OVERVIEW OF CATALYST TESTING AND COPROCESSING STUDIES AT SANDIA NATIONAL LABORATORIES*

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ABSTRACT

Prior to the initiation of Sandia's fine particle size catalyst testing project, it was not feasible to compare the activities of the many direct coal liquefaction catalysts developed in various laboratories. This was due to the wide variety of testing methods used by the different catalyst developers. Sandia developed a procedure that uses a bituminous coal (DECS-17 Blind Canyon coal), phenanthrene as the reaction solvent, and a factorial experimental design with three variables: temperature, time, and catalyst loading. Numerous catalysts have been evaluated. Pacific Northwest National Laboratories' (PNNL) 6-line ferrihydrite catalyst is the most active among the particulate catalysts. West Virginia University's (WVU) iron catalyst impregnated on Blind Canyon coal is the best iron catalyst evaluated to date. Because this catalyst was prepared by impregnation, which involves several preparation steps, it cannot be directly compared to particulate catalysts. In an effort to enable this comparison, WVU produced a particulate iron catalyst that has been tested at Sandia. In addition, Sandia has also evaluated several of Argonne National Laboratory's molybdenum and iron catalysts that were impregnated on Wyodak subbituminous coal from the Argonne Premium Coal Sample Program. Current activities are focused on developing capabilities for performing coprocessing experiments to support FETC's coprocessing thrust and a new project aimed at helping Puerto Rico solve its waste disposal problems.

INTRODUCTION

Sandia has previously evaluated an iron catalyst[1] that WVU had impregnated on the DECS-17 Blind Canyon Coal. Results showed this catalyst was the most active of those tested at Sandia. At the highest severity condition (400^{o}C, 60 minutes, 1 wt% catalyst) of the experimental design (Figure 1), it gave 93.0% tetrahydrofuran (THF) conversion, 24.9% heptane conversion, and 13.0% formation of 9,10-dihydrophenanthrene (DHP). The high amount of DHP indicates that this impregnated catalyst had significantly higher hydrogenation activity than the previously tested particulate catalysts. As with all the other fine particle catalysts evaluated at Sandia, there was no catalytic effect on gas formation, which was 1.65% based on dmmf coal. This impregnated catalyst was the only catalyst evaluated at Sandia that yielded a statistically significant impact on heptane conversion. In addition, Karl Vorres of Argonne National Laboratory has prepared both Mo and Fe impregnated catalysts on Wyodak subbituminous coal from the Argonne Premium Coal Sample Program. Sandia has evaluated several of these catalysts.

EXPERIMENTAL SECTION

<u>Materials.</u> Two coals have been used in this project: DECS-17 Blind Canyon coal (high volatile A bituminous, -60 mesh, 3.74% moisture, 0.36% iron, 0.02% pyritic sulfur, 7.34% mineral matter (dry basis)) from the Penn State Coal Sample Bank and Wyodak subbituminous coal (28.09% moisture, 0.17% dry pyritic sulfur, 9.82% mineral matter (on a dry basis using the Parr formula) from the Argonne

Premium Coal Sample Program). Phenanthrene is used as the reaction solvent. Elemental sulfur is used to sulfide catalyst precursors.

Microautoclave Reactors. Testing is performed using 43 cm^3 batch microautoclaves (liquid capacity of 8 cm^3) loaded with 1.67g coal and 3.34g phenanthrene. For catalytic reactions, either 0.5 wt% or 1.0 wt% catalyst (based on coal) is added to the reactor depending on reaction conditions. The amount of sulfur addition is usually determined by the catalyst developer. 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 every 30 seconds with a digital data acquisition system. At the end of the run, the reactors are rapidly cooled to room temperature in a water bath and a gas sample is collected. Reaction data is analyzed to determine actual reaction times and the averages and standard deviations for reaction temperature and pressure. Heat-up times and cooling times are also determined.

Product Workup Procedures. Reaction products are rinsed out of the reactors with 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. Filter cakes are rinsed twice with THF or heptane as appropriate. After filtrations are complete, the filter papers are dried under vacuum at 70^{o}C, cooled to room temperature, and weighed to determine the insoluble portions. THF soluble material is quantitatively sampled for gas chromatographic (GC) analysis that is used to determine the reaction solvent recovery and final composition. THF is removed from the solubles by rotary evaporation prior to determining heptane conversion. The quantity of gases (CO, CO_2, CH_4, C_2H_6) produced in a reaction is calculated using post-reaction 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. The factorial experimental design (Figure 1) evaluates the effects of three variables at two levels: temperature (350 to 400^{o}C), time (20 to 60 minutes), and catalyst loading (0 or 1 wt% based on weight of coal). With this full experimental design, the results are evaluated for all combinations of levels of the three variables so that 2^3 evaluations are required. Additional reactions are performed at the center point (375^{o}C, 40 minutes, 0.5% cat.) 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 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. The controlled factors used in the ANOVA are the measured average reaction temperature, measured reaction time, and the actual weight of catalyst used.

RESULTS AND DISCUSSION

Evaluation of WVU's Particulate Iron Catalyst. Dr. Dadyburjor (WVU) wanted Sandia to test WVU's particulate iron catalyst that was produced using a similar procedure to WVU's impregnated iron catalyst so that results could be compared. This particulate catalyst was evaluated at the highest severity condition (400^{o}C, 60 minutes, 1 wt% catalyst) used in our factorial experimental design.

Table 1 results show that WVU's impregnated catalyst (the only catalyst to yield a catalytic effect for heptane conversion) was significantly more active than their particulate catalyst as indicated by the higher amounts of THF conversion (91.4% versus 78.3%) and the quantity of DHP in the reaction product (12.8% versus 5.0%). Higher amounts of DHP (formed by catalytic hydrogenation of phenanthrene) in the product indicate a catalyst has higher hydrogenation activity. Heptane conversions and gas yields were similar for both catalysts. None of the catalysts that have been tested have shown a catalytic effect on gas yield.

TABLE 1: Comparison of WVU s Particulate Fe Catalyst to WVU s Impregnated Fe Catalyst and to Several Other Particulate Fe Catalysts Evaluated in this Project. Conditions: 400^{o}C, 60 min., 1% Catalyst, 1% Sulfur*

CATALYST	THF CONVERSION (%)**	HEPTANE CONVERSION (%)**	DHP (%)**	GAS YIELD (%dmmf coal)**
Pyrite***	73.4 (1.2)	27.9 (1.3)	4.0 (0.4)	Not Available
Univ. of Pittsburgh	81.7 (1.1)	31.8 (1.7)	5.4 (0.3)	1.93 (0.1)
PNNL	89.6 (1.1)	26.8 (1.1)	8.1 (0.1)	1.86 (0.3)
Univ. of KY Citrate Promoted	83.8 (0.5)	29.2 (3.1)	6.4 (0.7)	1.79 (0.3)
Univ. of KY SiO.5 Promoted	84.5 (0.6)	28.9 (0.1)	7.2 (0.0)	2.00 (0.1)
WVU PARTICULATE	78.3 (3.1)	26.7 (1.3)	5.0 (0.4)	1.73 (0.1)
WVU IMPREGNATED****	91.4 (0.6)	28.3 (2.5)	12.8 (0.5)	1.74 (0.2)

* Thermal runs for particulate catalysts with no sulfur addition = about 53% THF conversion and with sulfur addition = about 62% THF conversion due to formation of iron sulfides in the coal.
** Average of Measured Values with Standard Deviations in Parentheses.
*** No sulfur addition needed.
**** Sulfur impregnated onto coal.

Table 1 also compares WVU’s particulate catalyst to several additional particulate catalysts evaluated at Sandia. Of the particulate catalysts, PNNL’s had the best results with the highest THF conversion and the most DHP in the product. WVU’s particulate catalyst did not yield good activity. Differences between WVU’s impregnated catalyst and its particulate catalyst could be due to several factors such as differences in catalyst dispersion or changes in the coal due to the impregnation procedure.

<u>Evaluation of Argonne National Laboratory’s Impregnated Catalysts.</u> Karl Vorres of Argonne National Laboratory sent Sandia some of Argonne’s iron and molybdenum catalysts that were impregnated on Wyodak coal from the Argonne Premium Coal Sample Bank. These catalysts were prepared using several steps:

1) Screening the coal to -20+200 mesh, mixing it with distilled water, decanting off the fines, placing the product in a buret with fritted glass and passing distilled water through the sample until the water was clear, and then drying the sample in a vacuum oven for 24 hours.

2) Acid washing the product from step 1 with 0.1 N H_2SO_4 until the pH<4, then washing it with distilled water until the pH was about 4, and drying it in a vacuum oven at room temperature for about 24 hours.
3) Mo treated coal was prepared by adding ammonium heptamolybdate buffered at pH 2 and letting it stand for 2 days with occasional shaking, then filtering off the solution, and vacuum drying for 24 hours.
4) The Fe treated coal was prepared similar to the Mo treated coal except ferrous sulfate solution prepared at pH 3 was used.

Because of the various treatments used by Argonne to impregnate the metals on the Wyodak coal, it was necessary to determine the amounts of moisture remaining in the impregnated samples. Sandia worked with Karl Vorres to develop an appropriate procedure. The procedure consisted of 1) putting the sample under vacuum at room temperature for 3-4 hours; 2) heating it at 50^{o}C under vacuum for 2 hours; 3) heating it under vacuum at 110^{o}C overnight; 4) purging the sample with nitrogen and cooling it to 50^{o}C; and 5) weighing the dried sample. The values we obtained were 27.89% and 28.39%, which agree with the result (28.09%) reported in the Users Handbook for the Argonne Premium Coal Sample Program. Therefore, the two coal samples that were impregnated by Karl Vorres with either 0.9% Fe and 1.0% Mo (determined by Atomic Absorption Spectroscopy of the solutions from before and after the impregnation step) were analyzed for moisture contents by using this procedure. Results showed that the Fe impregnated coal had 6.79% moisture, and the Mo impregnated coal had 6.19% moisture.

Results of testing these impregnated coals are shown in Table 2. The coal used for the thermal reactions was dried to about the same moisture content as the impregnated coals. Unfortunately, there was not enough of the two impregnated coals to enable testing at all the points on the experimental design. Therefore, not all conditions were evaluated and few duplicates were performed. No reactions were performed at the center point because no coal impregnated with 0.5 wt% catalyst was obtained.

Analyses of the results from the thermal reactions in Table 2 show that THF conversions range from about 28% at the lowest severity condition (350^{o}C, 20 minutes, no catalyst) to 48% at the highest severity condition (400^{o}C, 60 minutes, no catalyst). For these same conditions, heptane conversions range from about 10% to 26%, and DHP in the reaction product ranges from a trace amount to 1.04%. In contrast, reactions with 1 wt% Mo addition show very significant improvements. At 400^{o}C for 60 minutes, THF conversion with 1 wt% Mo is 94% as compared to 48% for the thermal reaction. Heptane conversion is 60% compared to 26% for the thermal run, and DHP is 10.9% compared to 1.0%. Reactions with the Fe impregnated Wyodak coal gave much lower conversions than the Mo impregnated coal. At 400^{o}C for 60 minutes, THF conversion with the 0.9 wt% Fe catalyst averages about 56% compared to 48% for the thermal reaction. There does not appear to be any significant increases in heptane conversion or the amount of DHP in the product with the Fe impregnated coal.

<u>Coprocessing Studies at Sandia.</u> The goal of this work is to identify ways to reuse wastes produced on US islands such as Puerto Rico. The Governor of Puerto Rico has declared waste production and waste disposal as major problems for Puerto Rico. Landfilling, which is Puerto Rico's main method of waste disposal, is no longer a good method because the island has limited land mass and landfill space is rapidly diminishing. Therefore, it is necessary to identify possible scenarios for reusing waste materials rather than putting them in landfills. Sandia is participating in efforts to identify, initiate, and evaluate potential coprocessing activities that could be implemented in Puerto Rico. A workshop to identify options for

research and procedures for implementing successes is being planned for this fall. Success in this effort might be used on other US islands and might also be useful at some locations within the US.

Specific efforts will be concentrated on finding alternative uses for Puerto Rico's waste as well as coprocessing Puerto Rico's waste streams with low value materials (such as heavy resids, coal, and orimulsion). There is a petroleum refinery on the island so heavy resid could be available for coprocessing. Within a few years, coal will become available on the island because of plans to build a 2MW coal fired power plant. This raises the possibility of having a coal-waste coprocessing demonstration project on the island. Orimulsion (70% bitumen and 30% water) comes from Venezuela and is a very cheap resource that might be able to be upgraded to higher value products by coprocessing. Appropriate catalysts for use with the various waste streams will be identified. Additional efforts will focus on advanced catalyst development for coprocessing and upgrading. Sandia's work would be coordinated with efforts being performed in Puerto Rico. Success in this research could help solve Puerto Rico's waste disposal problem and also lead to a pilot plant demonstration project.

TABLE 2: Results of Thermal and Catalytic (Either 1.0 wt% Mo or 0.9 wt% Fe) Coal Liquefaction Experiments using Karl Vorres Impregnated Coal Samples. (Coal used in non-catalytic reactions was dried to approximately the same moisture contents as the impregnated coals (6.19 wt% for Mo & 6.79 wt% for Fe)).

AVER. TEMP (^{o}C)	TIME (min)	AVERAGE REACTION PRESSURE (psig)	CAT. (WT% COAL BASIS)	THF CONV. (%)	HEPTANE CONV. (%)	DHP (%)	GAS (%dmmf)
THERMAL REACTIONS + 1 wt% SULFUR (Average Values of 3 Runs)							
350.5	20.5	1224	NO	27.61	9.86	Trace	1.90
350.2	60.5	1265	NO	34.58	16.83	0.34	2.63
400.5	20.5	1247	NO	37.30	19.12	0.43	4.27
399.6	60.5	1356	NO	48.00	26.32	1.04	4.68
REACTIONS WITH 1 wt% Mo + 1 wt% SULFUR							
Reaction for 350^{o}C, 20 minutes, 1 wt% Mo gave very poor results							
350.2	61.0	1105	1 wt%	82.13	25.43	8.52	3.48
400.1	20.5	1161	1 wt%	90.12	38.61	9.72	4.42
399.4	60.5	1070	1 wt%	94.15	60.09	10.92	3.87
REACTIONS WITH 0.9 wt% Fe + 1 wt% SULFUR							
No reaction performed at 350^{o}C for 20 minutes with Fe							
No reaction performed at 350^{o}C for 60 minutes with Fe							
399.8	21.0	1303	0.9 wt%	44.25	18.51	0.67	4.39
400.2	60.5	1327	0.9 wt%	57.57	27.35	1.94	5.23
399.9	60.5	1295	0.9 wt%	53.66	27.05	1.15	5.24

CONCLUSIONS

Results of evaluating WVU's particulate Fe catalyst have shown that it is significantly less active than WVU's impregnated Fe catalyst that had been evaluated previously. At the highest severity test condition, the particulate catalyst yielded 78.3% THF conversion, 5.0% DHP in the reaction product, and 26.7% heptane conversion, whereas the impregnated catalyst yielded 91.4% THF conversion, 12.8% DHP, and 28.3% heptane conversion. These results indicate that the particulate catalyst has much lower activity than the impregnated catalyst and also has lower activity than most of the other particulate catalysts that have been evaluated.

Results of evaluating Argonne National Laboratory's impregnated Mo and Fe catalysts show that the 1% Mo impregnated catalyst gives 94% THF conversion at the highest severity condition whereas the 0.9% Fe impregnated catalyst gives only 56% THF conversion. The Fe impregnated catalyst only increased THF conversion by 8% (absolute) compared to a thermal reaction, indicating that this is a poor catalyst.

FUTURE WORK

The next catalyst to be evaluated using Sandia's standard coal liquefaction test procedure will be HTI's catalyst. After completing the analysis of this catalyst, Sandia will begin evaluating coprocessing options aimed at helping Puerto Rico solve its waste disposal problem.

REFERENCES

1. Stohl, F. V., Diegert, K. V., Goodnow, D. C., "Evaluation of West Virginia University's Iron Catalyst Impregnated on Coal", Proceedings Coal Liquefaction and Gas Conversion Contractors Review Conf., August 29-31, 1995, Pittsburgh, PA.
2. Stohl, F. V., Diegert, K.V., "Development of Standard Direct Coal Liquefaction Activity Tests for Fine-Particle Size, Iron Based Catalysts", Energy & Fuels, 1994, 8.

Acknowledgement: Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

FIGURE 1. FACTORIAL EXPERIMENTAL DESIGN
(Temp (^{o}C), Time (min.), Catalyst (% of coal))