

Assessment of Small Particle Iron Oxide Catalyst for Coal Liquefaction

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Introduction

Current efforts to lower the cost of producing coal liquids are concentrated on the use of low-rank coal feedstocks, and dispersed catalysts to promote coal dissolution in the first stage of a two-stage process. Molybdenum and iron are the most commonly investigated catalyst metals, and precursors of both can be converted to an active sulfide catalyst under liquefaction conditions.¹ Although iron catalysts are less active, they are preferred for reasons of economy. A great deal of research has been spent in attempting to understand the chemistry of liquefaction in the presence of iron catalysts. It has also been demonstrated that the use of powdered iron catalysts has allowed the liquefaction of subbituminous coals which could not otherwise be processed². Nevertheless, the activity of these catalysts is still much less than desired and means to enhance their activity are under investigation.

The catalyst activity is determined principally by its composition and the extent of its dispersion with the coal or coal-solvent slurry. The catalyst dispersion is dependent upon the form and mode of addition of the catalyst precursor. High activities are reportedly favored by catalysts introduced as oil-soluble organometallic precursors such as naphthenates and carbonyls.^{3,4,5} The results of some studies, however, indicate that even with these precursors, quite large crystallites or agglomerates can be formed during liquefaction and hence the potentially high dispersion is not maintained. There is some evidence to suggest that, if introduced as fine particulates, there is less tendency for agglomeration. Iron particles of about 50 nm mean diameter synthesized by a flame pyrolysis technique appeared to have retained their particle size and shape during presulfiding and coal liquefaction.^{6,7} Other work has shown that FeS is more active as a colloid than in powder form.⁸ A number of studies have reported enhanced catalytic activity by using methods of preparation that introduce nanometer size iron catalysts.^{9,10,11,12}

The work presented in this paper is concerned principally with a systematic evaluation of the effect of reaction parameters on the catalytic conversion of a subbituminous coal using a commercially produced nanometer size iron oxide catalyst. The work is part of a DOE program to evaluate process concepts that can alone, or in concert, significantly improve process economics. In order to make realistic assessments, studies have been made using process recycle oil from the Wilsonville Advanced Coal Liquefaction Research and Development Facility and Black Thunder subbituminous coal.

Materials

Reagents - Reagents were purchased as follows: Practical grade dimethyl disulfide (DMDS) from Fluka AG; 99% purity UV grade tetralin, high purity tetrahydrofuran (THF), and high purity pentane were Burdick & Jackson Brand from Baxter S/P; UHP 6000# hydrogen was supplied by Air Products and Chemicals, Inc. Coal, coal derived liquids and iron oxide used at the Wilsonville Advanced Coal Liquefaction Research and Development Facility were supplied by CONSOL, Inc.

Coal - Black Thunder subbituminous coal was ground to -200 mesh, riffled and stored under nitrogen at 4°C in a refrigerator.

Recycle oil - A reconstituted recycle oil was used in this program that had been produced at Wilsonville in runs where the plant was in the distillate production mode with all residual materials being recycled to extinction except for the organic matter occluded in the ash reject.¹³ The Wilsonville recycle oil, taken from Run 262 while operating on Black Thunder Coal, contained 43.8 wt% 1050°F distillate, 36.6 wt% residual organic material, 9.2 wt% cresol insolubles and 10.4 wt% ash.

The fractions that were used to form the recycle oil contained significant concentrations of both molybdenum and iron which were being added as catalysts in Run 262. The ashy resid contained 3.3 wt% iron plus 300 ppm molybdenum. The distillate contained only 200 ppm of iron and 2 ppm of molybdenum. It is assumed that these metals possess some indeterminate residual catalytic activity. However, in this research, these effects are integrated into the "thermal" baseline.

Catalysts - Two iron oxide catalyst precursors were used in this study. One was a sample of the iron oxide used at Wilsonville in Run 262 (WIO) while the other was a sample of superfine iron oxide (SFIO) provided by MACH I, Inc., King of Prussia, Pennsylvania. The latter has a bulk density 1/26th that of the WIO (.052 vs. 1.37 g/ml), and a very high surface area (318 vs. 9 m²/g for WIO).

Experimental

Equipment and Procedures - In a typical experiment 3 grams of coal, 5.4 grams of recycle oil, catalyst and DMDS (2.4 moles S/mole Fe added as catalyst) were added to the reactor. The reactor was sealed, pressurized with hydrogen to 1000 psig, and leak tested. Reactions were carried out in a fluidized sandbath set at the specified temperature while the reactor was continuously agitated at a rate of 400 cycles per minute. At the termination of the reaction period, the reactor was quenched to ambient temperature in a room temperature sand bath. The gaseous products were collected and analyzed by gas chromatography. A solvent separation technique, which is described in detail elsewhere,¹⁴ was used to separate both reactants and products. The solid-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 was comprised of IOM and ash, was dried (80°C/25 mm Hg) and weighed. The THF solubles were concentrated by removing excess THF in a rotary evaporator to which a 50:1 excess volume of pentane was added to precipitate the preasphaltenes and asphaltenes (PA+A). The mixture was placed in an ultrasonic bath for 3 minutes to facilitate the precipitation process before filtering off the PA+A. The PA+A fraction was dried and weighed. This then separates the product into oils, PA+A and IOM plus ash.

Material Balance and Product Yield Computational Methods - The calculation of the yield of products differs somewhat from those reported elsewhere, in that the feed is comprised of the multiple individual Wilsonville recycle oil fractions in addition to coal and catalyst. The product distribution was determined using this same fractionation scheme assuming complete recovery of the ash plus catalyst. In this method the iron is presumed to convert to pyrrhotite and the weight of catalyst reporting to the ash fraction is calculated as the corresponding weight of Fe_{0.9}S. By this method water produced during liquefaction is included in the oils fraction. Experimentally, complete recovery of ash and catalyst was demonstrated. Net product

yields are calculated by subtracting the amount of material contained in the feed fractions from the corresponding amounts found in the product fractions. The total of the net products equals the amount of maf coal in the feed and reflects the net make (or loss) of each of the solubility fractions while coal conversion equals 100 minus the yield of IOM.

Experimental Design - A major portion of the research reported here has been concerned with a detailed investigation of the influence of the reaction variables during coal liquefaction in the presence of added SFIO. An experimental approach was adopted that would maximize the amount of information gathered in a given series of experiments and provide a data set from which to draw valid comparisons. A full 2⁴ factorial experimental design was developed following the method described by Box, Hunter, and Hunter.¹⁵ The main effects and interactions of reaction temperature, catalyst concentration, and sulfur concentration were determined separately for each of several dependent variables including THF conversion, hydrogen consumption, CO+CO₂, hydrocarbon gas, oil and PA+A yields. This technique is particularly applicable to complex reaction systems, such as coal liquefaction, where the reaction mixture is comprised of recycle oil, which itself is a composite of three process materials, coal, catalyst and hydrogen.

Because of the high concentration of metals in the recycle oil, iron oxide concentrations were selected which could have a clearly discernible effect on coal liquefaction, ranging from 1 to 4 wt% Fe on as-fed coal. Added sulfur was selected to explore a wide range of S/Fe atomic ratios, with the centerpoint at 2:1. The reaction temperatures were 390 and 440°C, centered at 415°C.

Results

Comparison of Heavy Distillate and Recycle oil - Liquefaction of Black Thunder Coal in Wilsonville heavy 1050°F distillate at 415°C for 60 minutes gave 95 wt% THF conversion and 35.8 wt% oil yield with the addition of 1.1 wt% iron as WIO and excess DMDS for its conversion to pyrrhotite (see Table 1). The added iron catalyst had a significant effect on THF conversion and the yield of pentane solubles. Based upon previous results, distillate would exhibit little reactivity under these conditions and would not complicate the analysis of coal reactivity.¹⁶

However, coal liquefaction in the Wilsonville recycle oil produced THF conversions which regularly exceeded 100%. In a thermal run, without any added iron oxide, the THF conversion was in excess of 100%, and the oil yield was in excess of the yields observed in the run with distillate alone. The difference between the two solvents was that the recycle oil contained ashy material taken from the vacuum flash unit at Wilsonville and a smaller amount of deashed resid taken from the ROSE-SR deashing unit. The unusually high level of THF conversion and high oil yield indicated that the recycle oil IOM was being converted to soluble product.

Coal Conversion in Wilsonville recycle oil - Liquefaction of Black Thunder coal in the Wilsonville recycle oil, without added catalyst, showed steadily increasing THF conversion, oil and gas make with increasing reaction time at 415°C (see Table 2). The increases parallel the changes in yield obtained with added 1.1 wt% iron as WIO. The main effect of the catalyst was to produce a higher oil yield after 60 minutes. The results are in agreement with experimental data from pilot plant runs at Wilsonville, in which the addition of sulfided iron

oxide caused an appreciable increase in conversion.¹⁷

In both thermal and catalytic cases, the CO and CO₂ are formed at short times, and the yields increased only slightly between 15 to 60 minutes. In comparison, the hydrocarbon gas yield increased from 0.5 to 1.9 wt%. Much of this increase in hydrocarbon gas yield comes from the conversion of recycle oil.

Influence of Nanometer Size Iron Oxide (SFIO) - Sulfided iron oxide particles in the size range 50-80 nm, that were prepared by high temperature thermal oxidation, have been reported to show high activity for coal liquefaction.⁶ The catalytic effect has been attributed to the high surface area and small particle size of the pyrrhotite formed upon sulfiding in the presence of coal where the pyrrhotite particles retain the small particle size of the oxide precursor.¹⁸ The SFIO, whose very high surface area is consistent with nanometer size particles, may also, upon sulfiding, give rise to small particle, high surface area liquefaction catalysts.

The addition of SFIO, at a loading of 2.5 wt% iron on maf coal, produced 11 wt% more oils than in the thermal case (see Table 3). In addition there were slight increases in THF conversion and yield of hydrocarbon gases. These data represent the mid-point of the ranges for each of the three variables. The results of the comparison illustrate the potential advantage of processing with SFIO catalyst.

Impact of Reaction Variables on Liquefaction with SFIO - The R squared values for each dependent variable that was selected indicate the degree of fit by the linear model coefficients as shown in Table 4. Values for the coefficients for each of the simple linear models are summarized in Table 5. The P-value of each coefficient is shown in parentheses.

Of the independent factors, temperature has the strongest overall effect, as seen by the magnitude of the coefficients for THF conversion, hydrogen consumption, and the yields of oil and PA+A; the oil yield increases and PA+A decreases with increasing temperature. Increasing the catalyst concentration produces moderate effects on THF conversion, hydrogen consumption, and enhances the PA+A yield. However, there is no apparent effect of catalyst concentration on oil yield. It must be stressed that only two levels of catalyst concentration have been examined and the zero concentration case is not included: as shown in Table 3, the addition of catalyst significantly improves the oil yield over the thermal case. The effects of added sulfur are small, producing a weak negative coefficient with respect to THF conversion, and a negative coefficient with oil yield.

The average increase in oil yield obtained in the three centerpoint experiments was 11% over the thermal case. This is consistent with the increase of 10 wt% in oil yield predicted by the 2³ factorial design experiments and lends confidence to the linear model.

The addition of 1.1 wt% added iron as WIO, which was the ratio used in the Wilsonville plant, gave 5% more oil than in the thermal case, which agrees closely with the results observed at Wilsonville.¹⁷ The linear model predicts that SFIO at the lower concentration level (1.1 wt% Fe) will produce 15% higher oil yield than in the thermal case, with a decrease to the observed 11% gain at the center point due to the effect of added sulfur (see Table 6). However, the experimental check of this predicted outcome gave only 8% more oil than the thermal case. The catalytic activity of the SFIO for both oil formation and coal

conversion is greater than the corresponding activity of the WIO.

The negative effect of sulfur on THF conversion and on oil yield was unexpected based upon the results of Das Gupta, et al.,¹⁹ on the liquefaction of an iron deficient Indian coal. They found, through a non-linear parameter estimation procedure, that adding sulfur up to a S/Fe atomic ratio of 8 improved conversion. In this system adding sulfur at a S/Fe atomic ratio between 0.6 to 7.4 was detrimental. This effect could be related to adverse side reactions caused by the presence of excess sulfur.

The negative interaction between temperature and SFIO concentration for oil yield indicates that thermal effects begin to dominate catalytic effects at the higher temperature. Also, in addition to thermal conversion of PA+A, the magnitude of the catalyst coefficient for the PA+A model (4.80 vs. 4.08 for THF conversion) suggests that catalytic TOM dissolution reports mainly to the PA+A fraction.

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Table 1. Liquefaction of Black Thunder Coal with Wilsonville Oils^a

	Distillate ^b	Distillate	Composite ^b	Composite
Added Fe, wt% coal	none	1.1	none	1.1
% Yield, maf coal				
Gases	7.3	7.3	6.9	6.9
Oils	24.9	35.8	48.5	53.8
PA+A	54.5	51.9	52.2	45.3
IOM	13.3	5.0	-7.6	-6.0
THF Conv, wt%	86.7	95.0	107.6	106.0
Run No.	281-1	169-2	139-1/ 167-1	142-2/ 189-1

a. 415° C, 1 hour, 1000 psig H₂ cold, 5.4 grams recycle oil, 3.0 grams coal, 2.4 mole sulfur/mole iron.

b. No DMDS added.

Table 2. Liquefaction of Black Thunder Coal in Wilsonville Recycle Oil^a

Yields, wt %	No Catalyst Added			1.1 wt% Fe Added		
	15 min	30 min	60 min	15 min	30 min	60 min
HC Gases	0.5	1.1	1.9	1.1	1.6	2.1
CO+CO ₂	4.5	5.0	5.0	4.4	4.8	4.8
Oils	21.3	36.4	48.5	20.8	36.0	53.8
PA+A	57.6	56.2	52.2	58.1	59.3	45.3
IOM	16.1	1.3	-7.6	15.6	-1.7	-6.0
Coal Conv, wt %	83.9	98.7	107.6	84.4	101.7	106.0
Run Number	148-2	167-2	139-1/ 167-1	176-1	169-1	189-1/ 142-2

a. 415° C, 1000 psig H₂ cold, 5.4 grams recycle oil, 3.0 grams coal, 2.4 mole sulfur/mole Fe

Table 3. Effect of Superfine Iron Oxide on Liquefaction^a

	Thermal	SFIO	Δ
Iron, wt % coal	None	2.5	
Yields, wt% maf coal			
HC Gases	1.9	2.8	0.9
CO+CO ₂	5.0	4.7	-0.3
Oils	48.5	59.1	10.6
PA+A	52.2	43.3	-8.9
IOM	-7.6	-9.9	-2.3
THF Conversion	107.6	109.9	2.3
Run Number	139-1/167-1	174-2/ 190-1/190-3	

a. 415°C, 1 hour, 1000 psig hydrogen cold, 5.4 grams recycle oil, 3.0 grams coal, 2.0 mole sulfur/mole iron.

Table 4. Dependent Variables Evaluated

<u>Effect</u>	<u>Units</u>	<u>R Squared</u>
THF Conv	THF conversion, wt% maf coal	0.926
mg H ₂	H ₂ consumption, mg/g maf coal	0.973
HC Gas	Hydrocarbon gas yield, wt% maf coal	0.969
CO+CO ₂	CO and CO ₂ gas yield, wt% maf coal	0.944
TGas	Total gas yield, wt% maf coal	0.961
Oils	wt% maf coal	0.880
PA+A	wt% maf coal	0.922

Table 5. Summary of Estimated Coefficients^a

	Intercept	T ^b Coeff (P)	X ^b Coeff	S ^b Coeff	TxX ^b Coeff	TxS ^b Coeff	XxS ^b Coeff
THF Conv	107.40	4.54 (.003)	4.08 (.005)	-1.72 (.097)			-1.62 (.113)
mg H ₂	60.28	9.12 (.001)	2.66 (.014)		1.48 (.097)		-1.13 (.181)
HC Gas	3.50	1.86 (.001)		0.29 (.061)			
CO+CO ₂	5.06	0.84 (.001)		-0.20 (.046)			
TGas	8.57	2.71 (.001)					
Oils	58.61	13.87 (.001)		-5.67 (.054)	-4.60 (.100)		
PA+A	40.23	-12.03 (.005)	4.80 (.085)	3.85 (.141)	3.42 (.179)	3.52 (.169)	

- a. All three way interaction coefficients (TxXxS) are small and set equal to zero. Coefficient estimates are for coded variables (-1,0,+1).
- b. T = temperature; X = wt% Fe in SFIO on coal; S = wt% sulfur in DMDS on coal; TxX = two-way interaction of temperature with wt% Fe in SFIO on coal; TxS = two-way interaction of temperature with wt% sulfur in DMDS on coal; XxS = two-way interaction of wt% Fe in SFIO with wt% sulfur in DMDS on coal.

Table 6. Comparison of Wilsonville and Superfine Iron Oxide^a

	Thermal	WIO	Predicted ^b SFIO	Experimental SFIO
Fe, wt % coal	None	1.1	1.1	1.1
Yields, wt% maf coal				
HC Gases	1.9	2.1	2.6	1.2
CO+CO ₂	5.0	4.8	4.9	5.0
Oils	48.5	53.8	63.7	56.9
PA+A	52.2	45.3	35.1	45.1
IOM	-7.6	-6.0	-6.3	-8.2
THF Conv.	107.6	106.0	106.3	108.2
Run Number	139-1/167-1	142-2/189-1	N/A	272-1

- a. 415°C, 1 hour, 1000 psig H₂ cold, 5.4 grams Wilsonville recycle oil, 3.0 grams coal, 2.4 moles sulfur/mole iron.
- b. Predicted from model parameters. All curvature detected at the mid-range conditions is accounted for as resulting from temperature effects.