.200	0.200	0.203	0.264

Fuel usage is an adjustment to achieve a heat balanced yield.

3.1.3 Preliminary coal liquid evaluation studies

3.1.3.1 Distillate hydrotreating/catalytic cracking

As mentioned in section 3.1.2, the Task 4 pilot plant test results were used to create yield and property data that would be specific to DL1 heavy distillate hydrotreating and catalytic cracking. A diagram showing the possible processing options for the DL1 heavy distillate is shown in Figure 3-1.

This shows that the LP model is allowed to choose the most economical path for processing the heavy distillate. In general, each path has advantages and disadvantages.

- Sending the neat heavy distillate to diesel/fuel oil blending avoids the capital and operating costs of treating and cat cracking, but the product has a lower value than gasoline. In addition, the neat liquid may not meet diesel specifications even after blending with higher quality material.
- Treating the heavy distillate before sending it to blending may allow it to meet specifications, but there are significant treating costs and, again, the blended product has a low value.

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- Cat cracking the neat heavy distillate avoids the costs of treating and results in higher value gasoline blendstock, but the cat cracking gasoline yields are lower than the yields with treated feeds.
- Cat cracking the treated heavy distillate is the most expensive option from a capital and operating standpoint. The higher gasoline yields, however, may compensate for these costs.

A computer run was made under the refinery expansion scenario which showed that the neat heavy distillate should be sent to the catalytic cracker (option 3 above). This is because the improved cat cracker yields from the hydrotreated feeds are not enough to compensate for the additional hydrotreating capital costs.

Another run was made where the capital costs for hydrotreating were eliminated. In effect, this means that there is unused high pressure (~1500 psig) hydrotreating capacity available. Under these assumptions, the model chose to first treat the heavy distillate under the most severe conditions prior to cat cracking. This means that when compared to lower treating severity levels, the higher cat cracker yields from the high severity hydrotreating offsets the higher hydrogen consumption.

If this assumption of spare hydrotreating capacity is pursued further, then the capital cost for each severity level should not be the same as is currently assumed. The higher severity yields should be based on higher capital costs because of the requirement of a higher pressure reactor.

3.1.3.2 Coal liquid value determination

In determining the value of different feedstocks such as coal liquids it is important to understand the term objective function. Objective function is a linear programming term which is defined as follows:

$$\text{Objective Function} = \text{Revenues} - \text{Purchases} - \text{Utilities} - \text{Capital charges}$$

The linear program maximizes the objective function based on the constraints set by the model. An example of how the objective function is used to set product and alternate feed prices is given in section 4.7 of the topical report.

Similar to the alternate crude feedstocks, the value of the coal liquids was determined by using the linear programming model. The first step was to run the model without any coal liquid feed. This was followed by forcing in a given amount of the coal liquid into the model at zero value. The coal liquid value is the change in objective function divided by the amount of coal liquid feed. The end result is that if this value is then used in the model for the coal liquid, the objective function will be the same as for the zero coal liquid case.

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3.1.3.3 Preliminary coal liquid value determination

As mentioned previously, the coal liquid will be evaluated under a refinery expansion scenario which is discussed in detail in the topical report. The key assumptions in developing this scenario are as follows.

Case 1 involves a generic base refinery (prior to expansion) having the following characteristics:

- Nominal crude feed rate is 150,000 BPD
- Crude is heavier and higher in sulfur than current average PADD II crudes
- Unit capacities are adjusted from 1993 PADD II average capacities
- All process units are running at capacity
- Product slate and specifications are based on year 2000 estimates and the EPA Complex Model

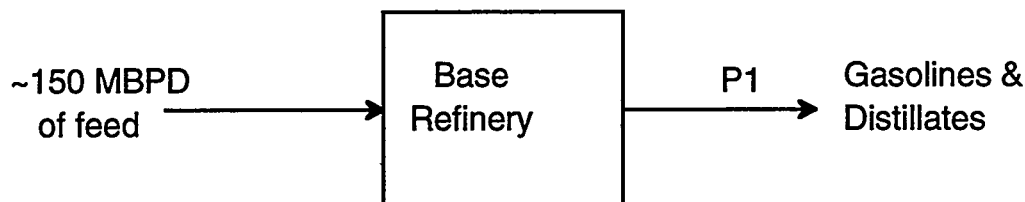
Case 2 involves expanding the Case 1 refinery:

- Nominal crude feed rate is increased to 200,000 BPD by increasing product demand by 33.3% (over Case 1)
- Process units are added or expanded as economically warranted. Capital costs are charged for expansion costs above Case 1 capacities
- The product slate is the same as for Case 1
- The crude feedstock is the same as for Case 1

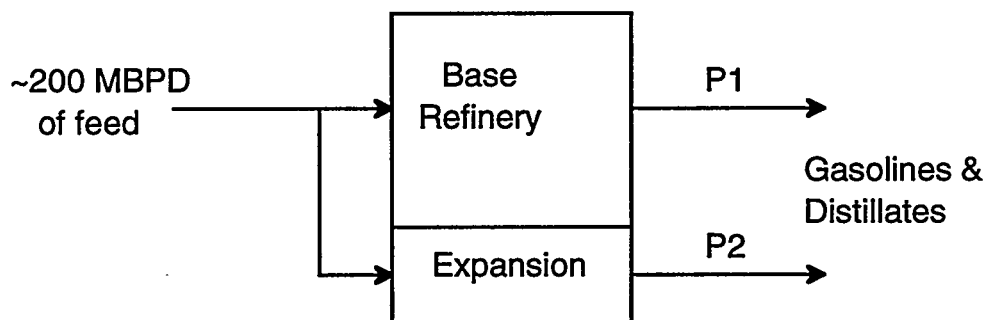
Except as noted, the coal liquids will be evaluated under the Case 2 - expansion allowed scenario.

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Case 1



Case 2



$$P2 = 1/3 \times P1$$

Figure 3-2 shows the results of the coal liquid evaluation work. With the base petroleum crude set at \$18/bbl, the DL1 coal liquid had a value varying from 21 to 22 \$/bbl, depending on the amount of coal liquid fed into the refinery. Under closer inspection, this coal liquid margin of 3-4 \$/bbl is due to a combination of capital avoidance and lower feedstock volumes.

The capital avoidance portion of the margin is distributed into a number of areas. In comparison to the Case 2 run with zero coal liquid, there is:

- Less cat cracking (less resid to process)
- Less alkylation (less olefins from cat cracking)
- Less kerosene/distillate treating (higher quality CL distillate allows bypassing)
- More naphtha HDT/reforming (more light material in CL)
- Less low value product

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At 50,000 BPD of coal liquid, the \$3.25/bbl margin over the base petroleum crude is due to:

Capital avoidance -	\$1.48
Utility charge	(\$0.10)
Additional feedstock	\$2.79
Additional product	(\$0.92)
Total	\$3.25

It should be noted that these preliminary coal liquid margins are based on analysis using the DL1 pilot plant test data available to date. Pilot plant data on naphtha hydrotreating and reforming and kerosene (light distillate) hydrotreating must still be added to the model. In addition, to complete a full evaluation of DL1 (including the calculation of the crude oil equivalent, COE), a complete heat and material balance of the coal liquefaction plant is required. This balance should be based on the operating conditions that were used to produce the DL1 liquid.

3.1.3.4 Expansion vs. no expansion allowed

The DL1 coal liquid was also evaluated under the Case 1 - no expansion scenario. The results are shown in Figure 3-3. The coal liquid margin is significantly lower (0.50 to 1.20 \$/bbl). This is because the model is much more restricted in the number of ways it can process the coal liquid. In particular, there is no credit for capital avoidance.

Figure 3-4 shows the significance of capital avoidance. For the Case 2 - expansion allowed scenario, the daily capital charges are plotted versus increasing amounts of coal liquid. This shows that at zero coal liquid the daily capital charges would be approximately \$274,000. This falls steadily to \$193,000 when 60,000 BPD of coal liquids are processed. This \$81,000 savings is directly due to the characteristics of the DL1 liquid.

3.1.3.5 Effect of Task 4 pilot plant data

Prior to the work detailed in section 3.1.2, direct coal liquid yields, properties, etc. were estimated based on preliminary characterization work and previous coal liquid upgrading studies. These studies in turn were based on using coal liquid feedstocks from early liquefaction processes such as Solvent Refined Coal (SRC) and Exxon Donor Solvent (EDS). These liquids were significantly inferior in quality to DL1 and, thus, required more extensive upgrading than DL1 requires.

The yield and property estimates were used in the model and several runs were made to determine the coal liquid values at several different feed rates.

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Figure 3-5 compares the results from these runs to the results from the runs made with the Task 4 pilot plant data. The lower curve are the coal liquid values with the original estimates for yields, properties, etc. The upper curve are the values based on the Task 4 data. This shows that using the pilot plant data results in about a \$1/bbl increase in coal liquid value. Overall this difference is due to the higher quality of DL1 which results in less upgrading required. In particular, DL1 does not require costly heavy distillate hydrotreating.

3.2 Kinetic correlation of hydrotreating data

3.2.1 Heavy distillate hydrotreating by SwRI

The SWRI hydrotreating data on heavy distillates (runs 49 and 50,) has been subjected to a simple pseudo first-order kinetic analysis. This type of approach has been found useful in the past for the analysis of sulfur and nitrogen removal kinetics for both petroleum and synthetic oil fractions. The severity factor concept, discussed in Section 2.4, has been used to analyze aromatics hydrogenation kinetics. Data were segregated into runs on the heavy petroleum distillate, the coal liquid heavy distillate and the blend of the two so that differences in kinetic rate constants could be identified.

The analysis is basically quite simple. First, it is assumed that both the desulfurization and denitrification reactions are first order. For desulfurization, a plot of $\ln(FS/PS)$ versus contact time would then be a straight line back to a FS/PS value of 1 (no conversion) at zero contact time. (FS is ppm sulfur in the feed, PS is ppm sulfur in the product liquid.) The slope of this line is the activity coefficient. The relationship $3600/LHSV$ is used as the measure of contact time. In order to bring data at different pressures into line, the contact time is multiplied by $48.6/P$. (P is pressure in atmospheres.) The resulting expression for the activity coefficient for sulfur removal, k_S , is given by:

$$k_S = LHSV/3600 \cdot 48.6/P \cdot \ln(FS/PS)$$

k_S is then plotted against $1000/T$ and the slope of the line is the activation energy in $kCal/gm$ mole. The analysis for denitrification is similar.

These results differ from those reported in the minutes of the January Progress Review Meeting because of the following changes:

- Since catalyst aging over coal liquid was detected in the repeat run on the distillate petroleum fraction, a simple aging correction was applied. This correction assumed a linear loss in activity with time on coal liquid (roughly 130 hours.) All results are then corrected back to a fresh catalyst basis. While probably oversimplified, the data did not permit any more detailed aging analysis.

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- Wherever SWRI has reported new values of sulfur and nitrogen in the product, these new values have replaced the old values in the correlations.
- Mathematical errors in the previous analysis have been corrected. $\ln(\text{FN}/\text{PN})$ replaces FN/PN and $\ln(\text{FS}/\text{PS})$ replaces FS/PS in the calculation of k_N and k_S . The logarithm of the ratio of k values, rather than the simple ratio, is divided by the difference in values of $1000/\text{Deg K}$ to calculate E , the activation energy. These corrections help to bring low conversion and high conversion data into line and lower the calculated activation energy considerably.

It would be highly unusual if the relationship $\ln(\text{FS}/\text{PS})$ vs. contact time were a straight line up to very high values of conversion. If adequate data were available, it would be better to assume that the more readily hydrogenated sulfur compounds are hydrogenated first and the more refractive compounds are hydrotreated last. The activity coefficient would thus be expected to decrease at high conversion levels where the more refractive species are being hydrogenated. The manner in which the data were collected does not permit such an analysis.

Figures 3-6 and 3-7 show the correlation of the SWRI sulfur removal and nitrogen removal kinetics in the manner described above. A linear pressure correction is used and there is some improvement due to this correction. Using the repeat run on petroleum distillate as a guide, the catalyst activity as a percentage of initial activity, after 130 hours on coal liquid, was 78% for sulfur removal and 15% for nitrogen removal.

As shown in Figure 3-6 there is no temperature effect on sulfur removal. This is not a normal result. In Section 2, the story is told about the contamination of the naphtha samples with elemental sulfur produced from H_2S by air oxidation in the handling of the samples. It is believed that there may have been a similar effect on the samples from heavy distillate hydrotreating. If this is true, then the actual sulfur levels in the products could have been appreciably lower than reported. It is thought that this could explain both the lack of a temperature effect and the difference in aging for sulfur vs. nitrogen removal. Nevertheless, reported sulfur levels were below the target value so that rerun of the data is not essential.

Nitrogen removal kinetics correlate reasonably well. Activation energy is between 18 and 24 kCal/mole, which is reasonable. Lower values of the activity coefficient were found for heavy distillate coal liquid than for either the petroleum heavy distillate or the blend. This is not unexpected since the coal liquid has already been subjected to high pressure hydrotreating conditions and only the more refractory compounds might be expected to survive this

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treatment. The most disturbing result is the severe loss in catalyst activity during the period on coal liquid.

Figure 3-8 shows the relationship between hydrogen pickup and the severity factor, $P^*T/LHSV$, as defined by SWRI. The only difference between this plot and Figure 2-9 is that the units of severity factor are different and more points are included. In particular, point 49R has been included which is representative of the very high severity sample sent to M. W. Kellogg for their catalytic cracking studies. This point provides a logical extension of the correlation line. A separate correlation is shown for the petroleum distillate and blend and the degree of hydrogenation is much greater at a given severity factor.

Figure 3-9 shows the relationship between density and hydrogen content in wt% for the feeds and products from distillate hydrotreating. A single correlation line is shown, though it might also have been reasonable to show individual lines for the coal liquid, petroleum distillate and blend feed materials.

3.2.2 Whole coal liquid hydrotreating by Sandia

Sandia reported on whole coal liquid hydrotreating at the January Progress Review Meeting. These data have been subjected to the same pseudo first-order kinetic analysis. Results are shown in Figures 3-10 and 3-11 for sulfur and nitrogen removal, respectively. Nitrogen removal correlated quite well in Figure 3-11, where a pressure adjustment has been made corresponding to $P^{1.5}$. The 1.5 exponent was found to best bring all points into reasonable correspondence. There seems to have been some initial aging and the initial data up to 5 days on stream have been omitted in drawing the correlation line. There is no evidence of aging after that. The equation of the correlation line is approximately:

$$k_N = 26 e^{(-14,000/RT)}$$

The correlation of sulfur removal in Figure 3-10 shows a greater degree of variance and very little temperature effect. The variance can be explained by the very high levels of conversion. The absence of a temperature effect is unexpected, but the SWRI data showed the same effect, where it was ascribed to possible sample contamination with elemental sulfur produced from H_2S in sample handling. Sandia did not caustic wash their samples, nevertheless it is recommended that Sandia also examine their sample handling procedures.

Figure 3-1
Distillate Hydrotreating/Catalytic Cracking

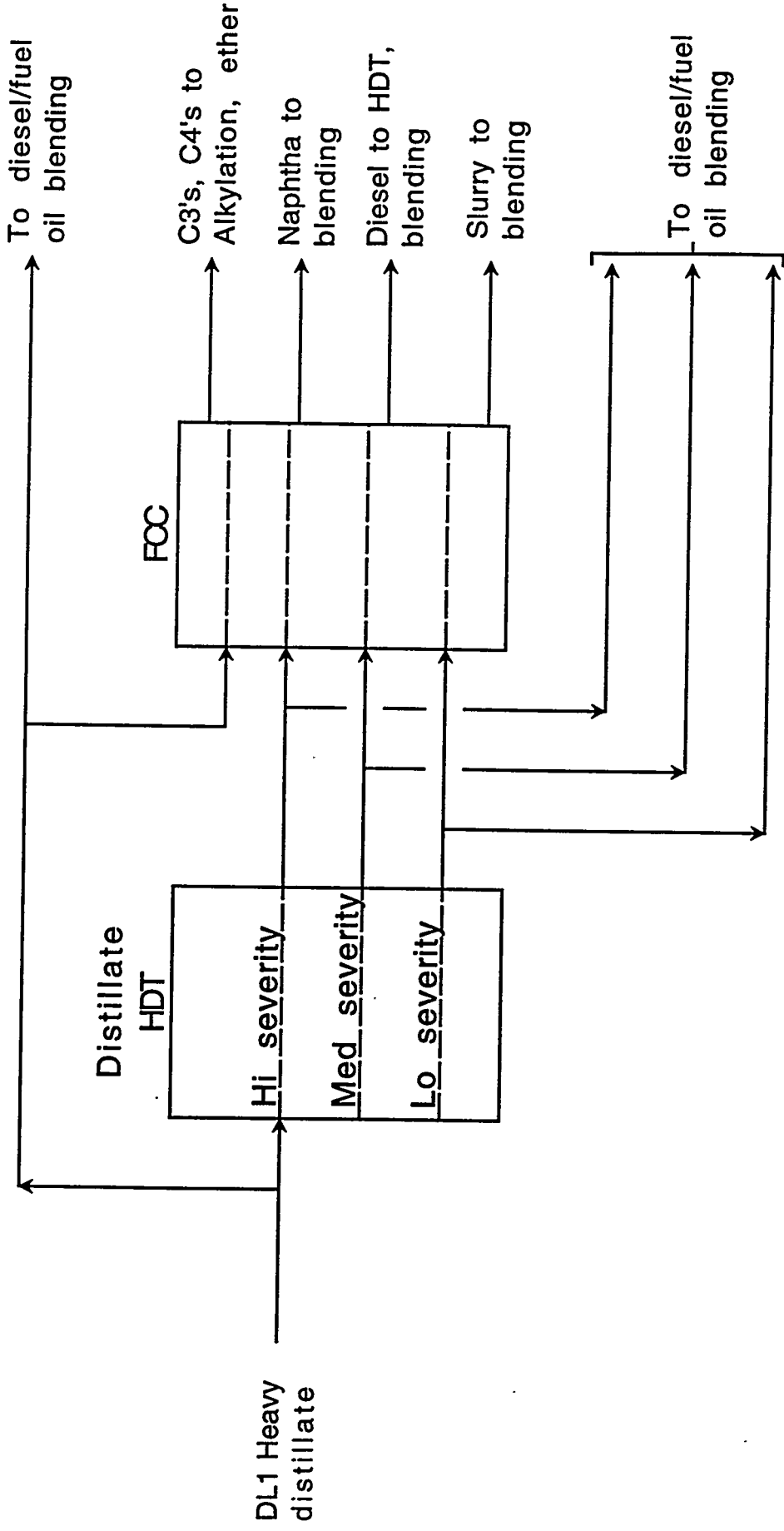
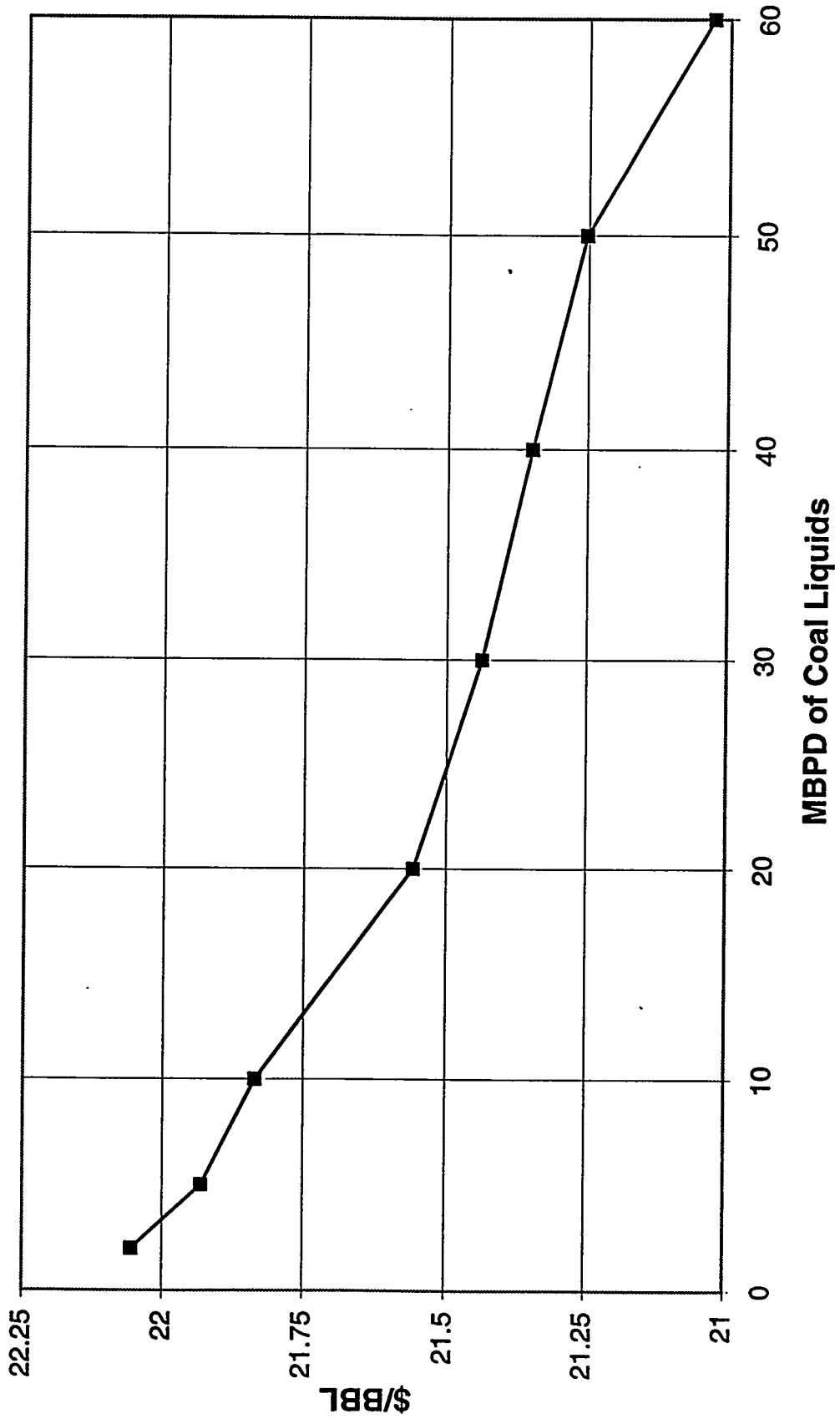


Figure 3-2
DL1 Coal Liquid Value



**Figure 3-3 DL1 Coal Liquid Value
Expansion vs. No Expansion**

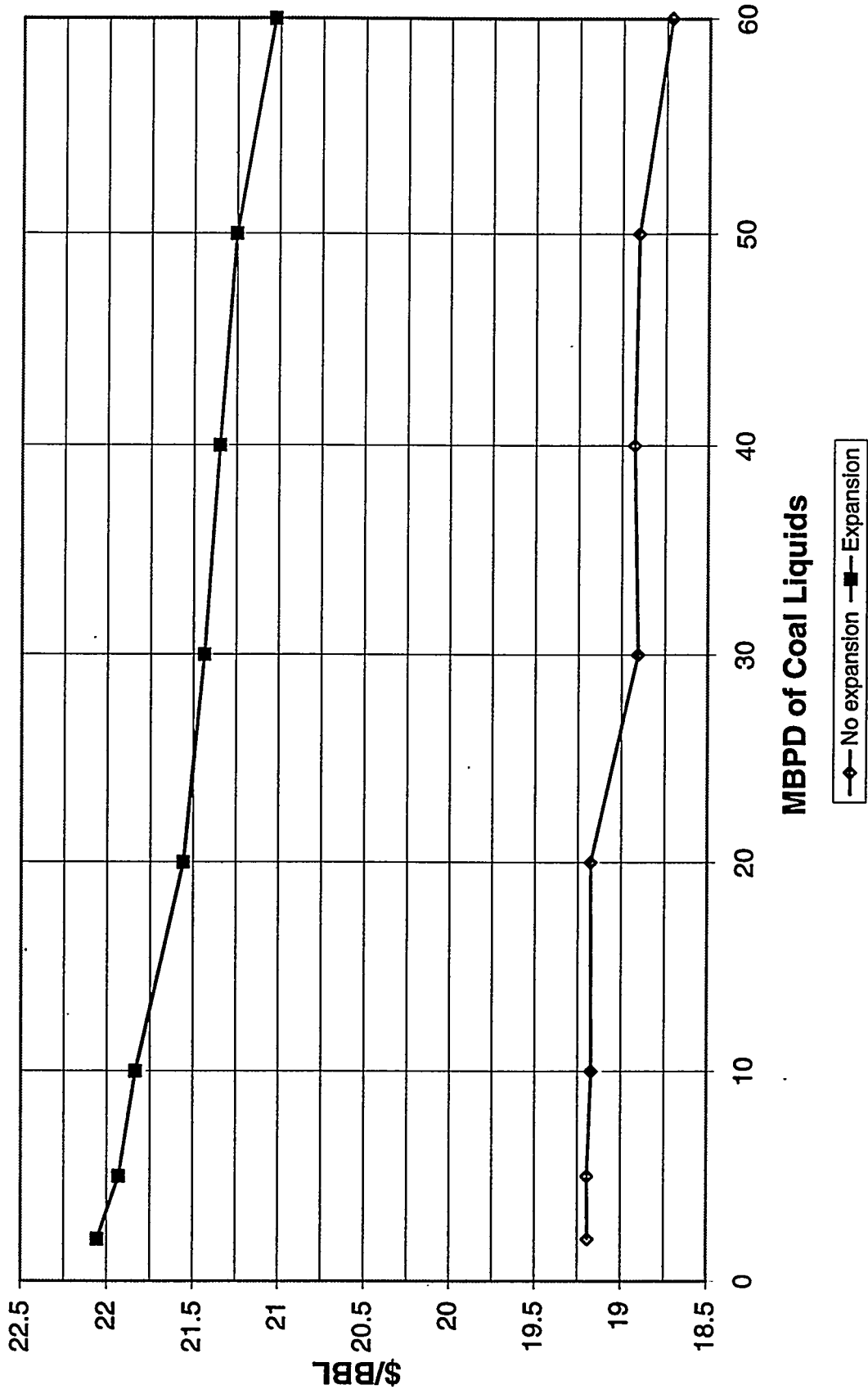
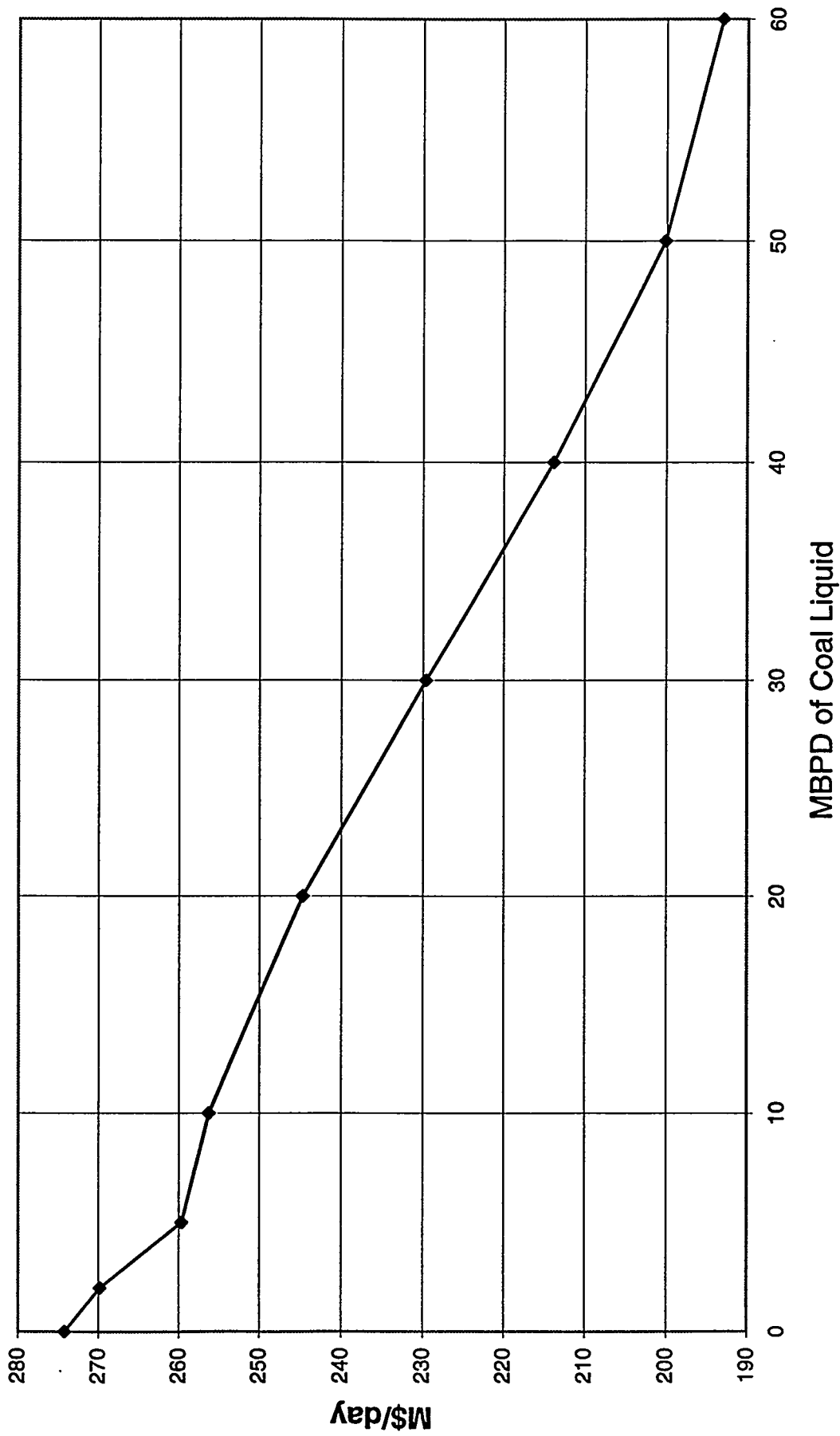


Figure 3-4
Capital Expenditures



**Figure 3-5 DL1 Coal Liquid Value
Effect of Pilot Plant Data**

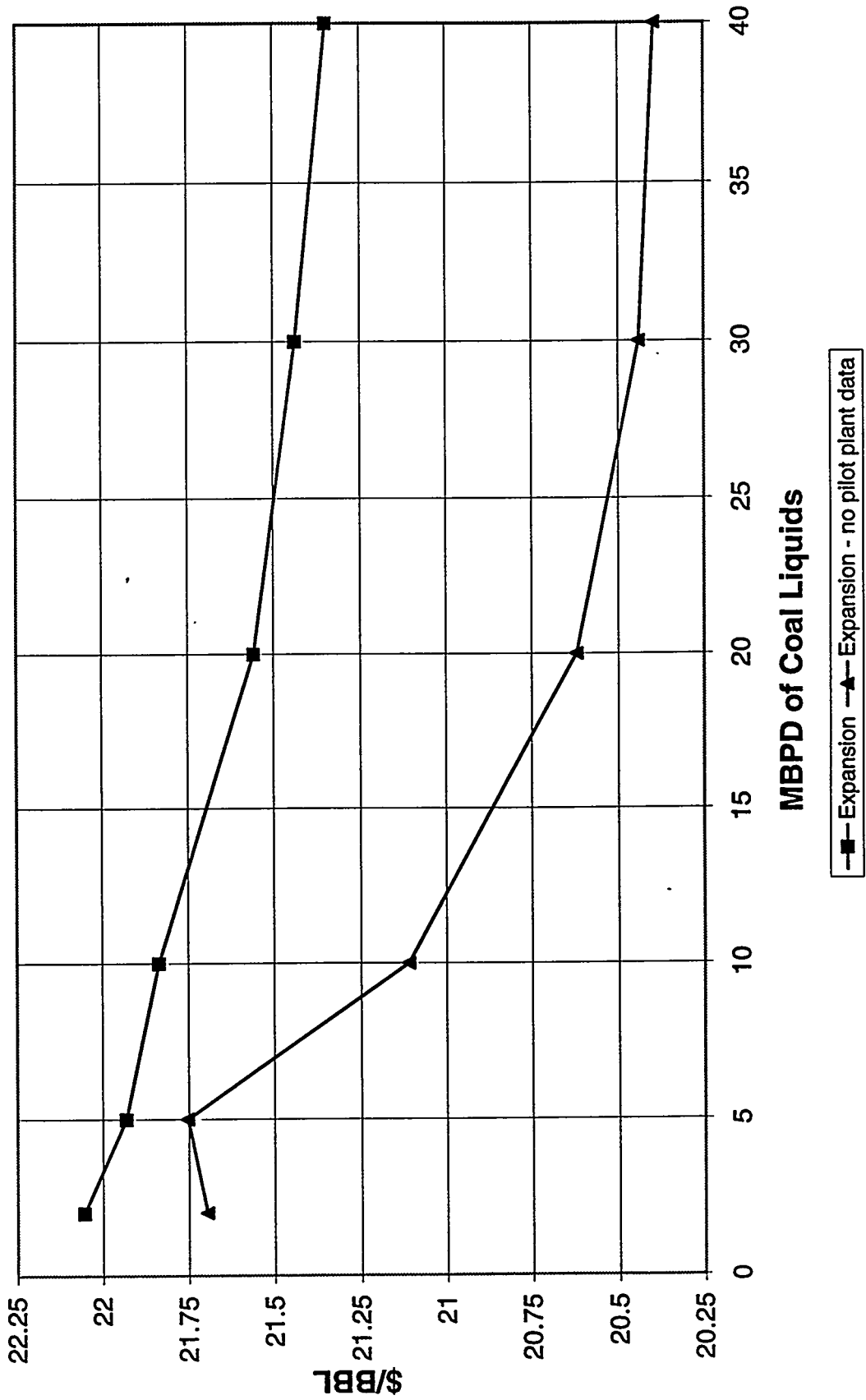


Figure 3-6

SWRI Distillate Hydrotreating
Sulfur Removal Kinetics with Aging Factor

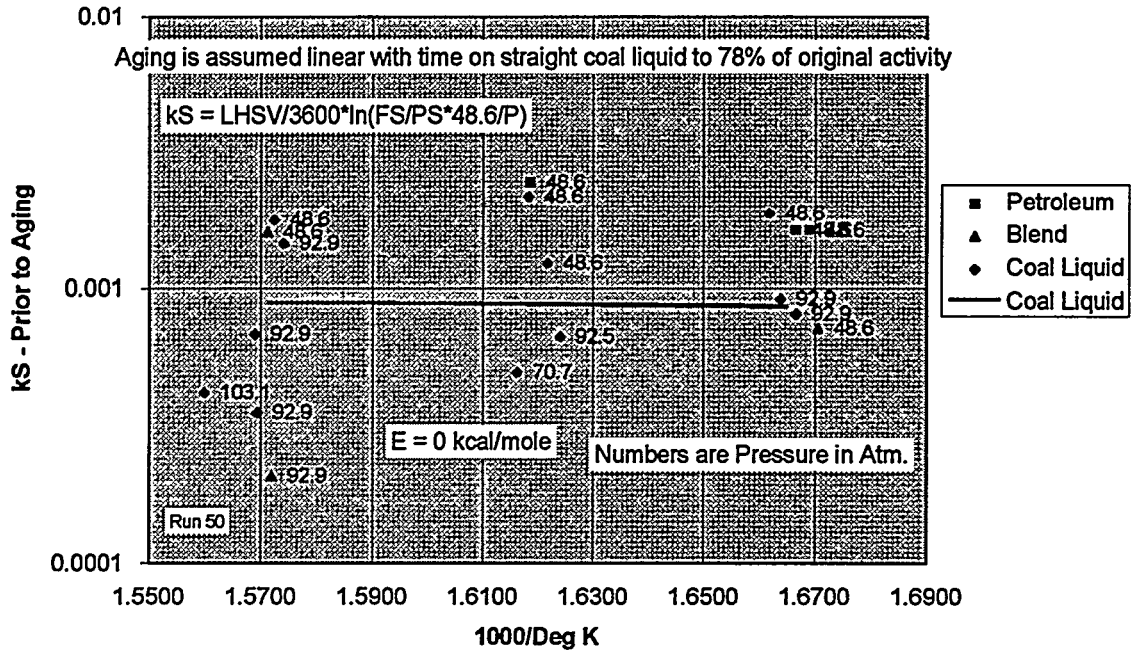


Figure 3-7

SWRI Distillate Hydrotreating
Nitrogen Removal Kinetics with Aging Factor

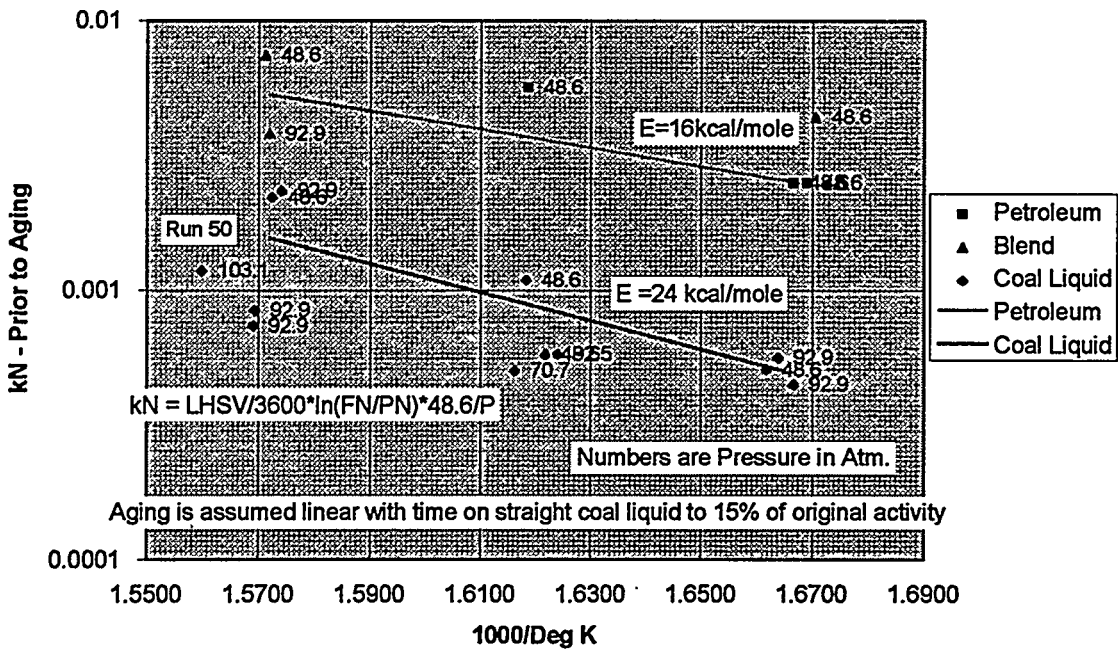


Figure 3-10

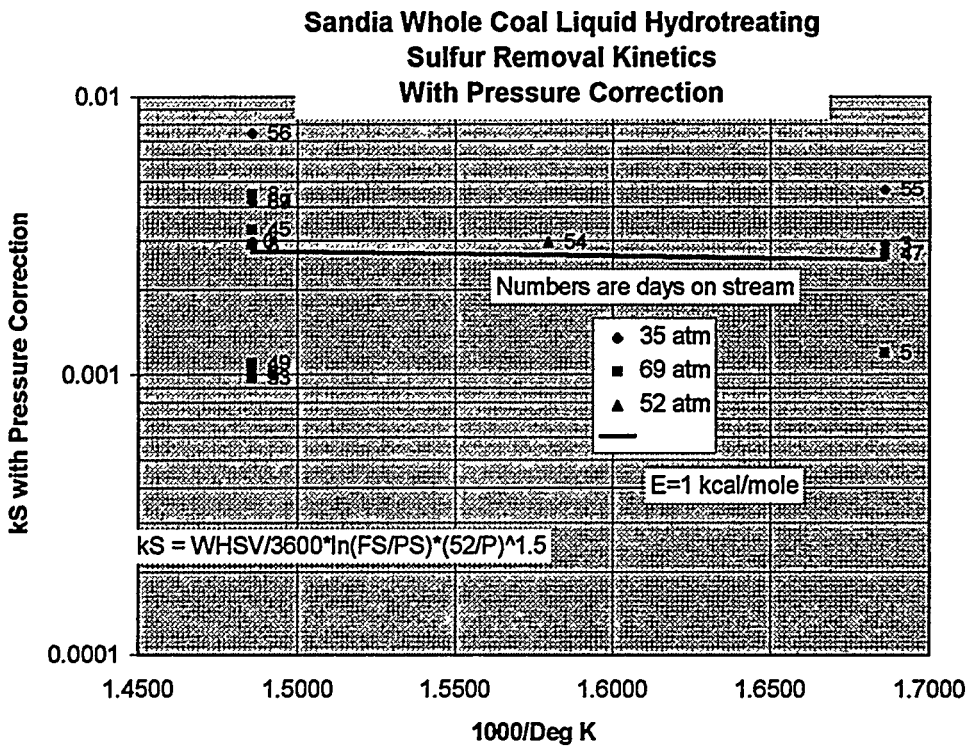


Figure 3-11

