

DEVELOPMENT OF AN ALL-SLURRY LIQUEFACTION TEST FOR SCREENING DISPERSED CATALYSTS

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ABSTRACT

Exceptionally high distillate yields have previously been achieved in the direct liquefaction of subbituminous coal using dispersed catalysts. As part of a program sponsored by the U. S. Department of Energy, selected dispersed catalysts are being evaluated in continuous bench-scale runs. In consequence, a laboratory test has been developed to screen candidate dispersed catalysts and determine the optimum range of operating conditions to maximize coal conversion and distillate yield. The objectives of the test are to simulate operation in an all-slurry mode with coal conversion and product selectivity at least as good as that achieved in 2-stage operation at the Wilsonville Advanced Coal Liquefaction Facility. Tests are conducted in microautoclaves using pilot plant derived solvents and a Wyodak coal in the ratio of 1.85/1. An Fe-Mo catalyst contained in a Wilsonville process solvent has been used as a reference. The influence of residence time at 440 °C on 524 °C+ resid conversion has been determined and evaluations of various Mo formulations will be discussed.

INTRODUCTION

A DOE sponsored program is currently being conducted, in part, at the CAER to develop viable slurry catalysts for producing a distillate product equivalent to that obtained in a run made at the Wilsonville Advanced Coal Liquefaction R&D Facility in 1992. In the Wilsonville study, Runs 262E and 263J, Wyodak coal from the Black Thunder mine was used as feed. Unlike those runs, which were made in a 2-stage configuration in which the 1st-stage was operated as a thermal reactor, with a Mo-Fe dispersed catalyst, and the 2nd-stage as an ebullated bed reactor, with a Ni-Mo extrudate catalyst,¹ the objective of the current work² is to develop a process involving an all-slurry reactor configuration using only dispersed catalyst. By eliminating the 2nd-stage catalyst, considerable cost reduction can be achieved if a dispersed catalyst can be found that can provide the same level of coal conversion and product selectivity that was obtained in the 2-stage Wilsonville operation.

Various methods for introducing dispersed catalyst precursors into the reaction system is being investigated in this project. One approach is to impregnate the catalytic metal precursors onto coal and activate these metals *in situ*. Such catalysts require that several interrelated process parameters be optimized in order to generate active catalysts. Although Mo is an active component in all these catalysts, the co-metals and their particular salt precursors must be defined as well as the concentration of metal on the coal substrate. In addition, limitations on the amount of the feed coal that must be impregnated, the conditions and reactants necessary to activate the catalyst as well as maintain its activity in the process, and the concentration of the catalyst in the recycle stream must be specified. The effect of each catalyst on product yields and quality must also be determined.

A catalyst screening test is being developed to facilitate the selection of catalysts and their concentration in the reaction system. The test simulates the liquefaction performance in an all-slurry liquefaction mode and expands upon the a catalyst screening test that was recently reported that simulates the first-stage reactor.³ The active catalyst, which is contained in the ashy resid portion of the recycle solvent from Wilsonville Run 262E, has been used as a reference catalyst. The performance of various test catalysts will be compared to the performance of the Run 262E catalyst, which appears to be far more active than any others that have been tested in our laboratory. Distillate yield and coal conversion are used as a measure of catalyst activity.

EXPERIMENTAL

Wyodak coal, obtained from the Black Thunder Mine in Wright, Wyoming, was ground to -200 mesh, riffled and stored under nitrogen at 4 °C. Proximate and ultimate analyses of the coal are presented in Table 1. Samples of the various components of the recycle solvents from Runs 258 and 262 were obtained from the Advanced Coal Liquefaction R&D Facility at Wilsonville, AL. All of these materials were produced at Wilsonville when the plant was operating in a close-coupled configuration and feeding Black Thunder coal. Run 262E recycle solvent contains sizable concentrations of iron and molybdenum resulting from addition of iron oxide and Molyvan L to the feed slurries. This solvent had previously been described in detail.⁴ Molyvan L is an organic-based Mo containing material supplied by R. I. Vanderbilt Co.

Based on previous Mössbauer studies on solids obtained from liquefaction of Black

Thunder coal in Run 262 solvent, the iron in the THF IOM was present in combination with sulfur as pyrrhotite. The molybdenum was presumed to be present as MoS₂. A sample of THF insoluble material in the Run 262 563 °C+ ashy resid was isolated by exhaustively extracting with THF for 2 days.⁵ Another sample of catalyst-enriched solids from Run 262 solvent was obtained by filtering a THF slurry at ambient temperature. In both cases the samples were dried overnight at 40 °C at 125 torr.

The catalyst screening tests are run in 50 mL microautoclaves in 2-3% H₂S in H₂ at a nominal total pressure at ambient temperature of 1350 psig which provides a hydrogen to feed coal ratio of about 18 wt % on dry coal. Total pressure at operating temperature is approximately 2500 psig. In the test, approximately 2.4 g dry coal is slurried in a solids-free solvent mixture comprising 33 wt % Run 258B heavy distillate (Wilsonville Vessel Number V-1074) and 67 wt % Run 258 ROSE deashed resid (Wilsonville Vessel Number V-130). Although the deashed resid is a bottoms cut from a 565 °C (1050 °F) vacuum tower, it still contains 8.3% 524 °C- (975 °F-) distillate and 16.0% of the 524-565 °C fraction, as determined in our laboratory. The various distillate cuts and feed coal concentrations in the starting mix are shown in Table 2. The ash contents of the deashed resid and distillate materials were determined to be quite small, i.e., 0.13 wt% and 0.12 wt%, respectively.

Reactions were conducted in 50 cc microautoclaves pressurized with hydrogen at ambient temperature. After pressurization, the reactor was placed in a fluidized sandbath set at the specified temperature and continuously agitated at a rate of 300 cycles per minute. At the end of the reaction period, the reactor was quenched to ambient temperature and the gaseous products collected and analyzed by gas chromatography. The solid and liquid products were scraped from the reactor using THF and the mixture was extracted in a Soxhlet apparatus for 18 hours. The THF insoluble material, which included IOM and ash, was dried (80 °C at 125 torr) and weighed. The THF solubles were concentrated by removing excess THF in a rotary evaporator and subjected to vacuum distillation using a modified D-1160 procedure, which is described elsewhere.⁶ The methods for calculating material balances are included in the previous descriptions. In the following discussion, coal conversion equals 100 minus the yield of THF-insoluble organic material (IOM). Resid conversions are calculated as shown below, while coal conversion is derived from the net yield of IOM.

$$\text{Resid Conv} = 100 \left[1 - \frac{[\text{IOM} + 524^{\circ}\text{C} \cdot \text{Resid}(\text{maf})]_{\text{Products}}}{[\text{Coal}(\text{maf}) + \text{IOM} + 524^{\circ}\text{C} \cdot \text{Resid}(\text{maf})]_{\text{Feed}}} \right]$$

RESULTS AND DISCUSSION

The objective of our program is to identify catalysts that warrant further testing in a continuous recycle bench-scale operation. The criteria for a screening test are to simulate, as closely as possible, actual process conditions that would exist under recycle operation. For that reason, solvents were used in the test that were actually generated from Wyodak Black Thunder coal in the Wilsonville plant. In our previous laboratory studies, the Mo catalyst contained in the Run 262E recycle solvent was found to be the most active of any catalyst we had tested. In our microautoclave reactors, we reported that the 565 °C+ (1050 °F+) resid conversion of Black Thunder Wyodak coal after 22 min at 440 °C was 32%.⁵ This essentially replicated the conversion observed in the 1st-stage reactor in both Wilsonville Runs 262E and 263J, which were essentially identical. The purpose for the catalyst screening test that is being developed in this program is to identify catalysts that can match the resid conversion that was obtained after the 2nd-stage of the Wilsonville operation with the Mo catalyst contained in the Run 262E recycle solvent.

Because of the complications associated with solids contained in the recycle solvents used in the Wilsonville plant, our intention was to devise a reformulated solids-free solvent containing a significant residual fraction but free of either mineral matter or accumulated catalysts. A solvent composition was chosen comprising a 565 °C- (1050 °F-) distillate material and a 565 °C+ (1050 °F+) solids-free resid, both taken from Wilsonville Run 258. The resid component was a solids-free 565 °C+ (1050 °F+) material produced by the ROSE-SR unit, which made up only about 7% of the total plant recycle solvent. The other major component in the Wilsonville recycle solvent was an ashy resid recycled from the vacuum distillation tower. In the screening test, the distillate and deashed resid components are blended with feed coal in a way to give a resid/maf coal ratio of approximately 1.1, which is similar to that contained in the feed in Run 263J. The composition of the reaction mixture in the catalyst screening test, as determined from distillations on the feed solvent in our laboratory, is shown in Table 2.

The reaction temperature of the catalyst screening test of 440 °C is the same as used in the Phase I test, however, the sulfiding agent was changed from dimethyl disulfide to 2% H₂S in H₂

with an initial starting pressure of 1350 psig. This provides a hydrogen to feed coal ratio of about 18 wt % on dry coal. Total pressure at operating temperature was approximately 2500 psig. The reaction time was selected from a series of experiments that were used to determine the time necessary to provide the same 565 °C+ resid conversion of Wyodak coal as observed in Run 263J. The microautoclave runs in our laboratory were made by adding 30 wt% dry Wyodak BT coal to Run 262E Mo-containing solvent, at a Mo concentration of 300 ppm on dry coal. The 565 °C+ resid conversion after 22, 30, 60 and 90 min were determined to be 32, 44, 47 and 52%, respectively (see Table 3). The source of the 22 min data was above. The corresponding resid conversions on an maf coal basis in these tests were quite high indicating a conversion even higher than observed at Wilsonville. In a plot of log unconverted resid versus reaction time, the 60 and 90 min conversions depart significantly from a plot of the 22 and 30 min reaction results, as shown in Figure 1. Since the resid conversions observed in Run 263J at Wilsonville was about 38%, a 30 min residence time was chosen for the test, since it most closely replicated those results.

To verify the validity of the catalyst test procedure for identifying active catalysts, samples of the catalyst dispersed in the Run 262E recycle solvent were isolated and evaluated in the screening test. This entailed isolating the catalyst-rich solids from the ashy resid portion of the solvent. One sample was prepared using a Soxhlet extraction technique with THF as the extracting solvent. Another sample was prepared by separating the solids from a THF-ashy resid slurry by filtration at ambient temperature. Both materials were dried overnight at 40 °C at 125 mm Hg. The filter cake obtained from the THF slurry was found to contain 740 mg Mo/kg, which provides a Mo/dry coal ratio of 300 ppmw in the test mixture.

In the catalyst screening test, both of these materials added to the reaction mixture at a Mo level of 300 ppmw on dry coal gave 524 °C+ resid conversions of 23-24%, which were significantly lower than the 40+% expected. Although the activities were less than expected, both samples showed activity that was well above the resid conversion activity of coal in the absence of any catalyst, i.e., 19%. By contrast, the coal conversion to THF solubles for the Mo-catalyst runs were much more in line with expected values, i.e., 99-101%.

As a check to determine if the unusually high 565 °C- distillate fraction in the Run 258 deashed resid or the composition of this fraction could be causing an unexpected result, a full range recycle solvent from Run 258, i.e., Wilsonville designation V-131B, was filtered and used as solvent in the screening test. Distillation indicated this material contained 50.2% 524 °C- distillate, 44.3% 524 °C+ resid, and 5.5% THF insolubles. The 524 °C+ resid conversion for Wyodak coal in this solvent, to which was added filter cake to a level of 300 ppm Mo on dry coal, was 26%, as shown in Table 4. This result is comparable to the result when using the deashed resid. For comparison, the 18% resid conversion in the absence of any added catalyst was essentially the same as when deashed resid was used as solvent.

Progress in developing this catalyst screening test will be discussed as well as possible reasons for this difference in activity for catalyst that was isolated from the reaction slurry versus catalyst that remained suspended in the solvent. In addition, results for various dispersed catalysts in this screening tests will be presented.

REFERENCES

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Proximate Analysis		Ultimate Analysis		Sulfur Types	
	wt%		wt%		wt%
Moisture	21.2	Carbon	68.68	Total	0.39
Ash	5.15	Hydrogen	4.76	Pyritic	0.07
Volatile Matter	34.4	Nitrogen	1.21	Sulfate	0.09
Fixed Carbon	39.3	Sulfur	0.56	Organic	0.23
		Oxygen (diff)	18.25		
		Ash	6.54		
		Ash, SO ₃ -free	5.42		

	Dry coal basis, wt %	
	565	524
Cut point, °C	565	524
Dry coal	35	35
Distillate, wt% at cut point	21.5	26.6
Deashed Resid, wt% at cut point	43.5	38.4

Run No.	I	II	III
Feed Composition			
Coal, mf, wt%	30.0		
565 °C- Heavy Distillate, wt%	30.5		
565 °C+ Ashy Resid, wt%	39.5		
Added Catalyst, wt%	none		
Mo Concentration, mg/kg mf coal	380		
Reaction Results			
THF Coal Conv	106	106	107
Gas Yield	22	32	32
565 °C+ Resid Conv	44	47	52
565 °C+ Resid Conv (on maf coal)	92	98	110
H ₂ consumption, wt%	4.6	5.4	5.9

Table 4. Catalyst Screening Test Results with Added Wilsonville Run 262E Mo-Containing Solids 440 °C, 30 min, 1350 psig, 2 vol% H ₂ S/H ₂					
Run No.	IV	V	VI	VII	VIII
Source of Run 262E extract	none	filtered	Soxhlet	none	filtered
Feed Composition					
Run 262E extract, wt%	none	12.4	12.6	none	12.4
Mo Concentration, mg/kg mf coal	none	295	300	none	300
Coal, mf, wt%	35	31	31	35	30
Run 258 565 °C- Distillate, wt%	21.5	18.8	22.4	-	-
Run 258 565 °C+ Deashed Resid, wt%	43.6	38.1	35.3	-	-
Run 258 Filtered Recycle Solvent, wt%	-	-	-	65	57.6
Reaction Results					
THF Coal Conv	68	99	101	77	111
Gas Yield	21	21	19	20	20
524 °C+ Resid Conv	19	23	24	18	26
524 °C+ Resid Conv (on maf coal)	41	57	59	35	58
H ₂ consumption, wt%	1.7	4.2	3.9	1.9	4.3

Figure 1
Resid Conversion in 262E Recycle Solvent

