# HYDROTREATING OF COAL-DERIVED LIQUIDS*

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## ABSTRACT

The objective of Sandia's refining of coal-derived liquids project is to determine the relationship between hydrotreating conditions and product characteristics. The coal-derived liquids used in this work were produced in HTI's first proof-of-concept run using Illinois #6 coal. Samples of the whole coal liquid product, distillate fractions of this liquid, and Criterion HDN-60 catalyst were obtained from Southwest Research Inc. Hydrotreating experiments were performed using a continuous operation, unattended, microflow reactor system. A factorial experimental design with three variables (temperature, (310°C to 388°C), liquid hourly space velocity (1 to 3 g/h/cm$^3$(cat)), pressure (500 to 1000 psig $H_2$)) is being used in this project. Sulfur and nitrogen contents of the hydrotreated products were monitored during the hydrotreating experiments to ensure that activity was lined out at each set of reaction conditions. Results of hydrotreating the whole coal liquid showed that nitrogen values in the products ranged from 549 ppm at 320°C, 3 g/h/cm$^3$(cat), 500 psig $H_2$ to <15 ppm at 400°C, 1 g/h/ cm$^3$(cat), 1000 psig $H_2$.

## INTRODUCTION

DOE/PETC's refining of coal liquids program is aimed at determining the most cost effective combination of existing refinery processes and blending options necessary to upgrade direct and indirect coal liquids into transportation fuels that meet year 2000 specifications. A main reason for this program is that coal liquefaction processing has improved significantly since the last refining evaluation was done by Sullivan and Frumkin (1) at Chevron in the early 1980s. In addition, a recent publication by Zhou, Marano and Winschel (2) indicates that blending coal liquids with petroleum may allow refiners to produce specification products with less refining than if each fraction was processed separately. Sandia's role in this program is to develop a database relating hydrotreating parameters to feed and product quality by experimentally evaluating options for hydrotreating whole coal liquids, distillate cuts of coal liquids, petroleum, and blends of coal liquids with petroleum. Sandia's project is unique because our small-scale, continuous operation flow reactor system enables us to evaluate many hydrotreating options in a cost effective manner while keeping waste production to a minimum. Sandia's project is integrated with other program participants including participants in the Refining and End-Use of Coal Liquids Study project (Bechtel, Southwest Research Inc. (SwRI), Amoco, M. W. Kellogg), Hydrocarbon Technology Inc. (HTI, formerly HRI) the MITRE Corporation, and PETC. Sandia's data will be used by other program participants in refinery linear programming models to identify the most cost effective options for introducing and processing coal liquids in a refinery. This paper will cover results obtained from hydrotreating whole coal liquid product from HTI's first proof of concept run with Illinois #6 coal.

## EXPERIMENTAL PROCEDURES

Sandia's experimental procedures included using a factorial experimental design, hydrotreating the whole coal-derived liquid, characterizing the feeds and hydrotreated products, and reporting results to other program participants.

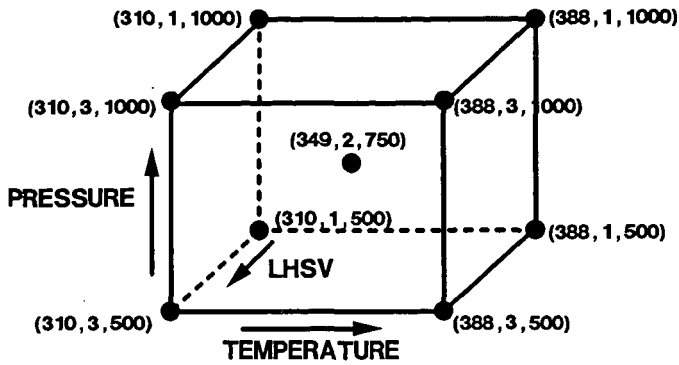
**Continuous Operation Reactor System:** Sandia's hydrotreating studies are being performed using a continuous operation, trickle-bed, microflow reactor system. The system has all required safety features to enable it to be operated unattended. The capabilities of this reactor system include catalyst loadings up to 25 cm$^3$, liquid flow rates from 0.05 to 4 cm$^3$/min, gas flows for hydrogen and nitrogen up to 2 l/min, gas flows for $H_2S/H_2$ up to 0.5 l/min, maximum temperature of 620°C, and a maximum pressure of 1800 psig. The reactor volume is 59 cm$^3$. Four samples can be collected automatically during unattended operation. For liquid hourly space velocities (LHSV) of 1 and 3 g/h/cm$^3$(cat), samples would weigh about 7 and 22 g respectively.

**Factorial Experimental Design:** Based on experience, three parameters were chosen for the factorial experimental design (Figure 1): temperature, pressure, and LHSV. The ranges of hydrotreating conditions used with the design were temperatures of 310 to 388°C, pressures of 500 to 1000 psig $H_2$, and LHSVs from 1 to 3 g/h/cm$^3$(cat). Evaluation of the first set of hydrotreating conditions (388°C, 500 psig $H_2$, 1 g/h/cm$^3$(cat)) was repeated once during the run and once at the end of the run so that effects of catalyst deactivation could be determined. Prior to the use of the testing using the factorial experimental design, two additional sets of reaction conditions were evaluated to see the effects of high pressure and temperature: 388°C, 1500 psig $H_2$, 1 g/h/cm$^3$(cat) and 362°C, 1500 psig $H_2$, 1 g/h/cm$^3$(cat).

**Reactor Feeds and Catalyst:** Sandia received (from SwRI) a sample of fresh Criterion HDN-60 catalyst and about 3.5 gallons of whole coal liquid product that was produced in HTI's first proof-of-concept run using Illinois #6 coal. The whole coal liquid product was collected when HTI's third stage reactor was not on line and while catalyst replacement was being used. Sandia's reactor was loaded with 10g of fresh catalyst that was sulfided in situ using temperature staging. The presulfiding procedure consisted of heating the catalyst to 177°C under He, starting the flow of a 10 mol% $H_2S/H_2$ mixture and maintaining

177°C for 1 hour. The catalyst was then heated to 288°C under flowing $H_2S/H_2$ and maintained at 288°C for 1 hour. Next the catalyst was heated to 404°C under flowing $H_2S$, the temperature was maintained at 404°C for 1 hour. $H_2S$ flow was stopped and $H_2$ flow started.

**Figure 1: Factorial experimental design (temperature = °C, LHSV = g/h/cm³(cat), pressure = psig)**




**Analytical Procedures:** Small samples were collected either manually or automatically throughout the run. Nitrogen and sulfur analyses were used to determine when line out was achieved at each reaction condition. These analyses were performed using an Antek 7000 Sulfur & Nitrogen Analyzer with an automatic sampler. Standards were prepared using phenanthridine for nitrogen, thianthrene for sulfur, toluene for the solvent, and four to five dilutions. Standards were measured at least twice and a polynomial fit of the intensity versus concentration data was used for analysis of unknowns.

## RESULTS AND DISCUSSION

Analyses of the whole coal liquid by HTI, SwRI, and Sandia are shown in Table 1. SwRI used their measured specific gravity. Sandia used 0.9 g/ml for the first and second samples. Data for the second sample was also calculated using SwRI's specific gravity to show the effect of different values. Results show some variability but indicate the whole coal liquid has about 600 ppm nitrogen and 400 ppm sulfur.

Table 1. Sulfur and nitrogen analyses of whole coal liquid. Specific gravities used: HTI unknown; SwRI = 0.8628 g/ml; Sandia = 0.9 g/ml (except as noted).

| HTI | | SwRI | | Sandia | |
|---|---|---|---|---|---|
| N | S | N | S | N | S |
| 581 | 345 | 529 | 405 | 616 | 428 |
| | | | | 621 | 399 |
| | | | | 649* | 417* |

* *Same data as second analysis but calculated with specific gravity = 0.8628.*

The first condition used in the run was 388°C, 1500 psig $H_2$, and LHSV = 1 g/h/cm³(cat). This condition was chosen to line out the freshly sulfided catalyst and to evaluate high severity conditions as a check on parameters for the factorial experimental design. Product analyses showed no detectable nitrogen or sulfur. Therefore, temperature was decreased to 362°C with pressure and LHSV remaining the same. At this condition, nitrogen and sulfur contents of the hydrotreated products were still very low (less than 5 ppm). Since hydrogen pressure is the most restrictive variable in a refinery and because low pressure gives more versatility for processing, the maximum pressure used in the factorial experimental design was decreased to 1000 psig $H_2$. In addition, the lower limit for temperature was also decreased. The goal was to have as broad a range of parameters as possible without decreasing sensitivity to the parameters. The order in which the various conditions were evaluated is shown in Figure 2.

Figure 2 shows the nitrogen contents that were obtained at the various processing conditions. Results were considered lined out when the temperature, pressure and LHSV were relatively constant and the nitrogen and sulfur results were relatively constant. The brackets above each grouping of nitrogen values show which results met these criteria. These results were used to determine the average nitrogen content at that condition. The average nitrogen contents and standard deviations are shown along the X-axis. In addition, the order in which conditions were evaluated is also shown. No data is shown for conditions 6 or 15 because the reactor went down before there were enough data points for analysis. Sample 17 was a large batch (about 890 ml) of hydrotreated product collected at the same condition used for sample 16 (368°C, 1000 psig $H_2$, 3 g/h/cm³(cat)). Sample 19 was a large batch (865 ml) collected at the same condition as sample 16 (368°C, 1000 psig $H_2$, and 1 g/h/cm³(cat)). These large batches were collected so that there would be enough hydrotreated product for additional analyses. Samples 17 had 151 ppm nitrogen, which is a little lower than sample 16, which had 178 ppm nitrogen. Samples 19 and 18 had similar nitrogen contents, 42 and 44 ppm respectively. Both samples 17 and 19 had <7 ppm sulfur.

Figure 2. Nitrogen (ppm) vs reaction conditions. Temperature (°C), Pressure (psig), LHSV g/h/cm³(catalyst). Dashed line = Reactor Shutdown.

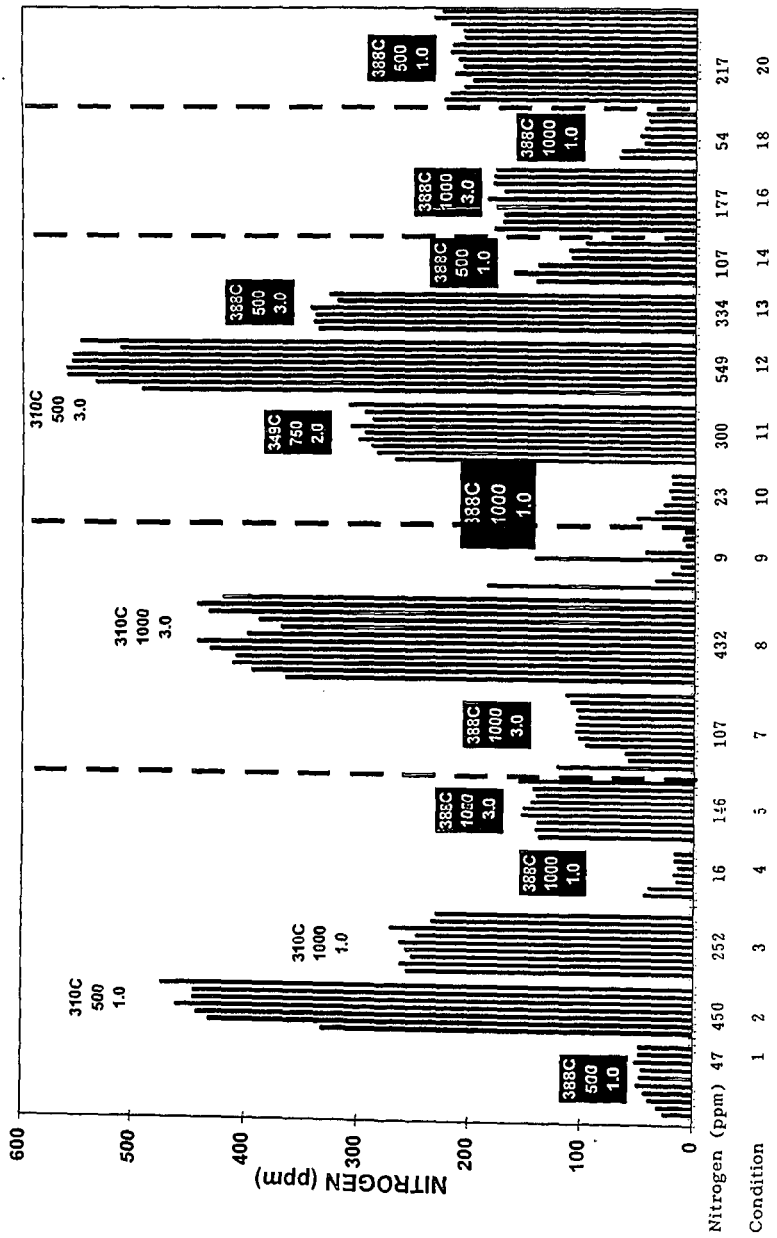



Figure 3 shows nitrogen contents as related to the conditions for the experimental design. Multiple values at a given condition show effects of catalyst deactivation. The total amount of reaction time (excluding down time) for this run was just over 32 days. Comparison of results for conditions 1 and 20 shows the effects of catalyst deactivation. Figure 4 shows the sulfur contents for the conditions of the factorial experimental design.

*Figure 3: Average nitrogen values (ppm) with standard deviations.*

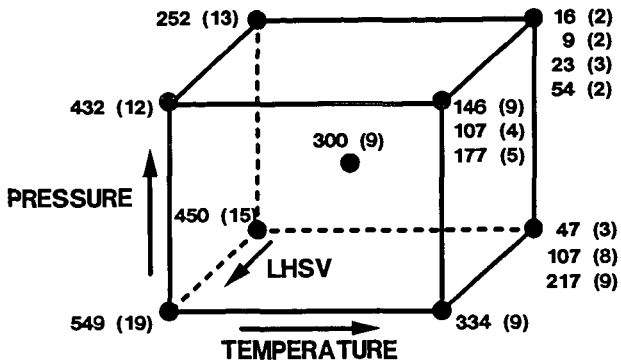
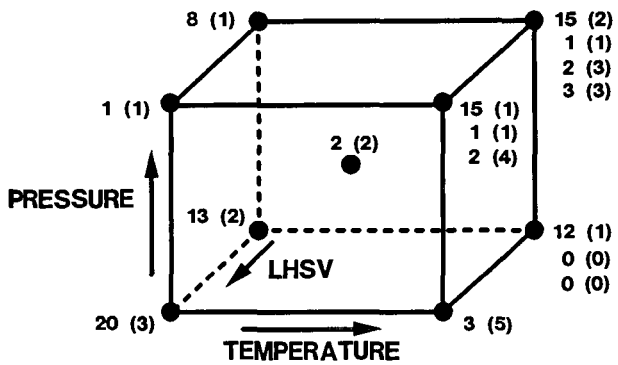



**Figure 4: Average sulfur values (ppm) with standard deviations.**




## CONCLUSIONS AND FUTURE WORK

Results of this work show that good denitrogenation and good desulfurization can be obtained under relatively mild conditions with coal liquids from current processes. At the lowest severity condition, there is only about 10% nitrogen removal, whereas at the highest severity condition, there is about 97% nitrogen removal. Sulfur removal is good over the whole range of conditions and is greater than 95%. Ongoing and future work will involve additional characterization of reaction products by techniques such as distillation, PONA or PIONA analyses, density determinations, and proton NMR for hydrogen distributions. Results will be corrected for catalyst deactivation and analyzed statistically to determine the effects of process conditions on product quality. Future hydrotreating experiments will be performed with distillate fractions of this coal liquid and with coal-derived liquids from subbituminous coal.

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**References:**

1) Sullivan, R. F., Frumkin, H. A., ACS Div. of Fuel Chem. Preprints 31(2), 325, 1986.
2) Zhou, P.-Z., Marano, J. J., Winschel, R. A., ACS Div. of Fuel Chem. Preprints 37(4), 1847, 1992.