

DISPERSED SLURRY CATALYSTS FOR HYDROCONVERSION OF CARBONACEOUS MATERIALS

L.K. Lee, V.R. Pradhan, G. Popper, and A.G. Comolli
Hydrocarbon Technologies, Inc.
Lawrenceville, NJ 08648

Keywords: Dispersed Catalysts, Coal Liquefaction, Coal/Waste Coprocessing

ABSTRACT

Dispersed slurry catalysts, based upon the *in situ* sulfided forms of transition metals such as iron and molybdenum, have been developed and successfully employed in the multi-stage hydroconversion of various carbonaceous materials including coal, heavy petroleum resid, waste plastics, and different combinations of these feedstocks. For example, using HTI's proprietary iron-based catalyst and commercial Molyvan-A additive, over 95 % maf coal conversion has been obtained accompanied by over 90 % maf conversion of 524°C+ residuum and over 65 % maf yield of C₄-524°C distillate yield in a fully back-mixed high pressure reaction system. The use of an in-line fixed-bed hydrotreater in such a hydroconversion process that relies only on dispersed slurry catalysts for conversion allows to selectively upgrade the light distillate products (IBP-400°C) from the process resulting in premium quality naphtha and mid-distillate products with less than 10 ppm nitrogen, an H/C ratio of 1.9, and about 20 ppm sulfur. The use of dispersed catalyst for such hydroconversion processes has a significant positive impact (as much as 20 % cost potential reduction) on the process economics because the reactor throughput can be increased by as much as 70 % while maintaining the equivalent residence time and the cost associated with the expensive high pressure catalyst addition/withdrawal system, used for supported extrudate catalyst, and that associated with expensive ebullating pumps can be reduced or eliminated completely.

INTRODUCTION

Two-stage catalytic conversion of coal and other carbonaceous feedstocks have been studied extensively using Ni/Mo or Co/Mo supported catalysts. The low/high temperature mode of operations was demonstrated in 3 ton/day scale at both the Wilsonville advanced Coal Liquefaction facility and Hydrocarbon Research, Inc. This mode of operations in combination with an in-line hydrotreater yields liquids of premium quality containing less than 20 ppm of nitrogen. The high conversion was achieved at the expense of high replacement rate of the supported catalysts which became deactivated with carbon and heavy metal depositions. The deactivation rate of supported catalysts for feedstocks, that contain high degree of heavy metals, such as vanadium and nickel and materials that have high tendency to form coke, is one of the key factor affecting the design and cost of the conversion facility.

Dispersed slurry catalysts, which offer better contact with the reactants than the supported extrudate catalysts, have drawn much attention in recent years. Hydrocarbon Technologies, Inc. has been studied the use of anion modified iron based catalyst at its bench scale (30 Kg/day) multi-stage unit located at Lawrenceville, New Jersey. It is observed that the use of dispersed catalyst, with or without supported catalyst, in conjunction with an in-line hydrotreater increase the throughput of a system significantly without compromising much in the product qualities. This paper discusses the use of HTI's proprietary dispersed catalysts in processing coal and other carbonaceous feedstocks, such as heavy oil and waste plastics. Due to the high activity of these dispersed iron-based catalysts, they can be used in small concentrations of 0.1-1.0 wt% iron relative to weight of feed for the various hydrogenation and hydroconversion reactions mentioned above, and are preferably recycled with the unconverted or partially converted high boiling fraction (454°C+) back to the reactor for further reaction. Because these dispersed fine-sized iron catalysts are produced based on use of available relatively inexpensive materials and since the principal component is cheap and environmentally friendly iron, they are usually disposable for large scale processes and do not require recovery and regeneration. HTI's proprietary dispersed catalyst can be used either as a wet cake consisting of a gel of precipitate particles in water containing 50-80 wt% water or as a dry powder obtained after drying and/or calcination of the oxyhydroxide precipitates. In the gel mode of usage, the precipitates from hydrolysis are not filtered or dried, but are used as is. The catalyst gel form reduces the catalyst cost significantly and also does not compromise at all on its activity for relevant hydroprocessing reactions. These catalysts, either in the dry powder form or in the wet-cake form, have been successfully tested (in the presence of a sulfiding source) both at a 20 cc microautoclave reactor scale and at a 30 kg/day continuous two-stage bench-scale operation, under hydrogen pressures of 5-20 MPa and operating temperatures of between 400 to 460°C. The key to the higher activity of these HTI's catalysts as compared with some other iron-based catalysts disclosed in literature, is believed to be their initial fine size, high surface area, a high extent of catalytic dispersion, and their ability to preserve the state of high dispersion under reaction conditions due to presence of anionic modifiers which are known to prevent sintering or agglomeration of fine-sized particles at high temperatures.

EXPERIMENTAL

The activity of catalyst was tested in a 20 cc vertically shaken microautoclave unit and in a two-stage bench scale continuous flow system of nominal capacity of 30 Kg/day. The bench-scale operations, employing dispersed catalysts, were conducted in HTI's fully back-mixed reaction system employing off-line pressure filtration for solids separation; a simplified schematic of the hydroconversion process used during this work is shown in *Figure 1*. As shown in *Figure 1*, the hydroconversion process, followed here, is based upon a catalytic multi-stage reactor system supported by an independent feed preparation/handling section, high pressure product fractionation section, light distillate refining and solids separation/heavy distillate recovery sections. The hydroconversion reactors could be operated in a close-coupled mode or an interstage product fractionator could be used for taking the lights off the feed going to the second stage hydroconversion reactor. The light product fraction (400°C-material) from the hydroconversion reactors was selectively processed through an in-line fixed-bed hydrotreating unit. This step achieves a significant function of improving the quality of distillable products from the process. The heavier product fraction (400°C+ material) is substantially recycled and unreacted feed (including solids in case of coal) is either partly recycled or rejected from the process completely with minimal loss of organics. The HTI iron based catalyst is an anion modified oxyhydroxide catalyst prepared in either a dry or a gel form which contains about 50-80 w% water. Molybdenum catalyst was added in form of Molyvan A at the desired concentration levels. Coal used in this study is from Wyoming Black Thunder Mine. The coal was prepared by Empire Coke Company of Alabama and was used in the last run of the DOE Proof of Concept program. The heavy oil is a California Hondo vacuum tower bottom, while the waste plastic was a curb side plastic waste containing mostly high density polyethylene, polystyrene and polypropylene.

RESULTS AND DISCUSSION

The activity screening of dispersed slurry catalysts, performed using shaken microautoclaves, is summarized in *Table 1*. From the *Table 1* results, it is seen that the HTI's dispersed slurry catalysts, used in either a wet cake (gel) form or a dried particulate form, provided hydroconversion results superior to those obtained using the two known iron oxide catalysts. Specifically, the percent coal conversion based on tetrahydrofuran (THF) solubility and percent conversion of 524°C+ resid fraction were both significantly greater than for the commercial iron oxide catalysts. The addition of about 100 ppm of molybdenum to HTI's iron catalyst improved both the coal and the resid conversions; the gel form of iron catalyst appeared slightly better than the dry powder form. The best performance of HTI's dispersed catalyst was almost equivalent to that obtained using a more active supported NiMo catalyst, Akzo AO-60, with which a shade better performance was obtained at same temperature but for a longer reaction time (60 minutes).

The dispersed iron-based catalysts described in this paper have been used extensively in continuous bench-scale two-stage operations with throughput up to 30 kg/day of moisture and ash-free (maf) coal feed for direct catalytic two-stage liquefaction of coal. As shown in *Table 2*, under the prevailing operating conditions, for the direct liquefaction of a sub-bituminous Wyoming Black Thunder Mine coal, dispersed catalyst containing 615-10000 ppmw of iron and 50-200 ppmw of molybdenum was used, relative to maf coal feed, in the form of HTI's iron-based dispersed catalysts. The dispersed catalysts were used either in an all-dispersed slurry catalyst mode, or in a hybrid system utilizing dispersed catalyst in one of two close-coupled hydroconversion reactors and the extrudate supported catalyst in the other reactor. The use of iron and molybdenum containing dispersed catalysts has resulted in a coal conversion range of 93-96 wt%, a 524°C+ residuum conversion range of 83-92 wt%, and C₄-524°C distillate liquid yields of 60-66 wt% (all on maf coal basis). When evaluated on the basis of the maf coal feed, this performance provides up to 4 barrels of C₄-524°C distillate liquid products per ton of the maf coal feed. Specifically, the direct comparison between the data from Bench Run 83 Condition 4 and Run 91 Condition 1B shows that in an hybrid catalytic mode of operation, higher molybdenum loading (100 vs. 50 ppm) results in better liquid distillate yields (66.3 vs. 63.4) and higher conversions of coal (94.7 vs. 92.8) and resid (90.0 vs. 87.4). The performance of HTI's dispersed slurry catalysts has been compared with some other dispersed and supported type catalysts for direct coal liquefaction as shown in *Figure 2*. The process performance has been compared on the basis of total coal conversion (based on quinoline solubility of the products), 524°C+ residuum conversion, and C₄-524°C distillate yield. The first bar (None-Cat) in *Figure 2* represents process performance with a thermal first stage reactor and an expanded supported catalyst bed in the second stage reactor; the second bar (Cat-Cat) represents process performance with supported catalysts in both the reactor stages; the third bar (Mo-Cat) represents molybdenum dispersed catalyst in first stage reactor and an expanded supported catalyst bed in the second stage reactor; the fourth bar (HTI-Cat) represents performance with HTI's iron-based dispersed catalyst in the first stage reactor and an expanded supported catalyst in the second stage reactor; the fifth bar (HTI-HTI) represents the performance of an all-dispersed slurry catalyst two-stage reactor system utilizing the HTI's dispersed catalyst. It can be clearly seen from *Figure 2* that the reactor configurations utilizing HTI's dispersed catalysts alone result in the highest extent of total coal and 524°C+ residuum conversion, and C₄-524°C distillate

yields. The result obtained with the 'all dispersed catalyst' mode of operation were also better than those obtained with 'Supported catalyst-catalyst' or 'hybrid mode' of operations. At 5000 ppm of iron and 50 ppm of molybdenum, 2 % higher coal conversion, higher light distillate products were obtained; the yield of light gases was also higher in an 'all dispersed' catalyst mode. The use of dispersed catalyst allows the higher volume of reactor for thermal cracking.

Bench-scale continuous multi-stage operations were also conducted to evaluate the performance of HTI's dispersed iron-based catalysts for hydroconversion of (a) heavy petroleum oil (California Hondo resid vacuum tower bottoms), (b) mixtures of heavy petroleum resid oil and mixed plastics (containing high density polyethylene, polypropylene, polystyrene, and other organic/inorganic impurities) from municipal solid waste streams, (c) mixtures of Wyoming Black Thunder Mine coal and Hondo resid, and (d) combinations of coal, Hondo resid, and the mixed plastics feeds. Significant process performance was obtained with all of these varied feedstocks with dispersed catalysts in each stage reactor, under conditions similar to those employed for direct coal liquefaction. The prevailing operating conditions, feed type and composition, dispersed catalyst metal loadings, and process performance and yields are summarized in Table 3. As shown in Table 3, consistently high feed conversions and light distillate oil yields have been realized in the bench-scale operations. With the bench-scale operations involving either heavy petroleum resid, Hondo resid alone or in a mixed feed with coal, as high as 99 wt% feed conversion to quinoline soluble products was obtained, with as high as 75 wt% C₄-524°C distillate liquid yields. During the operations, involving mixed plastics from a municipal solid waste stream, either with coal or with heavy resid or mixtures of coal and heavy resid, over 93 wt% total feed conversions were realized with about 75 wt% distillate liquid yields.

CONCLUSION

Based upon the data presented in this paper, it is evident that the sulfate-modified iron-based dispersed catalysts, HTI has developed, are very effective in achieving the levels of performance that is tantamount to or better than that obtained using the conventional supported extrudate catalysts. The iron-based dispersed slurry catalysts were also very effective for the hydroconversion of organic wastes such as heavy petroleum resids and MSW plastics, in combination with coal, into the value-added distillate products. The higher activity of these HTI's catalysts as compared with some other iron-based catalysts disclosed in literature, is believed to be due to their initial fine size, high surface area, a high extent of catalytic dispersion, and their ability to preserve the state of high dispersion under reaction conditions due to presence of anionic modifiers which are known to prevent sintering or agglomeration of fine-sized particles at high temperatures. The overall high levels of yields and conversions are obtained with HTI's proprietary dispersed catalyst, especially at the metal loadings that potentially make the use of these catalysts possible on a disposable basis. The replacement of supported extrudate catalysts by fine-sized dispersed slurry catalysts also allows for operations at significantly higher throughput under similar overall reaction severity. It is anticipated that the use of dispersed catalysts would lower the overall cost of hydroconversion of coal and other organic feeds discussed in this paper.

ACKNOWLEDGMENT

The financial support provided for this work by the U.S. Department of Energy under the Contract Nos. DE-AC22-93PC92147 and DE-AC22-92PC92148 is gratefully acknowledged.

Table 1. Activity of Dispersed Catalyst in Microautoclave Testing*

Coal: 2 g, Solvent: 6g, DMDS: 0.2 g 427°C @ 14 MPa for 30 min. Fe: 5000 wppm

Catalyst Type	THF Conversion [%]	524°C+ Conversion [%]
Fe ₂ O ₃ (Aldrich)	76.1	34.1
Fe ₂ O ₃ (Mach I)	80.6	42.8
Fe/SO ₄ ²⁻ (dry)	83.3	53.3
Fe/SO ₄ ²⁻ (gel)	86.2	55.1
Mo.Fe/SO ₄ ²⁻ (dry)	86.8	59.6
Mo.Fe/SO ₄ ²⁻ (gel)	89.9	63.3

*The THF Conversion under similar reaction conditions (but 60 minute long reaction time) for a supported extrudate NiMo/Al₂O₃ catalyst (fresh Akzo AO-60) was 92.1 w% and the 524°C+ residuum conversion was 64.4 w%.

**Table 2 Process Performance using Dispersed and Supported Catalysts
Wyoming Black Thunder Mine Coal
Dispersed Catalyst: HTI sulfated Iron; Supported Catalyst: Shell S-317**

Run I.D. Condition	CMSL-6 4	PB-02 1B	CMSL-11 1	PB-1 1
Process Conditions				
Mode	Thm/Cat	Thm/Cat	All Disp.	All Disp.
Recycle/Coal ratio	1.3	1.0	1.0	1.0
Space Velocity, Kg mf coalh/M ³	640	665	703	694
1st Stage Temperature, °C	449	447	441	433
2nd Stage Temperature, °C	429	427	449	449
Catalyst Concentration				
Iron, w%	0.0615	0.500	0.500	0.500
Molybdenum, wppm	100	50	50	50
Process Performance W% maf Coal				
C ₁ -C ₃	11.3	10.3	15.7	12.4
C ₄ -177°C	18.2	20.8	19.7	21.2
177°-343°C	33.5	26.4	32.1	28.0
343°-524°C	14.9	16.2	9.0	12.7
524°C+	4.5	5.4	3.7	6.6
C ₄ -524°C Distillate	66.6	63.4	64.6	61.9
Coal Conversion	94.5	92.8	95.5	94.7
524°C+ Conversion	90.0	87.4	91.5	88.0
H ₂ Consumption	7.0	7.3	6.9	6.4

Note: Thm/Cat = Thermal/Catalytic two-stage mode; All Disp. = All Dispersed Catalyst two-stage mode

Table 3 Hydroprocessing of Mixed Feeds using HTI's Iron Based Dispersed Catalyst

Run I.D. Condition	CMSL-9 9	CMSL-11 3A	CMSL-11 4B	PB-1 4	PB-1 9	PB-1 7
Feed Composition, w%						
Black Thunder	50	67	75	0	0	33.3
Waste Plastics	50	33	25	0	50	33.3
Hondo VTB	0	0	0	100	50	33.4
Process Conditions						
Space Velocity, Kg mf coalh/M ³	669	687	662	1059	1250	1033
1st Stage Temperature, °C	449	450	447	441	451	450
2nd Stage Temperature, °C	462	459	461	451	460	461
Catalyst Concentration						
Iron, w%	1.00	0.500	0.500	0.500	0.500	0.500
Molybdenum, wppm	300	100	100	50	50	50
Process Performance W% maf Coal						
C ₁ -C ₃	7.5	8.6	7.4	5.0	4.3	7.6
C ₄ -177°C	30.0	16.8	13.4	16.2	21.4	26.2
177°-343°C	26.2	24.9	26.1	27.7	24.3	24.6
343°-524°C	18.1	25.3	28.1	32.2	30.5	22.0
524°C+	8.9	11.4	11.2	16.5	15.7	10.9
C ₄ -524°C Distillate	74.3	67.0	67.6	76.1	76.2	72.8
Coal Conversion	97.0	95.3	94.7	N.A.	N.A.	96.3
524°C+ Conversion	88.1	83.9	83.5	83.3	84.0	85.4
H ₂ Consumption	3.5	4.1	4.9	1.7	1.8	3.4

Figure 1. Simplified Schematic of HTI's Catalytic Multi-Stage Hydroconversion Process

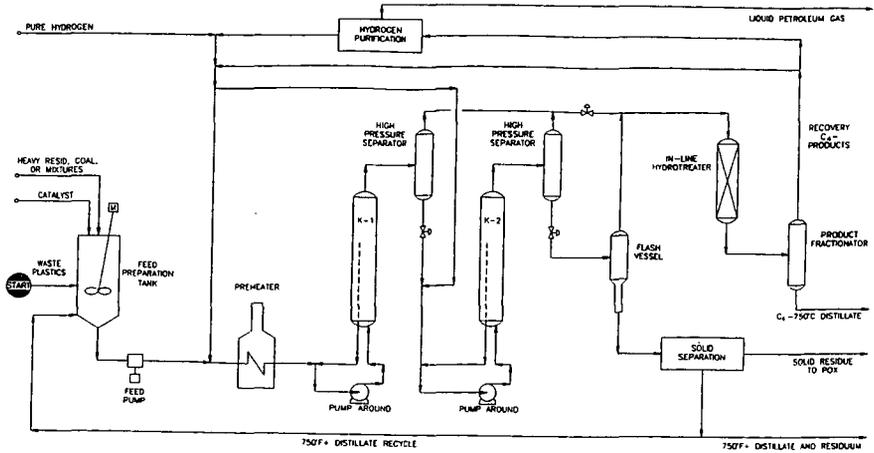


Figure 2. Comparison of Catalyst Performance in Bench-Scale Direct Coal Liquefaction

