DISPERSED MOLYBDENUM CATALYSTS FOR LIQUEFACTION OF ILLINOIS NO. 6 COAL

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ABSTRACT

Supported Ni/Mo catalysts have been used successfully for liquefaction of Illinois No. 6 bituminous coal at the Advanced Coal Liquefaction facility in Wilsonville, AL. In Run 261, coal conversions of 92-93% and C_4+ distillate yields of 64-65% were obtained with Akzo's EXP-A060 catalyst or Shell 324. These results are excellent, however, process costs could be decreased by use of a dispersed catalyst in a slurry reactor. Research was undertaken to evaluate dispersed Mo catalysts for liquefaction of Illinois No. 6 coal under DOE Contract DE-AC22-88PC88819.

Resid conversion improved when oil-soluble Molyvan L replaced Amocat™ 1C catalyst in the first stage (192 ppm Mo/coal). Raising the first stage temperature from 800°F to 820°F increased resid conversion further. Use of Molyvan L or Mo octoate (84-192 ppm Mo) as the only catalyst also gave high resid conversion. Furthermore, about the same yield structure was obtained at half the residence time and higher temperature. With the oil-soluble Mo catalysts, distilled fractions contained more heteroatoms, which must be removed in a subsequent hydrotreating step. Based on these tests, oil-soluble Mo catalysts are recommended for liquefaction of Illinois No. 6 coal.

INTRODUCTION

Illinois No. 6 coal has served as the reference liquefaction feedstock at the Advanced Coal Liquefaction facility in Wilsonville, Alabama for several years. The process has evolved over time from single-stage high-severity to two-stage, moderate severity. Significant improvements have been made in coal conversion, energy rejection during solids separation, distillate yield, and coal throughput. The best results to date were obtained using a new catalyst, EXP-AO-60, with a pore structure similar to Amocat™ catalysts, in the two stage catalytic process. It is becoming increasingly difficult to develop a new supported catalyst that gives a large beneficial effect on process economics. Improvements are more likely to come from significant process changes. With this in mind, oil-soluble molybdenum catalysts for liquefaction of Illinois No. 6 coal were tested in this work in place of the supported catalyst in one or both stages. Use of oil-soluble catalysts would simplify reactor design and decrease reactor cost. Molyvan L (8% Mo, $3.20/lb.) and molybdenum octoate (8% Mo, $2.00/lb.) are commercially-available oil-soluble lubricant additives. Molyvan L was used as a first stage catalyst for liquefaction of Black Thunder coal in Wilsonville run 262 (Shell 324 in stage 2) and the only catalyst in Wilsonville run 263. This paper describes use of Molyvan L and molybdenum octoate for liquefaction of Illinois No. 6 coal. Results were very promising, suggesting that oil-soluble molybdenum compounds are good alternative catalysts for a Wilsonville-type process with Illinois No. 6 coal feed.

EXPERIMENTAL

Analyses of the Illinois No. 6 coal feed, from Wilsonville Run 257, is given in Table 1. Liquefaction solvent was a blend of V-1074 and V-203 liquids from Wilsonville Run 257. The analysis is given in Table 2. The bench-scale liquefaction runs were made in AU-135L continuous, two-stage pilot plant with 1-liter stirred autoclave reactors. Feed slurries consisted of 33/67 mixtures of

coal/liquefaction solvent. Molyvan L or molybdenum octoate were added to the feed tank without additional sulfiding agent. Two runs with dispersed catalyst were completed, one with Molyvan L added to the feed as the first stage catalyst and Amocat™ 1C catalyst in the second reactor, and one with Molyvan L or molybdenum octoate and no supported second stage catalyst. Amocat™ 1C catalyst was presulfided with 8% hydrogen sulfide in hydrogen before use. Product solubility was determined by millipore filtration, distillate yields were determined by modified D-86 and D-1160 distillation, and distilled fractions were analyzed for C, H, S, N ,and O. Unconverted solids were analyzed for metals by ICP (inductively coupled plasma spectroscopy).

Molyvan L Catalyst in Stage 1/Amocat™ 1C Catalyst in Stage 2

Liquefaction of Illinois No. 6 coal may place greater demands on the catalyst for hydrogenation of aromatics than liquefaction of Black Thunder coal. This test used Molyvan L in the first stage and Amocat™ 1C catalyst in the second stage to keep hydrogenation activity high. Feed slurries contained 800 ppm of Molyvan L (192 ppm molybdenum as a fraction of coal). Operating temperatures were 800-820 °F for the first stage, and 760 °F for the second stage. Nominal residence times were 1.5 hour in each stage or 3 hours overall. The run was operated with slurry feed for 15 days, and then with solvent-only feed for 6 days.

RESULTS

Product yields are compared to those from Amocat 1C in Table 3. The run with Molyvan L in the first stage is labelled "T/C" and the run with Amocat™ 1C catalyst in the first stage is labelled "C/C". At 800°F, the resid yield was lower with Molyvan L than with Amocat™ 1C first stage catalyst (15% vs. 28%). Resid yield decreased to 7% with Molyvan L when the first stage temperature was raised from 800 to 820°F. Yields of 650-935°F distillate increased from 5% to 13% with Molyvan L, and yields of 360-650°F distillate increased from 35% to 43% at the higher first stage temperature. Hydrocarbon gas yields and hydrogen consumption increased only slightly at 820°F.

Analyses of distilled products are given in Table 5. Amocat™ 1C catalyst in the first stage gave better hydrogenation and heteroatom removal in the lightest (360-650°F) fraction than Molyvan L. This result is not surprising because smaller pore catalysts are most effective for hydrotreating light distillate fractions. The Molyvan L acts like a very large-pore catalyst.

Spent second stage catalyst analyses are given in Table 6. With Molyvan L in the first stage, second stage catalyst was in worse shape than when it was protected by Amocat™ 1C first stage catalyst. Carbon levels were higher (25% vs. 8%), the surface area was lower (84 vs. 151 m^2/g), the pore volume was lower (0.21 vs. 0.38 cc/g), and metal deposits were higher. Solids appear to deposit on the first supported catalyst that is available. In fact, spent second stage catalyst from the run with Molyvan L is similar to spent <u>first stage</u> Amocat™ 1C catalyst. The second stage catalyst replacement rate would have to increase if Molyvan L was used in the first stage.

Dispersed Molybdenum Catalysts in Stages 1-2

Molyvan L or molybdenum octoate were tested without supported catalyst for liquefaction of Illinois No. 6 coal at 192 ppm and 84 ppm Mo:coal (64 and 26 ppm Mo:slurry) for Molyvan L, and 96 ppm Mo:coal (32 ppm Mo:slurry) for molybdenum octoate. Operating temperatures were 800-820°F for both reactors. The nominal residence times were 0.75-1.5 hour in each stage or 1.5-3.0 hours overall. Each set of conditions was maintained for 3 days to obtain representative samples.

At the end of the run, a solvent-only feed was processed with Molyvan L catalyst (48 ppm Mo:solvent).

RESULTS

Product yields from all conditions were good, see Table 3, columns labelled "slurry". Resid yields were 3-8%, C_4-935°F distillate yields were 66-72%, and coal conversions were 94-96%, which was as least as good as from the first stage test with Molyvan L. Hydrogen consumption were somewhat lower (4.8-5.7%) than from Amocat™ 1C (5.6%) or for first stage Molyvan L (5.4-6.1%).

Product yields did not change when the molybdenum level was decreased from 192 ppm to 84 ppm. Product yields were also unchanged when and the residence time was decreased from 3 to 1.5 hours and the temperature was raised from 800 to 820°F. Molybdenum octoate gave less resid than Molyvan L at the same conditions, and would be the preferred oil-soluble molybdenum catalyst because it is less expensive.

Distillate product quality, Table 4, was not as good as when Amocat™ 1C catalyst was present, however. Nitrogen and oxygen levels were higher, but sulfur and hydrogen levels were about the same. It is interesting to note that the resid plus solid fraction has a higher H/C ratio (0.98) with Molyvan L catalyst at 800°F than with Amocat™ 1C catalyst(0.95-0.96). Better hydrogenation of the heaviest components by Molyvan L is indicated. At reactor temperatures of 820°F, the H/C ratio of the resid plus solids fraction dropped to 0.92, reflecting a shift in equilibrium toward dehydrogenation. Molybdenum octoate was not as active for hydrogenation of resid plus solids, giving a H/C ratio of 0.91 at 800°F.

CONCLUSIONS

Molyvan L Catalyst in Stage 1

Overall, a process with Molyvan L catalyst in the first stage and Amocat™ 1C catalyst in the second stage gave a higher distillate yields than a process with Amocat™ 1C catalyst in both stages. Because Molyvan L catalyst can be used in a less expensive slurry reactor, it would be the preferred first stage catalyst for liquefaction of Illinois No. 6 coal. With Molyvan L in the first stage, deactivation is more rapid for supported second stage catalyst, and the catalyst addition rate would have to be increased. Also, hydrogenation of light distillate was not as good, which would require additional hydrotreating.

Molyvan L Catalyst in Stage 1/Amocat™ 1C Catalyst in Stage 2

A process with dispersed molybdenum compounds as the only catalyst offers several advantages over liquefaction with Amocat™ 1C catalyst, including less expensive reactor design and simpler operation of the reactors. Product was better than when Amocat™ 1C catalyst was used in both reactors and as good as when Amocat™ 1C was used in stage 2 with Molyvan L in stage 1. Low levels of molybdenum, 84 ppm Mo:coal, were effective. Production of a low-resid product at 1.5 hours residence time and 820°F was demonstrated. Molybdenum octoate, a less expensive dispersed molybdenum catalyst, performed well, perhaps because of the high sulfur content of Illinois No. 6 coal. Use of dispersed molybdenum catalysts for liquefaction of Illinois No. 6 coal is recommended.

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TABLE 1
COAL ANALYSES

Coal	Illinois No. 6
As Received, Wt% H_2O	6.05
Dry, Wt%	
C	69.54
H	4.56
N	1.17
S	3.26
O (Difference)	12.03
Ash	9.44
Fe	1.19
Na	0.05
K	0.18
Ca	0.37
Mg	0.06
Al	0.99
Ti	0.05
Si	2.15

TABLE 2
SOLVENT ANALYSES

Wilsonville Run	257
Wilsonville Coal	Illinois No. 6
Elemental Analyses, Wt%	
C	89.26
H	8.83
N	0.57
S	0.08
O	1.26
Distillation, Wt%	
IBP-650°F	0.36
650-935°F	58.26
935+°F	40.45
Solubility, Wt%	
THF Insolubles	0.12
Toluene Insolubles	1.07
Hexane Insolubles	7.96

TABLE 3.
Liquefaction of Illinois No. 6 Coal: Distilled Product Yields

Process	C/C	T/C	T/C	Slurry	Slurry	Slurry	Slurry
Residence Time, Hours	3	3	3	3	3	1.5	3
Stage 1, °F	790	800	820	800	800	820	800
Stage 2, °F	760	760	760	800	800	820	800
Molyvan L, ppm MoOctoate, ppm	0 0	192 0	192 0	192 0	84 0	84 0	0 96
Catalyst Age, Hours	180	150	310				
Yields, Wt% of MAF Coal							
C_1-C_3	8.9	9.3	10.1	8.5	9.1	11.0	10.5
C_4-360°F	7	7	12	7	10	11	8
360-650°F	35	35	43	40	39	41	43
650-935°F	5	13	12	21	19	16	22
935°F+	28	15	7	8	8	5	3
C_4-935°F	47	56	67	68	66	68	72
Conversion	93.2	91.1	93.9	94.6	96.3	95.7	94.5
H_2 Consumption	5.6	5.4	6.1	5.1	5.7	4.9	4.8

C = With Amocat™ 1C catalyst T = Without Amocat™ 1C catalyst

TABLE 4.
Liquefaction of Illinois No. 6 Coal: Product Analyses

Process	C/C	T/C	T/C	Slurry	Slurry	Slurry	Slurry
Residence Time, Hours	3	3	3	3	3	1.5	3
Stage 1 °F	790	800	820	800	800	820	800
Stage 2 °F	760	760	760	800	800	820	800
Molyvan L, ppm MoOctoate, ppm	0 0	192 0	192 0	192 0	84 0	84 0	0 96
Catalyst Age, Hours	150	150	310				
Analyses, Wt%							
360-650°F Aromatic C	32	40	40	43	43	43	43
H/C	1.61	1.49	1.49	1.47	1.48	1.46	1.45
N	.25	.41	.48	.65	.56	.54	.51
O	1.5	2.3	2.4	2.9	3.3	3.1	3.1
650-935°F Aromatic C	42	47	47	47	48	50	51
H/C	1.28	1.28	1.27	1.25	1.27	1.22	1.22
S	.06	.07	.07	.08	.09	.09	.09
N	.30	.36	.47	.60	.61	.52	.49
O	.5	.8	.9	1.1	1.2	1.1	1.0
935°F+, Solids							
H/C	.96	.95	.96	.98	.98	.92	.91
S	.96	1.00	.92	1.01	.88	.35	.95
N	1.07	1.14	1.18	.97	1.06	1.09	1.12

C = With Amocat™ 1C catalyst T = Without Amocat™ 1C catalyst
Nominal residence time was about 3 hours for these periods.

TABLE 5.
Analyses of Spent Amocat™ 1C Catalyst Samples:
Illinois No. 6 Liquefaction

Stage	Fresh	1	2	2
Temperature, °F		790	760	760
Process		C/C	C/C	T/C
Oil-Soluble Mo, ppm				192
Run Length, Days	0	20	20	20
Elemental Analyses, Wt%				
Primary Metals				
Mo	9.10	5.9	8.10	6.50
Ni	2.22	1.25	1.63	1.37
Al	35.40	23.50	31.60	25.10
Si	1.39	.98	1.22	.99
Deposits				
C	--	25.35	7.86	24.98
H	--	1.59	1.50	1.42
S	.20	4.78	5.86	4.97
Ti	.00	1.54	.14	.58
Fe	.02	.44	.14	.17
Na	.08	.12	.11	.15
Mg	.00	.05	.01	.01
Ca	.00	.00	.00	.00
Pore Properties				
Vol. <1200 Å Diam., cc/g	.59	.16	.38	.21
BET Surface Area, m^2/g	200	65	151	84