

**CATALYTIC MULTISTAGE LIQUEFACTION OF BLACK THUNDER MINE COAL
USING BOTH SUPPORTED AND SLURRY CATALYSTS.**

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ABSTRACT

Catalyst cost has a significant impact on the economics of direct coal liquefaction. The catalyst cost is determined by its activity and deactivation. The use of an active slurry catalyst in low concentration, which gives equivalent performance to supported catalyst systems, would be potentially attractive. A slurried molybdenum catalyst, used with both iron impregnated coal and untreated coal, has been found to be an effective catalyst for the liquefaction of a sub-bituminous coal in HRI's Catalytic MultiStage Liquefaction process. The efficacy of the combined molybdenum/iron catalyst system in the first stage was investigated in HRI's ebullated bed bench unit. The combined catalyst system of molybdenum/iron (300 ppm Mo & 5000 ppm Fe) performed better than either iron or molybdenum alone in the first stage. The slurried catalyst, at these low concentrations, appeared to do as well a job of converting coal into liquids as a conventional supported catalyst (Ni-MO/Al₂O₃) in the first stage.

INTRODUCTION

The process performance parameters such as total coal conversion, 975+°F resid conversion and c4-975°F distillate yield can be used successfully as a measure of hydrogenation/hydrocracking activities of different catalyst systems. The catalyst activity and its deactivation-behavior can be compared for different catalyst systems by examining the resid conversion and the resid content of the heavy oil products as a function of catalyst age.

EXPERIMENTAL

This paper compares the results of three different bench-scale tests all run with Black Thunder Mine coal. The first test uses supported catalyst in both stages of a two reactor system. The other two tests use supported catalyst in the second stage and two different slurry catalyst additives in the first stage. The iron catalyst precursor was impregnated on the coal matrix using an incipient wetness technique developed by Pittsburgh Energy Technology Center¹ and previously scaled up by HRI for bench run CC-15². Black Thunder Mine coal was impregnated with hydrated iron oxide (FeOOH) at 5000 ppm of iron using this technique. The molybdenum catalyst was added as a 5 wt% solution of ammonium heptamolybdate at 300 ppm of coal.

HRI, Inc's Catalytic MultiStage Liquefaction (CMSL) technology was used as a basis for this test program. The reactor configuration consisted of an initial pre-treater stage, followed by a backmixed slurry reactor and then an ebullated bed reactor. The iron and molybdenum catalyst precursors were first activated to a sulfided form in the pre-treater stage prior to the two liquefaction stages. The first liquefaction stage operated as a slurry reactor (containing no supported catalyst) and the second stage as an ebullated bed containing Shell S-317 1/32" extrudate. Downstream product separation was accomplished by a hot separator and a cold separator. The bottoms from the hot separator were further processed off-line by batch pressure filtration. The pressure filter liquid (PFL) was used to slurry the feed coal and as a flush oil. The two catalyst precursors were activated with H₂S (3 wt% coal) at 300 °C in the pre-treater stage.

RESULTS AND DISCUSSION

Three runs with five different first stage catalyst conditions were compared; second stage catalyst always consisted of Shell S-317 1/32" extrudates (Table 1). Run CMSL-1 used both the slurry molybdenum catalyst with the iron impregnated coal as well as just the slurry molybdenum catalyst. Run CC-15 examined the use of both the iron impregnated coal and using no catalyst additive so that the first stage would be just a thermal reactor. Run CC-1³ is a base case for a catalytic/catalytic CTSLTM operation. Since each run consisted of a number of operating conditions, the exact periods chosen for comparison were based upon comparable second stage catalyst ages and similar high/low temperature staging of the final two reactors. The major significant difference among the runs is that CMSL-1 was run at a much higher space velocity, 1.45-1.66 times the base condition, giving only 60-69% of the nominal residence time of the base condition. This would normally lead to poorer performance in terms of coal conversion, resid conversion and total distillate yield and a higher level of resid in the pressure filter liquid.

The coal conversion for the four systems using a first stage catalyst are all roughly equal, within 1.5% (Figure 1). The conditions using the slurried molybdenum catalyst actually have the highest conversion, and the run with only a molybdenum additive has a higher conversion than when the iron is also present. All three slurry catalyst systems, the molybdenum/iron, the molybdenum alone and the iron alone, give favorable coal conversion compared to the base condition with the supported catalyst.

The resid conversion for the four catalytic systems also show only a small variation, with the molybdenum/iron system having the highest conversion and the iron system with the lowest (Figure 1). Both of the systems using the molybdenum additive show at least as good resid conversion as the base system does. Since the resid conversion is strongly dependent on the catalyst age, it is not surprising that the molybdenum/iron system, with a lower catalyst age by almost 1/2, has a higher conversion than the molybdenum

system does.

The total distillate yield (C4-975+F) also shows only small differences among the four catalytic conditions (Figure 1). This is the only measure of performance for which either of the molybdenum containing systems is worse than the base condition, and even then the molybdenum system is only 1.6 WT% lower than the supported catalyst; while the molybdenum/iron system is 1.2 WT% higher.

These three parameters, coal conversion, resid conversion and distillate yield, can be used to determine the performance of a catalyst in the CMSL process. The resid conversion and the total distillate yield being the two more catalyst dependent variables, but the coal conversion is not entirely independent of catalyst. For these three parameters there is little difference among the four different catalytic systems, the condition using no catalyst at all in the first stage having the poorest performance, as would be expected. These four conditions show equivalent performance even though the molybdenum/iron system was run at 1.66 times the reference space velocity and the molybdenum system was run at 1.45 times the reference space velocity. Also, there is little difference in the performance between the run with just a molybdenum catalyst and the run with the molybdenum and iron catalysts.

Another measure of catalyst performance is the distribution of the final products (Figure 2). The molybdenum/iron system gives the best overall product distribution with the highest light distillate yield and the lowest resid yield. Both the iron system and the molybdenum system compare well with the supported catalyst system, demonstrating higher light distillate yields with lower heavy distillate yields while the naphtha and resid yields are very close. The molybdenum and the molybdenum/iron systems both give better distillate distribution than the supported catalyst even though they are at a much higher space velocity, 1.45 and 1.66 times the reference space velocity respectively.

The activity and deactivation of a catalyst system is also critical to the long term operation of a liquefaction process. Figure 3 shows one measure of catalyst deactivation in terms of the resid conversion as a function of catalyst age. The CMSL-1 run using the molybdenum catalyst always gives a higher resid conversion than does CC-15 with the iron catalyst. Additionally the rate of deactivation as measured by the slope of the graph is also lower for the molybdenum system by 54%.

One of the more noticeable effects catalyst has is on the quality of the pressure filter liquid (PFL) used as a recycle oil to slurry the fresh coal feed. This is taken as the liquid bottoms from an atmospheric flash vessel usually operated at 315 °C. The better a catalyst is as a hydrocracker, the slower will the resid content of the PFL increase as the catalyst ages. Figure 4 shows the resid content as a function of catalyst age for the three runs. Run CC-1

data is not appropriate to this comparison past a catalyst age of 168 lbs dry coal/lb catalyst due to various recycle schemes that were used. Both CC-15 with the iron catalyst and CC-1 with the supported Shell S-317 catalyst show the same trend of resid buildup in the PFL. Run CMSL-1 with the molybdenum catalyst initially shows this same trend until a catalyst age of 300 lbs dry coal/lb catalyst is reached. At this point the resid content of the PFL is constant at 27 WT%. The molybdenum catalyst system achieves a steady level of resid content in the PFL sooner and at a lower level than does the iron system. The molybdenum system performs as well as either the supported catalyst system or the iron system does and at a much higher space velocity.

CONCLUSIONS

It has been shown that at comparable operating conditions the use of combined molybdenum/iron slurried catalysts in the first stage of the CMSL process results in an improved process performance for liquefaction of a sub-bituminous coal over that obtained from the use of either iron or molybdenum catalyst alone or the use of the supported Ni-Mo/Al₂O₃ catalyst in the first stage. The slurried catalysts, as compared to the supported catalyst (in the first stage) not only resulted in improvements in coal and resid conversion and C4-975+F distillate yield, they also subsidized the deactivation of the second stage supported catalyst, probably by maintaining the quality of the recycle oil in the first stage. This similar, if not better, overall performance was achieved while maintaining a 66% higher throughput.

REFERENCES

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TABLE 1: OPERATING PARAMETERS FOR COMPARISON RUNS						
RUN ID#		CMSL-1	CMSL-1	CC-15	CC-15	CC-1
PERIOD (DAY)		7	14	8	11	16
CATALYST AGE (LB COAL/LB CAT)		168	317	228	316	384
CATALYST 1 ST STAGE		MOLY & IRON	MOLY	IRON	NONE	SHELL S-317
2 ND STAGE		SHELL S-317	SHELL S-317	SHELL S-317	SHELL S-317	SHELL S-317
TEMP (°C)	RXN 1	444	440	427	427	436
(°F)		(832)	(824)	(801)	(801)	(817)
	RXN 2	413	413	412	413	408
		(775)	(775)	(774)	(775)	(767)
SPACE VELOCITY (SV _{REF} = 1.0)		1.66	1.45	0.91	0.96	1.00

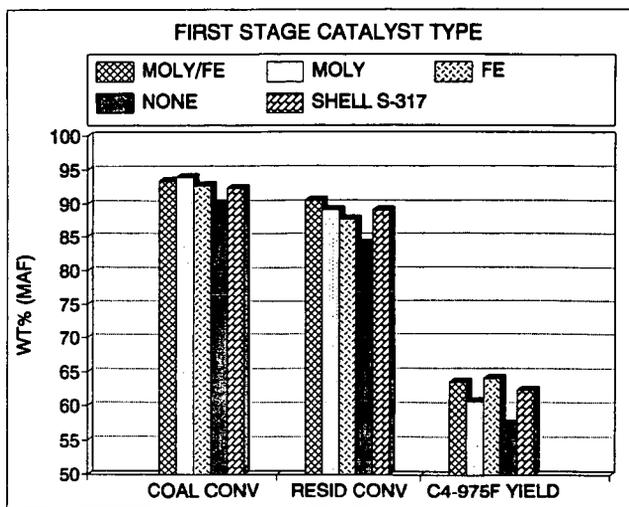


Figure 1. Process performance.

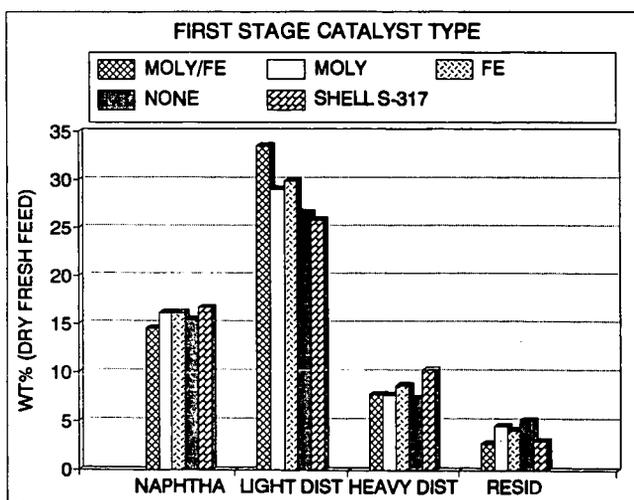


Figure 2. Final Product Distribution.

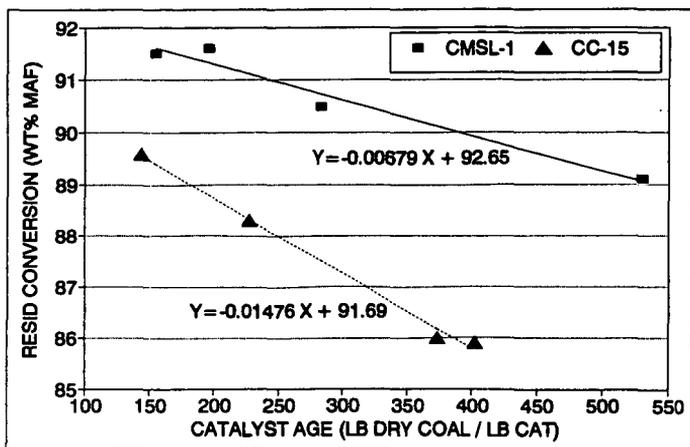


Figure 3. Resid conversion as a function of catalyst age for CMSL-1 and CC-15.

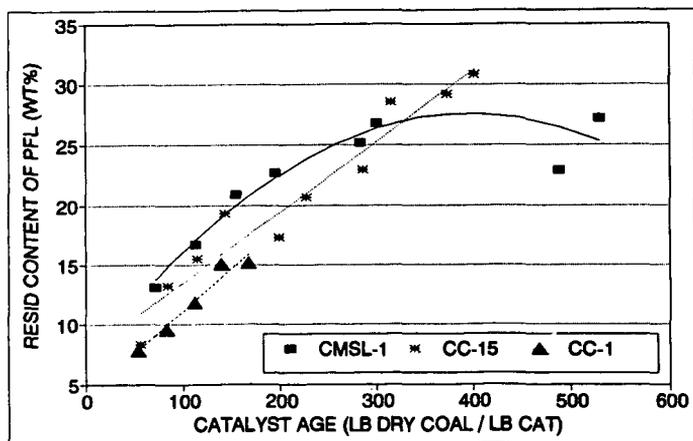


Figure 4. Resid content of the pressure filter liquid as a function of catalyst age.