

ACTIVITY TESTING OF FINE-PARTICLE SIZE,
UNSUPPORTED, IRON-BASED CATALYSTS*

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INTRODUCTION

The efficiency of the initial reactions of coal during coal liquefaction will have significant impacts on downstream processing (including catalyst usage, reaction severity, product yields, product quality) and hence on process economics. Reactions that result in compounds with low molecular weights and decreased boiling points are beneficial, whereas retrogressive reactions, which yield higher molecular weight compounds that are refractory to further processing, decrease process efficiency. Likewise, reactions that result in decreased sulfur, nitrogen, and oxygen contents and increased hydrogen contents in the products are beneficial. The use of unsupported fine-particle (<40 nm) catalysts during initial coal processing has the potential to enhance desired reactions and minimize retrogressive reactions. The potential advantages of using fine-particle size catalysts include improved dispersion of the catalyst, improved coal/catalyst contact, and the potential for using low amounts ($\leq 0.5\%$ based on the weight of coal) of these novel catalysts due to their very high surface areas. These catalysts could be combined with the coal or coal-solvent mixture as either active catalysts or catalyst precursors that would be activated in situ. Several methods of combining catalyst and coal, such as physical mixing or using a catalyst-hydrogen donor slurry, are possible. Ideally the fine-particle catalysts would be inexpensive enough to be disposable.

The Pittsburgh Energy Technology Center's (PETC) Advanced Research (AR) Coal Liquefaction Program has many research projects to develop fine-particle size catalysts that are active for reactions of interest in direct coal liquefaction: hydrogenation, carbon-carbon bond breakage, and heteroatom removal. However, it is difficult to compare results among researchers because of the variety of testing procedures used including different reactors, reaction temperatures, reaction times, pressures, hydrogen donor solvents, solvent to coal ratios, and workup procedures. In addition, some catalyst developers in the AR program do not have any testing capabilities for direct liquefaction. The objectives of the work reported here are to develop standard coal liquefaction test procedures and to perform the testing of the novel fine-particle size catalysts being developed in the PETC AR Coal Liquefaction Program.

EXPERIMENTAL PROCEDURES

Materials

The coal being used in this project is the DECS-17 Blind Canyon Coal obtained from The Penn State Coal Sample Bank. The coal, which is packaged under an

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inert atmosphere in sealed foil bags with a plastic liner, is stored in a refrigerator prior to use. The coal is a HVA 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. The coal is riffled three times with remixing prior to taking splits. 1,2,3,6,7,8-hexahdropyrene (H_6Py) and 9,10-dihydrophenanthrene (DHP) were evaluated as hydrogen donors for use in the standard tests. H_6Py was obtained from Aldrich (98% purity), and DHP was obtained from either Aldrich (94% purity) or Janssen Chimica (97% purity). Pyrite (99.9% pure on a metals basis) with a -100 mesh particle size was obtained from Johnson-Matthey. An X-ray diffraction pattern taken on this material showed only pyrite. The surface area of the pyrite is 0.7 m^2/g as measured using BET techniques. Stabilized tetrahydrofuran (THF) and heptane are used in product workups.

Reactors

The testing is being performed using batch microautoclaves consisting of a 0.75" OD Swagelok "T" connected to 0.375" OD high pressure stainless steel tubing. A Whitey plug valve at the top of the tubing is used for pressurizing and depressurizing the reactors. A thermocouple was inserted into the reactor, and a pressure transducer was attached. The total volume for a reactor is 43 cm^3 with a liquid capacity of up to 8 cm^3 . Four reactions can be run simultaneously. After being charged with the reactants (coal, hydrogen donor solvent, high pressure gas, and other additives required by the experimental design such as catalyst or sulfur), the reactors are rapidly heated to temperature in a fluidized-sand bath while being agitated at 200 cycles/sec with a wrist-action shaker. Temperatures and pressures are recorded with a digital data acquisition system during the course of the experiments. Following the heating period, the reactors are rapidly quenched in a water bath to ambient temperature, a gas sample is taken, and the liquid and solid products are removed for analysis.

Product Analyses

The primary criteria for evaluating catalysts are based on coal conversion. Reaction product analyses that are performed routinely include THF and heptane solvent solubility determinations, gas chromatographic (GC) analyses of the hydrogen donor, and analyses of gas products. Solvent solubilities are done using pressure filtration procedures with a Millipore 142 mm diameter pressure filtration device and Duropore (0.45 micron) filter paper. Quantitative GC analyses using methylnaphthalene as an internal standard are performed on the THF soluble material to determine the recovery of the hydrogen donor and the amounts of both DHP and phenanthrene present in the product. The quantity of each gas in the product is calculated using the ideal gas law, the mole percent in the gas sample as determined from a Carle GC using standard gas mixtures, and the post-reaction vessel temperature and pressure.

RESULTS AND DISCUSSION

Two important aspects of the catalyst testing program are the development of standard test procedures and the development of a statistical experimental design.

Standard Test Procedures

The standard test procedures cover both performing the reactions and doing product workups. H_6Py and DHP were evaluated for use as hydrogen donors in the standard tests. DHP was chosen because it is less expensive than H_6Py and has a lower melting point (32-35°C) that could help ensure good mixing. It also performed well in experiments. Current coal liquefaction processing

configurations use approximately a 2:1 hydrogen donor solvent to coal ratio. In addition, some of the better recycle solvents from large-scale processes contain about 1% donatable H₂, which is considered very good. Use of DHP at a 2:1 donor solvent:coal ratio gives about 1% donatable hydrogen and a high liquid:coal ratio for aiding catalyst dispersion.

Procedures have been set up to obtain excellent temperature control during the course of the reactions. The average temperature is routinely within one degree of the desired temperature and the standard deviation is <1°C. Heat-up times are about 3.5 minutes for 400°C reactions and quench times to temperatures <50°C are about 2 minutes.

After the gas samples are collected, the reactors are opened and the Swagelok tees and end caps containing the product are sonicated in THF, soaked in THF overnight, and then sonicated again prior to filtration. The total time the liquid products are in THF is about 17 hours. The volume of THF used in this reactor cleaning is 200 ml. Typically, three filter papers are used for THF filtration. The filter cake is rinsed with THF prior to opening the device. After the filtration is complete, the filter paper is dried in a vacuum oven, cooled to room temperature and weighed to determine the insoluble portion. The THF solubles are then rotoevaporated to about 50 to 60 ml volume, quantitatively transferred to a 100 ml volumetric flask and brought to 100 ml volume after the solubles have cooled to room temperature. A 1 ml portion is removed and used for determination by GC of the hydrogen donor recovery, including both DHP and phenanthrene. The remaining 99 ml is rotoevaporated until there is no weight loss after 10 minutes of rotoevaporating. A stirring bar is added to the flask and 200 ml heptane is added with constant stirring. This heptane/product mixture is then pressure filtered to obtain the weight of heptane insolubles.

Statistical Experimental Design

There are two main reasons for using an experimental design: to enable good comparisons among novel catalysts and to obtain more information with fewer experiments. This procedure will give statistical information regarding the results and will yield optimum processing conditions for each catalyst over the ranges of the variables studied. The statistical experimental design (Figure 1) that was chosen evaluates the effects of three variables: time (20 to 60 minutes), temperature (350 to 400°C) and catalyst loading (0 to 1 wt% on a weight of as-received coal basis). These conditions are consistent with process conditions used in coal liquefaction. An additional advantage of using an experimental design is that the impacts of additives, such as sulfur required to activate an Fe₂O₃ catalyst, can be easily evaluated by adding sulfur to the thermal baseline reactions.

Evaluation of the Statistical Design

This experimental design was evaluated by each of two operators using pyrite. Pyrite was chosen because it is a known iron catalyst in coal liquefaction, is commercially available, and is easy to work with.

The hydrogen donor recoveries (including both DHP and phenanthrene) were greater than 90% for all the reactions. At the lower severity conditions about 83% of the donor product was DHP, whereas at the higher severity conditions only 24% was DHP. The non-hydrogen gases detected in the reaction products were CO₂, CO, CH₄, and C₂H₆. The quantities of these gases produced ranged from 0.23% (dmwf coal basis) for the lowest severity conditions to 2.21% for the highest severity conditions. Table 1 shows the measured, gas

corrected THF conversions and heptane conversions obtained by each operator for the nine sets of process conditions in the experimental design. It also gives the average conversions and the standard deviations. The THF results show good reproducibility. The largest standard deviation is 4.09 for the center point of the cube. This high value is consistent with the fact that both operators indicated the products from runs made at these conditions are the most difficult to filter. The equation obtained by fitting the THF conversion data to a linear model is as follows:

$$\text{THF Conv}(\%) = 70.908(+/-)16.938(+/-)6.931(+/-)1.091(+/-)(+/-)(-1.956)$$

Where:

70.908	Center Point Conversion
16.938	Temperature Effect
6.931	Time Effect
1.091	Pyrite Effect
-1.956	Time x Temperature Interaction

The r^2 value for the fit of the THF data to this equation is 0.987. To calculate the THF conversion for a given set of reaction conditions choose either the + or - in each (+/-). Use + for each high value: 400°C or 60 minutes or 1 wt% catalyst. Use - for each low value: 350°C or 20 minutes or no catalyst. This analysis shows that the largest effect is due to temperature, followed by time and finally pyrite addition. There is also some interaction between temperature and time. No other interactions were observed. The calculated THF values for the points on the cube are shown in Figure 2. The results show that the impact of a 1% pyrite addition is to increase the THF conversion by 2.2%, which is a statistically significant increase. It also shows that the effect is the same at both the lowest and highest severity conditions.

The measured heptane conversions in Table 1 show much greater variability than the THF conversions. Approximately halfway through the experimental design, it was observed that there was a systematic difference between the heptane conversion values obtained by the two operators. Therefore, the procedure was revised to ensure that both operators were doing the workups the same way. The results for the runs that were made after this change are indicated with an "*". A comparison of the results from the revised procedure to those from the old procedure shows significant improvement in reproducibility. All of the measured heptane conversions were used in the linear modeling effort because there would not be enough data if the old workup procedure results were discarded. The equation obtained by fitting the heptane conversion data to a linear model is as follows:

$$\text{Heptane Conv}(\%) = 19.958(+/-)13.020(+/-)5.255(+/-)(+/-)2.406$$

Where:

19.958	Center Point Conversion
13.020	Temperature Effect
5.255	Time Effect
2.406	Time x Temperature Interaction

The r^2 value for the fit of the heptane conversion data to this equation is 0.957. The calculated heptane values are shown in Figure 3. This analysis indicates that the largest effect is due to temperature, followed by time. Pyrite addition had no effect on heptane conversion. There is also an

interaction between temperature and time. No other interactions were observed. The estimates of standard errors associated with this data could probably be improved by repeating the experimental design using the new workup procedure for all experiments. This might show somewhat different results. The heptane conversion (4.09%) for 350°C for 20 minutes is equal to that obtained from the as-received coal.

Operator effects were also analyzed as part of the statistical analysis of the results. Operator effects include both effects between operators and within each operator. The results were as follows:

<u>SOURCE</u>	<u>ESTIMATES OF STANDARD DEVIATION</u>	
	<u>THF CONVERSIONS</u>	<u>HEPTANE CONVERSIONS</u>
Between Operators	0.23	0.31
Within Operators	1.78	0.95

These results show good reproducibility both between operators and within each operator and thus indicate that there are no systematic differences in the procedures used by the operators. Only the results from the new workup procedure were used in this analysis of the heptane conversions.

SUMMARY

The results of the experiments performed using pyrite have shown that small differences in activity can be detected by using a statistical experimental design. The differences in THF conversion were 2.2% between thermal and catalytic reactions. This difference was unaffected by changes in reaction time and temperature over the parameter ranges used in this study. The results also show that the experimental procedures (with the revised heptane conversion techniques) can be well duplicated between operators and within a single operator.

FUTURE WORK

Future work will include repeating the statistical experimental design to determine if the revised heptane procedure impacts the conclusions. The hydrogen donor to coal ratio will also be varied to determine the effects on catalyst activity. Efforts will be made to develop a procedure for obtaining information on the quality of the reaction products by performing elemental analyses on the THF and heptane insoluble materials. Testing of a novel catalyst being developed by I. Wender at the University of Pittsburgh will be initiated. This will be the first novel catalyst that will be evaluated using this experimental design.

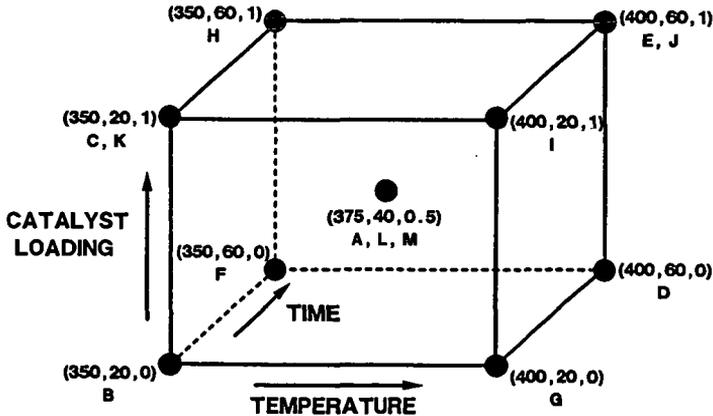
Acknowledgement

I would like to express my thanks to Jeff Kawola and Richard Jensen for performing the experimental work associated with this project. I would also like to thank Kathleen Diegert for determining the best experimental design and analyzing the results and Carlos Quintana for his efforts in setting up the new testing facility.

TABLE 1. MEASURED CONVERSIONS

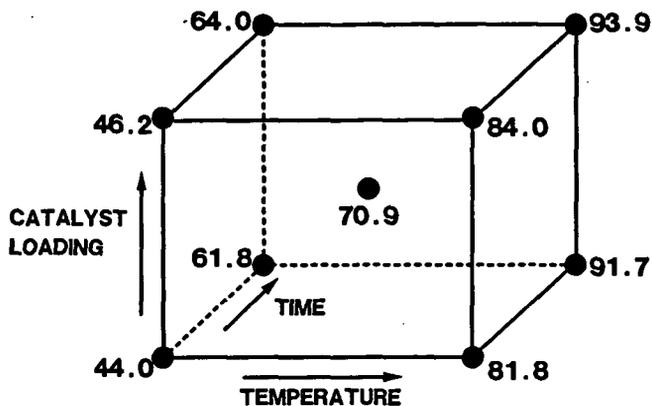
TEMP (°C)	TIME (min)	CAT (wt%)	THF RESULTS				HEPTANE RESULTS			
			OPERATOR		AVERAGE	STD DEV	OPERATOR		AVERAGE	STD DEV
			#1	#2			#1	#2		
350	20	0	42.5	44.0	43.2	1.05	3.0	6.6	4.8	2.55
400	20	0	82.2	79.2	80.7	2.16	25.6*	25.1*	25.3	0.33
350	60	0	61.4	60.9	61.1	0.34	6.6	13.0	9.8	4.53
400	60	0	93.0	91.6	92.3	0.72	37.8	48.4	42.1	4.58
			91.7				39.9*			
			92.9				42.5*			
375	40	0.5	74.6	74.9	71.8	4.09	15.7	22.2	17.2	3.07
			65.1				17.6*			
			70.6	73.7			14.1*	16.4*		
350	20	1	47.2	45.9	46.1	1.20	2.4	3.9	4.6	2.05
			44.5	46.9			4.9*	7.3*		
400	20	1	84.0	83.9	83.9	0.03	26.7*	27.4*	27.0	0.45
350	60	1	62.1	64.9	63.5	2.02	11.3*	11.7*	11.5	0.26
400	60	1	93.2	92.6	92.8	0.28	35.0	40.4	40.0	3.53
			92.7	92.7			41.9*	42.9*		

* - Revised work up procedure



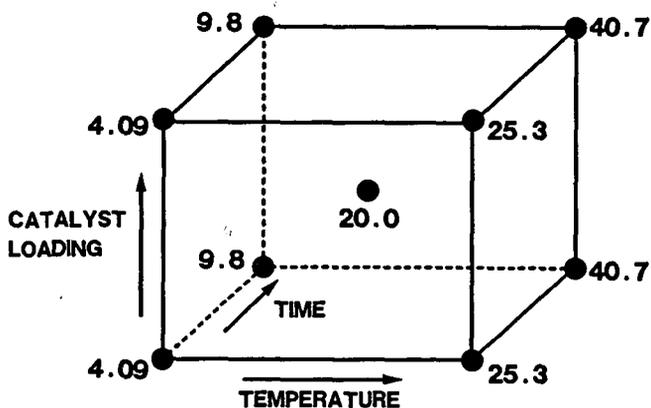
(TEMPERATURE = °C; TIME = MINUTES; CATALYST LOADING = WT % AR COAL)
LETTERS = ORDER IN WHICH REACTIONS WERE PERFORMED

Figure 1: Statistical experimental design



(TEMPERATURE - °C; TIME - MINUTES; CATALYST LOADING - WT % AR COAL)

Figure 2. THF conversions: Calculated from the linear model



(TEMPERATURE - °C; TIME - MINUTES; CATALYST LOADING - WT % AR COAL)

Figure 3. Heptane conversions: Calculated from the linear model