Title: **EVALUATION OF WEST VIRGINIA UNIVERSITY'S IRON CATALYST IMPREGNATED ON COAL**

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Objective: To evaluate and compare the activities/selectivities of fine-particle size catalysts being developed in the DOE/PETC Advanced Research (AR) Coal Liquefaction program by using standard coal liquefaction activity test procedures.

Accomplishments: Previously reported results have described the standard test procedure developed at Sandia to evaluate fine-particle size iron catalysts being developed in DOE/PETC's AR Coal Liquefaction Program and described the evaluation of several catalysts (commercially available pyrite, University of Pittsburgh's (U. of Pitt.) catalyst, Pacific Northwest Laboratories' (PNL) catalyst) using these procedures. The test uses DECS-17 Blind Canyon Coal, phenanthrene as the reaction solvent, and a factorial experimental design that enables evaluation of a catalyst over ranges of temperature (350 to 400°C), time (20 to 60 minutes), and catalyst loading (0 to 1 wt% on an as-received coal basis). Recent work has focused on the evaluation of West Virginia University's (WVU) iron catalyst that WVU impregnated on DECS-17 Blind Canyon coal. Results showed good activity for this catalyst including the highest amount of 9,10-dihydrophenanthrene (13.2%) observed in a reaction product and a small but significant catalytic effect for heptane conversion (0.5%). Additional experiments are being performed to enable comparison with previously tested catalysts. Tetrahydrofuran (THF) insolubles from selected reactions have been sent to the University of Kentucky for Mossbauer characterization of the iron phases present.

Plans: Ongoing work includes completion of the statistical analysis of WVU's impregnated catalyst and comparison of this catalyst's results with results from previously tested catalysts. Future work will include testing additional catalysts being developed in the AR Coal Liquefaction Program (including catalysts impregnated on Wyodak coal), developing procedures to characterize reaction products, and determining the kinetics of the reactions.

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INTRODUCTION

There are several potential advantages of using cheap, unsupported, fine-particle size (less than or equal 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 (less than or equal to 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.

Sandia has previously reported(3) a standard test procedure using a factorial experimental design for the evaluation of fine-particle catalysts. This test has been applied to evaluate several different catalysts including a commercially available pyrite(3), a sulfated iron oxide catalyst(4) from the University of Pittsburgh and several different formulations of a 6-line ferrihydrite(5,6) prepared at Pacific Northwest Laboratories (PNL). This paper will describe the recent results obtained from evaluating West Virginia University's (WVU) iron catalyst that was impregnated on DECS-17 Blind Canyon coal.

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. Sandia sent four packets of this coal to WVU for impregnation with their catalyst. Phenanthrene is used as the reaction solvent.

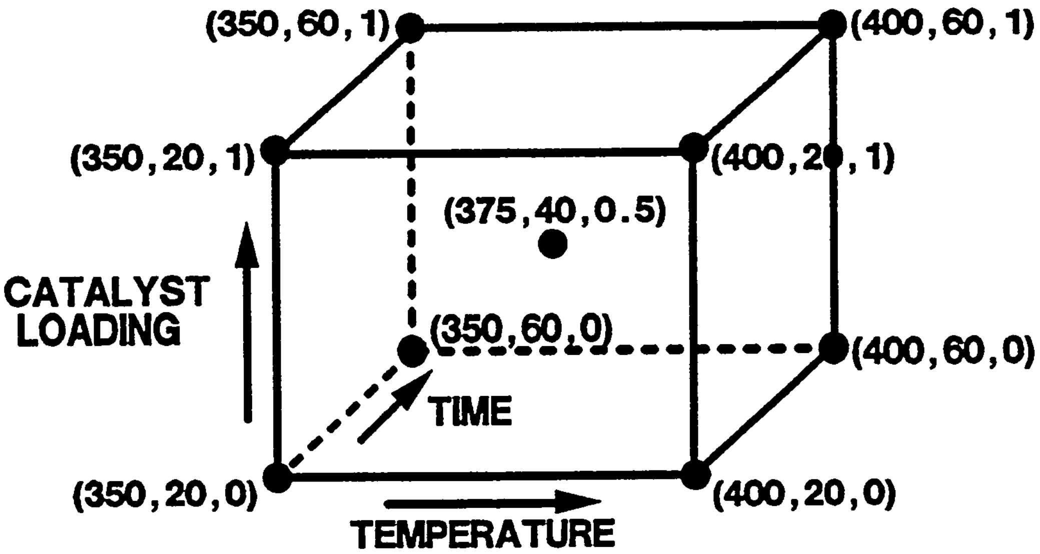
Microautoclave Reactors. The testing is performed using batch microautoclaves made of type 316 stainless steel components. The total volume of a reactor is 43 cm^3 with a liquid capacity of 8 cm^3. The reactors are loaded with 1.67g coal and 3.34g reaction solvent. If the reaction is catalytic, the catalyst loading will be either 0.5 wt% or 1.0 wt% on an as-received coal basis. The reactors are charged to 800 psig H_2 (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, CO_2, CH_4, C_2H_6) 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 2^3 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 conditions(7). The controlled factors used in the ANOVA are the measured average reaction temperature, measured reaction time, and the actual weight of catalyst used.

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



Catalyst. Sandia sent DECS-17 coal samples to D. Dadyburjor for impregnation with an iron catalyst. Calculations were performed by both Sandia and WVU to ensure that the correct amounts of catalyst were impregnated on the coal so that comparisons with other catalysts could be done. Dadyburjor (WVU) supplied Sandia with impregnated coals that had both 1 wt% and 0.5 wt% catalyst loadings on an as-received coal basis. No pretreatment, additives or special handling were required during testing. Impregnated coals were stored under argon to minimize changes with time.

RESULTS and DISCUSSION

Experimental Results of Testing WVU's Impregnated Catalyst. The measured results of testing WVU's impregnated catalyst are shown in Table 1 along with the average reaction temperature, and the actual reaction time. The standard deviation of the reaction temperature is almost always less than or equal to 1°C. Heat-up times are less than or equal to 3 minutes. Table 2 shows the averages and standard deviations for the data in Table 1. 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 a preliminary statistical analysis of the data with an asterisk in Table 1 are given in Tables 3 and 4. 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 used in this statistical analysis, and R^2 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 are derived from the experimental error, which pertains to a single measurement.

Procedure for Estimating Experimental Results from the Linear Model. To use one of the linear models in Tables 3 or 4 to estimate 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 the reaction at 375°C for 40 minutes with 0.5 wt% catalyst:

$p_{TIME} = (40\text{ min}-20\text{ min})/(60\text{ min}-20\text{ min}) = 0.5$
$p_{TEMP} = (375^{\circ}C-350^{\circ}C)/(400^{\circ}C-350^{\circ}C) = 0.5$
$p_{CAT} = (0.5\text{ wt\%}-0\text{ wt\%})/(1.0\text{ wt\%}-0\text{ wt\%}) = 0.5$

These calculated p's are used in the following equation (see Table 3):

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

where K is the estimated constant (24.9%), a is the estimated time effect (5.7%), b is the estimated temperature effect (21.1%), c is the estimated catalytic effect (9.5%), d is the estimated time-catalyst interaction (11.1%), and e is the estimated temperature-catalyst interaction (20.7%). The calculated THF conversion is 51.0% as shown in Table 3. 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.

Results of the modeling (Table 3 and 4) show that temperature has the largest effect on THF conversion (21.1%), followed by the temperature-catalyst interaction (20.7%), the time-catalyst interaction (11.1%), the catalyst effect (9.5%), and the time effect (5.7%). Calculated estimates of the THF conversions for the nine experimental sets of conditions can be compared with the average measured data shown in Table 3. Results show that the largest difference is for the center point of the cube (51.0% versus 63.3%). Modeling the measured heptane conversions shows that temperature (12.1%), the time-temperature interaction (9.6%), time (2.4%) and the catalyst (0.5%) have a statistically significant effect on heptane conversion. This is the first time a catalytic effect was observed for heptane conversion. There is good agreement between the measured and calculated heptane conversions in Table 3. The significant effects for gas yield are temperature (0.73%), the time-temperature interaction (0.42%), and time (0.23%). The 9,10-dihydrophenanthrene (DHP) formed by hydrogenation of phenanthrene during the reaction has the most complicated model with six parameters having significant effects: temperature-catalyst interaction (6.06%), time-catalyst interaction (4.24%), catalyst (1.01%), time-temperature interaction (0.96%), temperature (0.12%), and time (-0.07%). The amount of DHP obtained at 400°C for 60 minutes (13.04%) was the highest amount observed for any catalyst tested so far. The R^2 values for the fits of these models ranged from 0.91 for heptane conversion to 0.98 for the gas yield.

Comparison of Catalysts. A preliminary comparison of results (Table 5) from WVU's impregnated catalyst with results from PNL's catalyst, the U. of Pitt.'s catalyst and pyrite at the highest severity conditions (400°C, 60 minutes) indicates that WVU's catalyst has performed very well. The calculated THF conversion is at least as good as that obtained with PNL's catalyst if not better. WVU's catalyst has also yielded the highest amount of DHP at the highest severity condition; it's about 50% higher than obtained with PNL's catalyst. WVU's catalyst has shown a small but significant catalytic effect (0.5%) on heptane conversion, which has not been seen previously with other catalysts that have been evaluated. These results of the statistical analysis for WVU's catalyst are based on the data in Table 1 that has an asterisk. Since this statistical analysis was performed, some additional reactions have been performed. Therefore, a new statistical analysis of WVU's catalyst will be performed using all the data in Table 1.

Two catalysts in Table 5 (PNL's catalyst and the U. of Pitt.'s catalyst) were analyzed using a baseline with sulfur addition (either 1% or 2% based on as-received coal). For WVU's impregnated catalyst and pyrite, Sandia did not add sulfur to the reactions so the baseline was a thermal reaction. To get a good comparison, among these four catalysts, it is necessary to perform comparisons with the same baseline, i.e. the thermal baseline. This will be done when the statistical analysis of WVU's complete data set in Table 1 is done.

CONCLUSIONS

Results of the evaluation of WVU's iron catalyst that was impregnated on the DECS-17 Blind Canyon coal showed that it is a very good catalyst. At 400°C for 60 minutes, it yielded 93.0% THF conversion, which is as good or better than PNL's catalyst, and it yielded the highest amount of DHP (13.04%) observed in the reaction product indicating significantly better hydrogenation activity than the other catalysts tested. WVU's catalyst also showed a small (0.5%) catalytic effect for heptane conversion, whereas other catalysts tested to date have not shown any catalytic effect for heptane conversion. At 400°C for 60 minutes, THF conversion obtained with PNL's catalyst was 89.4% versus 82.3% with the U. of Pitt.'s catalyst, and 73.4% with pyrite. Analyses of DHP in the reaction products showed that PNL's catalyst gave 8.41% DHP, versus 5.35% for the U. of Pitt.'s catalyst, and 3.88% for pyrite. No catalytic effects have been detected for gas yield. Future work will include completing a statistical analysis of the complete data set in Table 1, comparing all catalysts tested to date using a thermal baseline, testing additional catalysts being developed in DOE/PETC's program, and continuing to evaluate better analytical methods for determining product quality.

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Table 1. Measured experimental results.

	TEMP (°C)	TIME (min)	CAT.	THF CONV. (%)	HEPTANE CONV. (%)	GAS (%dmmf)	DHP(%)
*	350.4	20.5	NO	24.13	2.64	0.29	0.25
*	350.3	20.5	NO	25.01	2.46	0.27	0.23
*	350.3	20.5	NO	27.91	4.85	0.28	0.25
	350.0	20.5	NO	19.93	1.69	0.41	NA
	350.1	20.5	NO	21.92	2.43	0.41	0.18
	350.3	20.5	NO	20.67	NA	0.65	NA
*	350.0	20.5	YES	32.29	-0.80	0.28	1.69
*	350.1	20.5	YES	28.97	-2.56	0.30	1.45
*	349.9	20.5	YES	34.68	-1.46	0.32	1.60
	350.2	20.5	YES	26.97	NA	0.48	1.22
*	350.2	60.8	NO	23.74	0.67	0.59	NA
*	350.2	60.5	NO	24.86	1.08	0.57	0.45
*	350.1	60.5	NO	28.85	5.03	0.49	0.43
*	350.2	60.5	NO	27.54	4.63	0.48	0.47
	350.4	60.5	NO	27.75	6.28	0.67	0.38
	350.6	60.5	NO	26.90	5.09	0.67	0.43
*	350.2	60.5	YES	NA	NA	0.42	5.95
*	350.3	60.5	YES	51.91	3.43	0.50	5.69
*	349.8	60.5	YES	49.09	3.47	0.53	5.27
*	350.4	60.5	YES	52.57	1.79	0.53	5.59
*	375.0	40.5	YES	66.02	8.73	0.73	7.29
*	374.8	40.0	YES	63.09	7.17	0.79	6.38
*	375.1	40.5	YES	60.73	10.47	0.81	6.67
*	400.4	20.5	NO	39.65	10.17	0.84	0.65
*	399.8	20.5	NO	46.61	17.72	1.04	0.68
*	400.1	20.5	NO	41.09	13.09	1.13	0.61
	400.2	20.0	NO	38.74	13.69	1.22	0.63
	400.3	20.5	NO	38.37	12.68	1.13	0.60
*	399.6	20.5	YES	76.98	12.99	0.98	8.10
*	400.0	20.5	YES	77.16	10.51	0.99	8.10
*	400.1	20.5	YES	74.63	12.93	1.20	6.84
*	400.0	20.5	YES	75.35	14.12	0.97	7.43
*	399.5	60.5	NO	54.00	23.83	1.63	1.20
*	400.9	60.8	NO	52.63	19.01	1.68	1.52
*	400.0	60.5	NO	50.69	19.61	1.69	1.11
	399.9	60.5	NO	48.93	20.98	1.87	1.21
	399.7	60.5	NO	46.83	20.95	1.83	1.19
	400.3	60.5	NO	49.52	NA	1.95	1.47
*	400.2	60.5	YES	92.17	30.69	1.63	13.09
*	400.5	60.5	YES	91.68	28.79	1.72	13.37
*	399.9	60.5	YES	91.02	24.75	1.74	13.10
*	399.9	60.5	YES	90.65	29.02	1.57	12.36
	400.3	60.5	YES	91.51	NA	2.02	12.22

* Reactions used in preliminary statistical analysis (see Tables 3 and 4). ** = Not Available.

Table 2. Averages and standard deviations for all reaction conditions and all results in Table 1.

	TEMP (°C)	TIME (min)	CAT.	THF CONV. (%)	HEPTANE CONV. (%)	GAS (%dmmf)	DHP (%)
AVER =	**350.2**	**20.5**	NO	**23.3**	**2.8**	**0.4**	**0.23**
Std Dev =	0.2	0.0		3.0	1.2	0.1	0.001
AVER =	**350.1**	**20.5**	YES	**30.7**	**-1.61**	**0.3**	**1.5**
Std Dev =	0.1	0.0		3.4	0.89	0.1	0.2
AVER =	**350.3**	**60.6**	NO	**26.6**	**3.8**	**0.6**	**0.4**
Std Dev =	0.2	0.1		1.9	2.3	0.1	0.2
AVER =	**350.2**	**60.5**	YES	**51.2**	**2.9**	**0.5**	**5.6**
Std Dev =	0.3	0.0		1.8	1.0	0.0	0.3
AVER =	**375.0**	**40.3**	YES	**63.3**	**8.8**	**0.8**	**6.8**
Std Dev =	0.2	0.3		2.6	1.7	0.0	0.5
AVER =	**400.2**	**20.4**	NO	**40.9**	**13.5**	**1.1**	**0.6**
Std Dev =	0.2	0.2		3.4	2.7	0.1	0.0
AVER =	**399.9**	**20.5**	YES	**76.0**	**12.6**	**1.0**	**7.6**
Std Dev =	0.2	0.0		1.2	1.5	0.1	0.6
AVER =	**400.1**	**60.6**	NO	**50.4**	**17.4**	**1.8**	**1.3**
Std Dev =	0.5	0.1		2.6	8.7	0.1	0.2
AVER =	**400.2**	**60.5**	YES	**91.4**	**22.7**	**1.7**	**12.8**
Std Dev =	0.3	0.0		0.6	12.8	0.2	0.5

Table 3. Results of preliminary statistical analyses for THF and heptane conversion data shown with an asterisk in Table 1.

	THF Conversion (%)			HEPTANE Conversion (%)		
Parameter	Model Estimate	Meas'd Average	Std. Error	Model Estimate	Meas'd Average	Std. Error
Constant*	24.9		2.7	0.3		1.4
Time	5.7		3.1	2.4		1.8
Temperature	21.1		3.1	12.1		1.8
Catalyst	9.5		3.8	0.5		1.2
Time-Temp. Int.				9.6		2.5
Time-Cat. Int.	11.1		4.2			
Temp.-Cat. Int.	20.7		4.2			
Experimental Error	5.4			3.1		
350°C, 20min, 0%	24.9	25.7	2.0	0.3	3.3	1.3
350°C, 60min, 0%	30.6	27.1	2.0	2.7	3.6	2.2
400°C, 20min, 0%	46.0	42.4	3.7	12.5	13.7	3.8
400°C, 60min, 0%	51.7	52.4	1.7	24.4	20.8	2.6
375°C, 40min, 0.5%	51.0	63.3	2.7	10.2	8.8	1.6
350°C, 20min, 1%	34.4	32.0	2.9	0.8	-1.6	0.9
350°C, 60min, 1%	51.2	51.2	1.8	3.2	2.9	1.0
400°C, 20min, 1%	76.2	76.0	1.2	13.0	12.6	1.5
400°C, 60min, 1%	93.0	91.4	0.7	24.9	28.3	2.5
R^2	0.95			0.91		

* Value calculated for a thermal reaction at 350°C for 20.

Table 4. Results of preliminary statistical analyses for gas yields and amounts of DHP in reaction product (based on data with an asterisk in Table 1).

	GAS YIELD (%dmmf coal)			DHP (%)		
Parameter	Model Estimate	Meas'd Average	Std. Error	Model Estimate	Meas'd Average	Std. Error
Constant*	0.27		0.03	0.72		0.60
Time	0.23		0.04	-0.07		0.78
Temperature	0.73		0.04	0.12		0.78
Catalyst				1.01		0.78
Time-Temp. Int.	0.42		0.06	0.96		0.87
Time-Cat. Int.				4.24		0.87
Temp.-Cat. Int.				6.06		0.88
Experimental Error	0.12			1.1		
350°C, 20min, 0%	0.27	0.28	0.01	0.72	0.24	0.01
350°C, 60min, 0%	0.50	0.51	0.05	0.65	0.45	0.02
400°C, 20min, 0%	1.00	1.00	0.15	0.84	0.65	0.04
400°C, 60min, 0%	1.65	1.67	0.03	1.73	1.28	0.22
375°C, 40min, 0.5%	0.86	0.78	0.04	4.07	6.78	0.46
350°C, 20min, 1%	0.27	0.30	0.02	1.74	1.58	0.12
350°C, 60min, 1%	0.50	0.52	0.02	5.90	5.52	0.22
400°C, 20min, 1%	1.00	1.03	0.11	7.92	7.62	0.61
400°C, 60min, 1%	1.65	1.67	0.08	13.04	12.98	0.43
R^2	0.98			0.95		

* Value calculated for a thermal reaction at 350°C for 20 minutes.

Table 5. Calculated results (400°C, 60 minutes).

	THF Conv. (%)	DHP (%)*
1wt%** WVU Impregnated Catalyst***	93.0	13.4
Thermal	51.7	1.73
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 percent based on as-received coal.

*** Based on preliminary statistical analysis (results with asterisk in Table 1).