

COMPARISON OF THE ACTIVITIES OF FINE-PARTICLE SIZE CATALYSTS*

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ABSTRACT

The objectives of Sandia's fine-particle size catalyst testing project are to evaluate and compare the activities of the fine-particle size catalysts being developed in DOE/PETC's Advanced Research Coal Liquefaction Program by using standard coal liquefaction test procedures. The standard procedures use Blind Canyon coal, phenanthrene as the reaction solvent, and a factorial experimental design with temperatures from 350°C to 400°C, reaction times from 20 to 60 minutes, and catalyst loadings up to 1 wt%. Catalytic activity is measured in terms of tetrahydrofuran conversion, heptane conversion, the amount of 9,10-dihydrophenanthrene in the product, and the gas yield. Several catalysts have been evaluated including a commercially available pyrite, a sulfated iron oxide from the University of Pittsburgh, and several preparations of 6-line ferrihydrites from Pacific Northwest Laboratories. Results have demonstrated that significant differences in activity can be detected among these catalysts.

INTRODUCTION

There are several potential advantages of using cheap, unsupported, fine-particle size (<40 nm) catalysts in direct coal liquefaction. These include improved coal/catalyst contact due to good dispersion⁽¹⁾ of the catalyst, and the potential for using low quantities of catalyst ($\leq 0.5\%$ based on the weight of coal) because of their very high surface areas. These catalysts could be combined with the coal as either active catalysts or catalyst precursors that would be activated in situ. Research efforts that have been performed to develop fine-particle size, unsupported catalysts for direct coal liquefaction⁽²⁾ indicate that the use of these catalysts could result in significant process improvements, such as enhanced yields of desired products, less usage of supported catalyst, and possibly lower reaction severities. These improvements would result in decreased costs for coal liquefaction products.

The Advanced Research (AR) Coal Liquefaction Program, which is managed by the United States Department of Energy's Pittsburgh Energy Technology Center (PETC), is funding numerous research efforts aimed at developing these types of catalysts for direct liquefaction. Although most catalyst developers have the capability of testing the performances of the catalysts they develop, it is difficult if not impossible to compare results among researchers because of the different testing procedures used. Therefore, to guide the research and development efforts for these fine-particle size, unsupported catalysts, it is necessary to evaluate each catalyst's performance under standard test conditions so that the effects of catalyst formulations from different laboratories can be compared.

The objectives of this project are to develop standard coal liquefaction test procedures, to perform the testing of the novel fine-particle size liquefaction catalysts being developed in the PETC AR Coal Liquefaction program, and to evaluate reaction mechanisms. Previously reported work^(3,4) described the reaction procedures, product workups, and the factorial experimental design to be used in this project as well as results obtained by testing a commercially available pyrite and the University of Pittsburgh's sulfated iron oxide catalyst. This paper will describe the recent results obtained from evaluating a Pacific Northwest Laboratories' (PNL) catalyst.

EXPERIMENTAL SECTION

Materials. The coal being used in this project is the DECS-17 Blind Canyon Coal obtained from the Penn State Coal Sample Bank. It is a high volatile A bituminous coal with 0.36% iron, 0.02% pyritic sulfur, and 7.34% mineral matter (on a dry basis). The particle size is -60 mesh. Phenanthrene is used as the reaction solvent. Elemental sulfur was added to the reactors to sulfide the catalyst precursors.

Microautoclave Reactors. The testing is performed using batch microautoclaves made of type 316 stainless steel components. The total volume of a reactor is 43 cm³ with a liquid capacity of 8 cm³. The reactors are loaded with 1.67g coal and 3.34g reaction solvent. If the reaction is catalytic, the catalyst loading will be either 0.5 wt% or 1.0 wt% on an as-received coal basis. The amount of sulfur addition is specified by the catalyst developer. The reactors are charged to 800 psig H₂ (cold charge) and heated to reaction temperatures in fluidized-sand baths. Temperatures, pressures and times are recorded with a digital data acquisition system every 30 seconds during the course of the reactions. Following the heating period, the reactors are rapidly cooled to ambient temperature in a water bath and a gas sample is collected. The reaction data is analyzed to determine the actual reaction time and the averages and standard deviations for reaction temperature and pressure. Heat-up times and cooling times are also determined.

Product Workup Procedures. The reaction products are rinsed out of the reactors with tetrahydrofuran (THF). THF and heptane solvent solubilities are measured using a Millipore 142 mm diameter pressure filtration device with air pressurization and Duropore (0.45 micron) filter paper. The filter cakes are rinsed twice with THF or heptane as appropriate. After the filtrations are complete, the filter papers are dried under vacuum at 70°C, cooled to room temperature and weighed to determine the insoluble portions. The THF soluble material is quantitatively sampled for gas chromatographic (GC) analysis, which is used to determine the reaction solvent recovery and composition. The THF is removed from the solubles by rotary evaporation prior to determining the heptane conversion. The quantity of gases (CO, CO₂, CH₄, C₂H₆) produced in a reaction is calculated using the postreaction vessel temperature and pressure with the ideal gas law and the mole percents in the gas sample as determined using a Carle GC and standard gas mixtures.

Factorial Experimental Design and Analysis. The factorial experimental design (Figure 1) evaluates the effects of three variables at two levels: temperature (350 and 400°C), time (20 and 60 minutes), and catalyst loading (0 and 1 wt% based on as-received coal). With this full factorial experimental design, the experimental results are evaluated for all combinations of levels of the three variables so that 2³ evaluations are required. Additional reactions are also performed at the center point of this cubic design. An Analysis of Variance (ANOVA) is performed to estimate the effects of the experimental variables and to statistically test their significance. Replication of the experiments is used to estimate measurement error and to reduce its effect on the estimated effects of the variables. Models are constructed using the estimates of the effects of the variables to calculate the expected experimental results for specified sets of reaction conditions⁵⁾. The controlled factors used in the ANOVA are the measured average reaction temperature, measured reaction time, and the actual weight of catalyst used.

Catalyst. J. Linehan (PNL) supplied Sandia with the -325 mesh fraction of a 6-line ferrihydrite catalyst precursor for evaluation using the full factorial experimental design. No pretreatment was required. Linehan recommended testing this material with a 1:1 sulfur to catalyst precursor ratio on a weight basis. All reactions including thermal reactions had the same amount of added sulfur, so the impact of sulfur could be determined.

RESULTS and DISCUSSION

Experimental Results of Testing PNL's 6-Line Ferrihydrite Catalyst

The testing of PNL's 6-line ferrihydrite catalyst precursor plus sulfur was performed by two operators: operator 1 (a previous operator) and operator 2 (the current operator). The measured experimental results obtained by operator 2 using the full factorial experimental design are given in Table 1. The reproducibility of the measured THF conversions is good for most of the data. However, results at 350°C for 60 minutes show high variability. These reaction products were significantly more difficult to filter than those from other conditions; the reason for this is unknown. Negative values for heptane conversion occur because the values are very close to zero, and the variability is high.

Modeling of Experimental Results

Results of the statistical analyses of the data in Table 1 are given in Tables 2 and 3. These tables show calculated estimates of the effects of the variables and the interactions among variables over the region bounded by the cubic design, calculated estimates of the mean values of the reaction results at the nine sets of reaction conditions, standard errors of the estimates, the means of the measured values in Table 1, and R² values for the fit of the model to the data. The constant represents the estimate of the reaction results when all variables are at their low levels: temperature=350°C, time=20 minutes, and catalyst loading=0%. The variables with statistically significant effects are listed under the constant; the larger the estimated value, the greater the effect. The estimate of experimental error, which is presented as a standard deviation, accounts for all variability in the data not accounted for by the fixed and random effects of the model. Included in this estimate are variabilities due to measurement, process and material inconsistencies, and modeling inadequacies. The estimates of reaction results at the nine sets of reaction conditions are calculated from the model and can be compared to the means of the measured values. The standard errors of the estimated results at cube corners are derived from the experimental error, which pertains to a single measurement.

The results of the modeling show that temperature has the largest effect on both the THF (33.6%) and heptane (17.5%) conversions. The catalyst has the second largest effect on THF conversion (16.6%) but no significant effect on heptane conversion. The lack of catalytic effect on heptane conversion was also observed when pyrite and the University of Pittsburgh's catalyst were evaluated.^{6,4)} The other significant parameters for THF conversion are time (11.5%) and the temperature-catalyst interaction (9.3%). For heptane conversion the other significant parameters are the time-temperature interaction (7.5%) and time (2.8%). The significant effects for gas yield are temperature (0.91%), the time-temperature interaction (0.43%) and time (0.23%). The 9,10-dihydrophenanthrene (DHP), which was formed by hydrogenation of phenanthrene, in the reaction product has the most complicated model with six parameters having significant effects: temperature-catalyst interaction (2.83%), time-catalyst interaction (2.39%), temperature (1.03%), catalyst (0.85%), time-temperature interaction (0.52%), and time (0.40%). The R-square values for the fit of the models were 0.94 for THF conversion and 0.96 for the other three models.

Procedure for Estimating Experimental Results from the Linear Model. To use one of the linear models in Tables 2 or 3 to determine an estimate for an experimental result within the cube, first calculate proportional levels for each variable that has a significant effect. For example, to calculate THF conversion for a reaction at 375°C for 40 minutes with 0.5% catalyst:

$$P_{TIME} = (40 \text{ min} - 20 \text{ min}) / (60 \text{ min} - 20 \text{ min}) = 0.5$$

$$P_{TEMP} = (375^\circ\text{C} - 350^\circ\text{C}) / (400^\circ\text{C} - 350^\circ\text{C}) = 0.5$$

$$P_{CAT} = (0.5 \text{ wt}\% - 0 \text{ wt}\%) / (1.0 \text{ wt}\% - 0 \text{ wt}\%) = 0.5$$

These calculated p's are used in the following equation (see Table 2):

$$K + P_{TIME} \cdot a + P_{TEMP} \cdot b + P_{CAT} \cdot c + P_{TEMP} \cdot P_{CAT} \cdot d$$

where K is the estimated constant (18.5%), a is the estimated time effect (11.5%), b is the estimated temperature effect (33.6%), c is the estimated catalytic effect (16.6%) and d is the estimated temperature-catalyst interaction (9.3%). The calculated THF conversion is 51.7, which agrees within round off errors with the value in Table 2. For calculating a result for any point within the region

bounded by the cube, the p values will range from 0 to 1. Extrapolation beyond the limits of the cube is usually not recommended.

Evaluation of Operator Effects

To compare results from the University of Pittsburgh's catalyst and PNL's catalyst, it is necessary to evaluate operator effects. The testing of PNL's catalyst using the full experimental design (Table 1) was performed by operator 2, whereas operator 1 performed the evaluation of the University of Pittsburgh's catalyst as well as a limited number of reactions on PNL's catalyst. The experiments performed by each operator on PNL's catalyst are shown in Table 4. A statistical analysis of the THF conversion results for operator 2 (Table 1) showed that a model (Table 2) with significant effects for temperature, catalyst, time and the temperature-catalyst interaction fit the data well ($R^2=0.94$). To compare the results from the two operators, operator 2's data for reactions at 350°C for 20 minutes were not used because operator 1 had not performed these reactions. Results of the comparison are shown in Table 5. The values in Table 5 for the model of THF conversion obtained by operator 2 are slightly different from those in Table 2 because Table 2's results included reactions performed at 350°C for 20 minutes.

Comparison of the constants for the two operators shows that there are significant differences in THF conversions at 350°C for 20 minutes without catalyst. Using these two models to calculate THF conversion at 375°C for 40 minutes with 0.5% catalyst (the center point of the experimental design) gave 56.7% for operator 1 and 49.9% for operator 2. Calculating results at 400°C for 60 minutes with 1wt% catalyst gave a THF conversion of 88.4% for operator 1 and a similar value of 87.5% for operator 2. Comparison of these three sets of calculated results shows that the biggest differences between the two operators were at the lowest severity conditions. Because of these differences, only the high severity results are compared in Table 6. The estimates of error variability (within their respective data sets) were comparable for the two operators. Similar conclusions were obtained for comparison of heptane conversion results between the two operators. Operator 1 had higher conversions than operator 2, particularly at low temperature. Unfortunately, a model for heptane conversion could not be fit for operator 1 results, because the time-temperature interaction is important for heptane conversion, and operator 1 did not perform tests at 350°C for 20 minutes.

Comparison of Catalysts

A comparison of results (Table 6) from PNL's catalyst with results from the University of Pittsburgh's catalyst and pyrite at the higher severity conditions indicates that PNL's catalyst is the most active. THF results show that PNL's catalyst increases conversion by 25.8% over its thermal baseline with 1% sulfur addition. The University of Pittsburgh's catalyst and pyrite increase conversion above their respective baseline values by 19.3% and 18.5% respectively. Comparison of the three baseline results shows that sulfur addition has an effect on THF conversion. Therefore, the best comparison among these three catalysts is obtained by using the thermal baseline without sulfur addition (54.9%). Using this baseline gives 34.5% total conversion for PNL's catalyst, 27.4% conversion for the University of Pittsburgh's catalyst and 18.5% for pyrite.

The model for the amount of DHP (Table 3) in the recovered reaction solvent from experiments performed with PNL's catalyst involved the three main effects (time, temperature, catalyst) as well as the three two-way interactions (time-temperature, time-catalyst, temperature-catalyst). This model is somewhat simpler than those obtained for pyrite and the University of Pittsburgh's catalyst, because it doesn't have the three-way interaction. The amount of DHP present in the product from the 400°C reaction for 60 minutes with PNL's catalyst was 8.41%. The University of Pittsburgh's catalyst yielded 5.35% DHP and pyrite yielded 3.88%. These results indicate that PNL's catalyst has the highest hydrogenation activity.

CONCLUSIONS

Results of the evaluation of PNL's 6-line ferrihydrite with 1 wt% sulfur addition have shown that it is more active than either the University of Pittsburgh's sulfated iron oxide with 2 wt% sulfur addition or pyrite. At 400°C for 60 minutes, THF conversion obtained with PNL's catalyst was 89.4% versus 82.3% with the University of Pittsburgh's catalyst, and 73.4% with pyrite. Analyses of DHP in the reaction products show that PNL's catalyst has the highest hydrogenation activity. PNL's catalyst gave 8.41% DHP, versus 5.35% for the University of Pittsburgh's catalyst, and 3.88% for pyrite. There were no catalytic effects for either heptane conversion or gas yield. Future work will involve testing additional catalysts being developed in DOE/PETC's program and evaluating better analytical methods for determining product quality.

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REFERENCES

1. Huffman, G. P.; Ganguly, B.; Zhao, J.; Rao, K. R. P. M.; Shah, N.; Feng, Z.; Huggins, F. E.; Taghiei, M. M.; Lu, F.; Wender, I.; Pradhan, V. R.; Tierney, J. W.; Seehra, M. S.; Ibrahim, M. M.; Shabtai, J.; Eyring, E. M.; Energy Fuels 1993, 7, 285-296.
2. Pradhan, V. R.; Tierney, J. W.; Wender, I.; Energy & Fuels 1991, 5, 497-507.
3. Stohl, F. V.; Diegert, K. V.; Energy & Fuels 1994, 8, 117-123.
4. Stohl, F. V.; Diegert, K. V.; Gugliotta, T. P.; Proc. Coal Liquefaction and Gas Conversion Contractors' Review Conf., September 27-29, 1993, Pittsburgh, PA. p. 123-135.
5. John, P. W. M.; *Statistical Design and Analyses of Experiments*; MacMillan Co., New York, 1971.

Figure 1. Factorial experimental design (temperature = °C, time = minutes, catalyst loading = wt% of as-received coal).

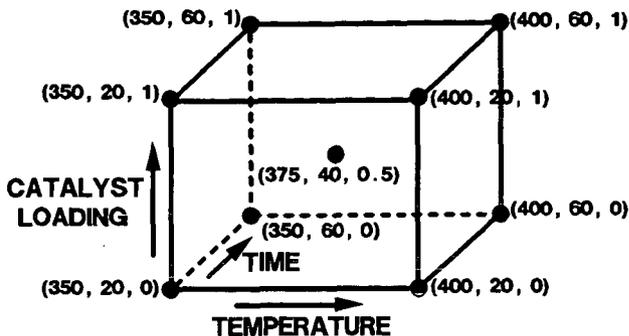


Table 1. Measured experimental results from operator 2.

| TEMP. (°C) | TIME (min) | CAT. (mg) | THF Conv. (%) | Heptane Conv. (%) | Gas (%dmmf) | DHP (%)* |
|------------|------------|-----------|---------------|-------------------|-------------|----------|
| 350.9 | 20.5 | 0 | 21.86 | -2.63 | 0.34 | 0.33 |
| 349.4 | 20.5 | 0 | 17.28 | -4.92 | 0.30 | NA** |
| 350.4 | 20.5 | 0 | 21.14 | -1.56 | 0.25 | NA |
| 350.2 | 60.5 | 0 | 26.39 | 2.47 | 0.60 | 0.63 |
| 350.2 | 60.7 | 0 | 31.49 | 1.69 | 0.52 | 0.72 |
| 350.5 | 60.5 | 0 | 23.31 | -2.15 | 0.44 | 0.60 |
| 349.9 | 59.0 | 0 | 26.98 | 1.43 | NA | 0.54 |
| 400.0 | 20.5 | 0 | 50.06 | 14.05 | 1.23 | 1.09 |
| 399.8 | 20.5 | 0 | 47.33 | 13.00 | 1.16 | 1.05 |
| 400.1 | 60.5 | 0 | 63.86 | 23.40 | 1.98 | 2.27 |
| 399.7 | 60.5 | 0 | 61.69 | NA | 1.82 | 2.36 |
| 375.1 | 40.5 | 8.4 | 63.52 | 7.90 | 0.83 | 3.97 |
| 374.8 | 40.5 | 8.6 | 56.89 | 8.59 | 0.78 | 4.00 |
| 374.8 | 40.5 | 8.1 | 62.12 | 5.19 | 0.76 | 3.78 |
| 375.1 | 41.0 | 8.3 | 57.11 | 8.02 | 0.75 | 2.96 |
| 375.4 | 40.5 | 8.4 | 54.24 | 8.48 | 0.78 | 3.67 |
| 350.5 | 20.5 | 16.6 | 35.01 | 0.56 | 0.31 | 1.04 |
| 351.2 | 20.5 | 17.2 | 32.04 | -3.15 | 0.29 | 0.95 |
| 350.0 | 61.5 | 17.4 | 53.57 | -1.09 | 0.54 | 4.10 |
| 350.2 | 61.0 | 16.8 | 52.96 | 3.22 | 0.56 | 4.30 |
| 351.2 | 60.5 | 17.3 | 38.82 | 0.10 | 0.48 | 4.03 |
| 350.0 | 61.0 | 17.0 | 42.26 | -3.34 | 0.49 | 4.46 |
| 399.7 | 20.5 | 16.7 | 72.80 | 16.92 | 1.11 | 5.04 |
| 400.2 | 20.5 | 17.0 | 75.90 | 16.63 | 1.33 | 5.27 |
| 399.9 | 60.5 | 16.5 | 88.85 | 26.04 | 2.06 | 8.03 |
| 400.2 | 61.0 | 16.6 | 90.38 | 27.65 | 1.65 | 8.16 |

* Percent in recovered reaction solvent.

** NA= Not available.

Table 2. Results of the statistical analyses of operator 2's measured THF and heptane conversion data.

| Parameter | THF Conversion (%) | | | HEPTANE Conversion (%) | | |
|--------------------|--------------------|----------------|------------|------------------------|----------------|------------|
| | Model Estimate | Meas'd Average | Std. Error | Model Estimate | Meas'd Average | Std. Error |
| Constant* | 18.5 | | 2.5 | -2.9 | | 1.0 |
| Time | 11.5 | | 2.5 | 2.8 | | 1.2 |
| Temperature | 33.6 | | 3.5 | 17.5 | | 1.5 |
| Catalyst | 16.6 | | 3.1 | | | |
| Time-Temp. Int. | | | | 7.5 | | 2.0 |
| Temp.-Cat. Int. | 9.3 | | 5.0 | | | |
| Experimental Error | 5.6 | | | 2.1 | | |
| 350°C, 20min, 0% | 18.5 | 20.1 | 2.5 | -2.9 | -3.0 | 1.0 |
| 350°C, 60min, 0% | 30.0 | 27.0 | 2.4 | -0.1 | 0.9 | 0.7 |
| 400°C, 20min, 0% | 52.1 | 48.7 | 3.0 | 14.6 | 13.5 | 1.1 |
| 400°C, 60min, 0% | 63.6 | 62.8 | 3.0 | 24.8 | 23.4 | 1.2 |
| 375°C, 40min, 0.5% | 51.6 | 58.8 | 1.1 | 9.1 | 7.6 | 0.4 |
| 350°C, 20min, 1% | 35.1 | 33.5 | 1.8 | -2.9 | -1.3 | 1.0 |
| 350°C, 60min, 1% | 46.6 | 46.9 | 2.3 | -0.1 | -0.3 | 0.7 |
| 400°C, 20min, 1% | 77.9 | 74.4 | 3.0 | 14.6 | 16.8 | 1.1 |
| 400°C, 60min, 1% | 89.4 | 89.6 | 3.0 | 24.8 | 26.8 | 1.2 |
| R ² | 0.94 | | | 0.96 | | |

* Value calculated for a thermal reaction at 350°C for 20 minutes with 1% sulfur addition.

Table 3. Results of the statistical analyses of operator 2's measured gas yields and DHP in the recovered solvent.

| Parameter | GAS YIELD (%dmmf coal) | | | DHP (%) | | |
|--------------------|------------------------|----------------|------------|----------------|----------------|------------|
| | Model Estimate | Meas'd Average | Std. Error | Model Estimate | Meas'd Average | Std. Error |
| Constant* | 0.25 | | 0.05 | 0.40 | | 0.42 |
| Time | 0.23 | | 0.07 | 0.40 | | 0.46 |
| Temperature | 0.91 | | 0.08 | 1.03 | | 0.49 |
| Catalyst | | | | 0.85 | | 0.48 |
| Time-Temp. Int. | 0.43 | | 0.11 | 0.52 | | 0.49 |
| Time-Cat. Int. | | | | 2.39 | | 0.49 |
| Temp.-Cat. Int. | | | | 2.83 | | 0.48 |
| Experimental Error | 0.12 | | | 0.49 | | |
| 350°C, 20min, 0% | 0.25 | 0.30 | 0.05 | 0.40 | 0.33 | 0.42 |
| 350°C, 60min, 0% | 0.48 | 0.52 | 0.04 | 0.80 | 0.62 | 0.24 |
| 400°C, 20min, 0% | 1.15 | 1.20 | 0.06 | 1.43 | 1.07 | 0.32 |
| 400°C, 60min, 0% | 1.82 | 1.90 | 0.06 | 2.35 | 2.31 | 0.32 |
| 375°C, 40min, 0.5% | 0.92 | 0.78 | 0.02 | 2.97 | 3.78 | 0.11 |
| 350°C, 20min, 1% | 0.25 | 0.30 | 0.05 | 1.25 | 0.99 | 0.32 |
| 350°C, 60min, 1% | 0.48 | 0.52 | 0.04 | 4.04 | 4.22 | 0.23 |
| 400°C, 20min, 1% | 1.15 | 1.22 | 0.06 | 5.10 | 5.16 | 0.32 |
| 400°C, 60min, 1% | 1.82 | 1.86 | 0.06 | 8.41 | 8.10 | 0.31 |
| R ² | 0.96 | | | 0.96 | | |

* Value calculated for a thermal reaction at 350°C for 20 minutes with 1% sulfur addition.

Table 4. Number of reactions completed by each operator for PNL's catalyst.

| TARGET CONDITIONS | | | NUMBER OF REACTIONS | |
|-------------------|------------|-----------------|---------------------|------------|
| TEMP. (°C) | TIME (min) | CATALYST (wt%)* | OPERATOR 1 | OPERATOR 2 |
| 350 | 20 | 0 | 0 | 3 |
| 350 | 60 | 0 | 1 | 4 |
| 400 | 20 | 0 | 1 | 2 |
| 400 | 60 | 0 | 2 | 2 |
| 375 | 40 | 0.5 | 0 | 5 |
| 350 | 20 | 1 | 0 | 2 |
| 350 | 60 | 1 | 1 | 4 |
| 400 | 20 | 1 | 1 | 2 |
| 400 | 60 | 1 | 3 | 2 |

* Precursor based on as-received coal.

Table 5. Models for THF conversion without the 350°C, 20 minute experimental results.

| PARAMETER | ESTIMATES (%) | |
|----------------------|---------------|------------|
| | OPERATOR 1 | OPERATOR 2 |
| Constant* | 28.0 | 17.0 |
| Time | 12.0 | 11.9 |
| Temperature | 25.0 | 32.7 |
| Catalyst | 17.2 | 16.4 |
| Temperature-Catalyst | 6.2 | 9.5 |
| Experimental Error | 3.2 | 4.3 |

* Value calculated for a thermal reaction at 350°C for 20 minutes with 1% sulfur addition.

Table 6. Calculated results (400°C, 60 minutes).

| | THF Conv. (%) | DHP (%)* |
|---|---------------|----------|
| 1wt%** PNL Cat. Precursor + 1wt%** Sulfur | 89.4 | 8.41 |
| Thermal + 1wt% Sulfur | 63.6 | 2.35 |
| 1wt% U. of Pitt. Cat. Precursor + 2wt% Sulfur | 82.3 | 5.35 |
| Thermal + 2wt% Sulfur | 63.0 | 2.43 |
| 1wt% Pyrite | 73.4 | 3.88 |
| Thermal | 54.9 | 1.08 |

* Percent of recovered reaction solvent.

** Weight percents based on as-received coal.