

CATALYST PERFORMANCE IN ASHY-RESID CONTAINING RECYCLE OILS

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INTRODUCTION

In recent years, the objective for coal liquefaction has switched from producing primarily a resid to making exclusively distillate product. In this revised configuration, improving conversion of the residual fraction becomes essential for developing a viable process.¹ Since resid conversion under typical process conditions does not proceed to any significant extent in the absence of a catalyst,^{2,3} developing improved catalysts is a key element for improving the process. Although there is continuing interest in developing catalysts for coal liquefaction,⁴ much of this research effort has not been specifically directed toward conversion of coal in media incorporating coal-derived resid.⁵ The criteria for optimizing resid conversion is to maximize distillate yields at low hydrogen consumption levels while limiting gas make.⁶ Therefore, viable catalysts must be capable of meeting these criteria for resid conversion as well as attain maximum dissolution of the coal.

Both particulate and highly dispersed catalysts have been used for converting residual feeds to distillate products.⁷ At the Advanced Coal Liquefaction Research and Development Facility at Wilsonville, Alabama, in thermal/catalytic or catalytic/thermal Runs 260, 262 and 263, an organically dispersed molybdenum catalyst (Molyvan L) plus iron oxide was used along with a particulate nickel-molybdenum catalyst.⁸ This system of dispersed iron and molybdenum catalysts along with a supported particulate catalyst gave higher yields of C₄⁺ distillate than either system alone and among the highest ever observed. To realistically evaluate catalysts for processing resid containing feedstocks, it is necessary to measure their activity in feeds containing significant concentrations of residual material. This paper presents the results of a study in which catalyst candidates were evaluated in resid containing process solvents that were obtained from Wilsonville.

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. This material was supplied by CONSOL Inc. Proximate and ultimate analyses of the coal are presented in Table 1. A sample of V-131B recycle oil from Run 258 was obtained from Wilsonville. Samples of the individual components that were combined into the Run 262 recycle oil were obtained from CONSOL Inc. These included the V-1074 heavy distillate from the vacuum tower, the V-130 deashed resid product from the ROSE-SR deashing unit, and the V-1082 ashy resid feed to the deashing unit. All of these materials were produced at Wilsonville when the plant was operating in a close-coupled configuration and feeding Black Thunder coal. Analyses of these recycle oils given in Table 2 show that both contain sizable concentrations of iron resulting from addition of iron oxide to the feed slurries. Run 262 process oil also contains a sizable concentration of Mo since Molyvan L, an organic-based Mo containing material, was being added during this run. Based on previous Mössbauer studies on similar material, the iron is present in combination with sulfur as pyrrhotite. The molybdenum was presumed to be present as MoS₂. Each of the recycle oils was characterized by separating into tetrahydrofuran (THF) insoluble, THF soluble-pentane insoluble, and pentane soluble fractions (see Table 2). A sample of THF insoluble material in the Run 262 V-1082 ashy resid was isolated by exhaustively extracting with THF for 2 days and drying overnight at 40 °C at 125 torr. A sample of the iron oxide catalyst (IO) that had been used at Wilsonville was supplied by CONSOL Inc. Molyvan L was supplied by R. I. Vanderbilt Co. A sample of superfine iron oxide (SFIO), which was described previously, was supplied by Mach I Company, King of Prussia, Pa.⁹ Impregnated coals were prepared as previously described.¹⁰

Reactions were conducted in 50 cc microautoclaves pressurized to 1000 psig hydrogen at ambient temperature. In coal reaction experiments, 5.4 g of solvent, 3 g of coal, catalyst and dimethyl disulfide were added to the reactor. After pressurization, the reactor was placed in a fluidized sandbath set at the specified temperature and continuously agitated at a rate of 400 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 either a solvent separation scheme, which was described previously,⁹ or vacuum distillation using a modified D-1160 procedure, which is described elsewhere.¹¹ 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).

Reactivity of Residual Feeds

Samples of Wilsonville produced recycle oils or their individual components were used for evaluating catalysts. These oils contained slightly more than 40 wt% 1050 °F heavy distillate and 30-35 wt% resid, as shown in Table 2. The combined mineral matter and IOM made up the remaining 25-30 wt% of this material, nearly equivalent to the feed coal used at Wilsonville in these runs. The higher oil and lower IOM concentrations in the Run 262 recycle oil, relative to the Run 258 recycle oil, indicates the higher level of conversion obtained in the presence of the added Mo catalyst. Each of the components in the Run 262 recycle oil were also subjected to solvent separation, the sum of which agreed with results from solvent separation of the combined Run 262 recycle oil. The Run 258 recycle oil was used as received.

The composition of the Run 262 recycle oil changes quite significantly at temperatures above 300 °C. As shown in Table 3, at 415 °C, the IOM in these recycle oils decreased from 14.0 wt% to 10.8 wt% after 30 min at 6.89 MPa H₂ (cold). A net conversion of both PA + A and IOM to pentane soluble oils occurred, both of which had been observed previously.^{12,2} Formation of hydrocarbon gases and CO+CO₂ was minimal. In a series of similar runs at 415 °C ranging from 3.8 min to 60 min, the THF-IOM concentration decreased rapidly from 14.0 wt% in the starting material to approximately 10 to 11 wt%, even at the shortest time (Table 4). This same level of reactivity was observed at 300 °C, both in the presence and absence of hydrogen overpressure. The product from this latter run indicated a somewhat smaller shift to oil product. Similar reactivity was observed in the ashy resid fraction in the absence of any distillate solvent. The IOM decreased from an initial 26.8 wt% in the starting ashy resid to 20.5 wt% after 15 min at 415 °C in 6.89 MPa H₂ (cold). This corresponded to 24 wt% conversion of the IOM. Therefore, most of the reaction is occurring in the residual fraction in the absence of donor solvent and independent of the presence of gaseous hydrogen, which appears to have a slightly positive effect. A sample of IOM that had been isolated from the ashy resid was subjected to reaction in tetralin at 415 °C for 15 min with 6.89 MPa H₂ (cold). Because only 5.2 wt% was solubilized, it appears this material does not respond to normal liquefaction conditions.

This change in ashy resid solubility in THF may be due to disassociation of the material making it more soluble in THF. Earlier results on vacuum tower bottoms and ROSE-SR ash concentrate showed that pyridine and mixed cresylic acids were significantly better solvents than THF.¹³ However, a comparison of the insoluble organic matter in the Wilsonville filter feed stream determined with each of these solvents showed that pyridine, quinoline and mixed cresylic acids gave essentially the same result.¹⁴ In our laboratory, we determined the solubility of ashy resid in pyridine, THF and cresylic acids using a Soxhlet technique for pyridine and THF and the Wilsonville procedure for cresylic acid.¹⁵ The insolubles in THF, pyridine and cresylic acids were 26.8, 23.1 and 24.0 wt%, respectively. In refluxing pyridine at 114 °C, as compared to the 84 °C temperature attained when using the Soxhlet, the insolubles decreased further to 21.4 wt%, which was very close to the 20.5 wt% THF IOM obtained after reacting the ashy resid at 415 °C for 15 min in 6.89 MPa H₂ (cold).

The reactivity of the distillate fraction further complicated use of these materials in evaluating catalyst performance. The THF IOM fraction of this material was 3.1 wt% of which 1.8 wt% remained insoluble after heating at 300 °C in hydrogen for 15 minutes. This amount, though relatively small on a percentage basis, makes a larger impact on the amount of IOM in the sample that is converted and affects the overall conversion numbers.

Reactivity of Coal in Recycle Oil

The conversion and product yields of Black Thunder Wyodak coal were determined using these Wilsonville derived recycle oils. Both oils contained sizable amounts of iron while the Run 262 oil also contained 163 ppmw molybdenum. For a 30 wt% coal concentration in the feed, this corresponds to a 300 ppmw Mo concentration on moisture and ash-free coal. Various iron and iron-molybdenum catalysts were added to these reaction systems; iron up to 1.0 wt% and Mo up to 1000 ppmw, based on maf coal, were added as shown in Table 5. Reactions were run at 440 °C for 22 min after which they were analyzed either by solvent separation or vacuum distillation. The amount of conversion was, of course, influenced by the IOM present in the starting recycle oil that became solubilized, which explains the > 100% values. Vacuum distillation was also used to measure the amount of conversion to distillable oils. A corresponding THF conversion value was also obtained using this technique since THF insolubles were removed prior to distillation.

Although there is considerable scatter in the data, it is clear that as Mo concentration increases, reactivity improves. In Figure 1 THF conversion increases quite sharply from a low of 96 wt% in the

absence of Mo. Similarly, C₃ solubles also increase as shown in Figure 2. This value increases from a low of 32 wt% in the absence of Mo up to 59 wt% upon addition of 1000 ppmw Mo. The corresponding 1050 °F value also varies similarly but with somewhat more scatter, as shown in Figure 3. These data indicate that distillate yield levels out at a Mo addition level of about 500 ppmw for the Run 258 recycle oil. All of the distillate yields taken in Run 262 recycle oil that already contained recycled Mo, were at a maximum, indicating that recycle oil performance had been optimized in Run 262.

The most striking example that fails to fall within this pattern is the reaction in the presence of SFIO to which no Mo had been added. Of the 2.9 wt% Fe present in the reaction feed, only 0.8 wt% was SFIO. Surprisingly, its THF conversion, C₃ solubles and 1050 °F distillate yield appears to be equivalent to addition of approximately 500 ppmw Mo in the Run 258 recycle oil. These data support a significant activity for this nanometer size material.

Conclusions

The assessment of the activity of fresh catalysts for liquefaction of Wyodak coals in Wilsonville recycle oils is complicated by the presence of resid, unconverted coal, ash and dispersed catalyst. The presence of a THF-insoluble fraction that easily converts at temperatures above 300 °F in an inert atmosphere to a THF-soluble fraction results in apparent conversions of coal in excess of 100%, even under the mildest of conditions. Solubilization of this material was observed in refluxing pyridine at 114 °C, as well as this material is not susceptible to reaction in tetralin and hydrogen at reaction conditions to form a THF soluble material. Addition of Mo to Mo-free recycle oils resulted in increased THF-conversion, pentane solubles yield, and 1050 °F⁺ conversion. Accumulated Mo catalyst in recycle oils, taken from runs at Wilsonville where dispersed Mo was being added, masks the effect of added fresh Fe or Mo catalysts. Catalyst testing in these systems requires careful control of the components in the residual fraction.

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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		

	Run 262 V-131B ^a	Run 258 V-131B
1050°F Distillate	44.2	46.6
Ash	8.3	8.1
THF IOM	12.8	15.1
PA+A	18.6	22.1
Oils	60.3	54.7
Iron	1.7	1.2
Molybdenum, ppmw	163	3

a. Prepared by blending V-1074 heavy distillate, V-130 deashed resid and V-1082 ashy resid in ratio 42.7:6.6:50.7, respectively.
b. Not available

wt% af WRO	Reactants	415°C for 30 min	300 °C for 15 min
HC Gases	0.0	0.1	-
CO+CO ₂	0.0	0.1	-
Oils	65.7	71.2	69.5
PA+A	20.3	17.8	19.6
IOM	14.0	10.8	11.0
IOM Conversion	-	23	21

a. No coal, 5.4 g Run 262 recycle oil, 6.89 MPa H₂ cold.

Temperature, °C	Gas ^b	Time, min	THF IOM ^c
415	H ₂	0	14.0
415	H ₂	3.8	11.3
415	H ₂	7.5	11.1
415	H ₂	15	10.9
415	H ₂	30	10.8
415	H ₂	60	10.1
300	H ₂	15	11.0
300	N ₂	15	11.7

a. Recycle oil contains 1.8 wt% Fe on ash-free basis.
b. Pressure 6.89 MPa (cold).
c. Weight percent ash-free solvent on SO₃-free ash basis.

No.	Recycle Oil Wilsonville Run No.	Form of Catalyst	Added Catalyst ^a			
			Fe, wt%	Fe carrier	Mo, ppmw	Mo Carrier
1	258	none	-	-	-	-
2	258	Particulate	1	IO	100	MVL
3	258	Impregnated	0.78	FOH	-	-
4	258	Impregnated	0.8	FeIII	-	-
5	258	Particulate	0.8	SFIO	-	-
6	258	Impregnated	0.8	FeIII	250	AM
7	258	Impregnated	0.8	FeIII	500	AM
8	262	Impregnated	0.8	FeIII	550 ^b	AM
9	262	Impregnated	0.8	FeIII	800 ^b	AM
10	258	Impregnated	0.8	FeIII	1000	AM

a. IO = iron oxide from Wilsonville; MVL = Molyvan L; FOH = FeOOH formed by base precipitation of ferric nitrate; SFIO = superfine iron oxide; AM = ammonium molybdate impregnated on coal as aqueous solution; FeIII = $Fe_2(SO_4)_3 \cdot 5H_2O$ impregnated on coal as aqueous solution.

b. Includes Mo in recycle oil, 300 ppmw on maf coal.

Figure 1. THF Conversion

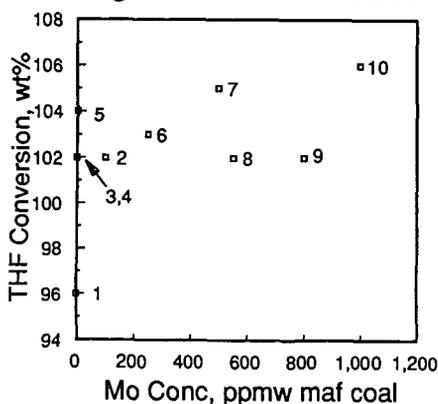


Figure 2. Pentane Soluble Oil

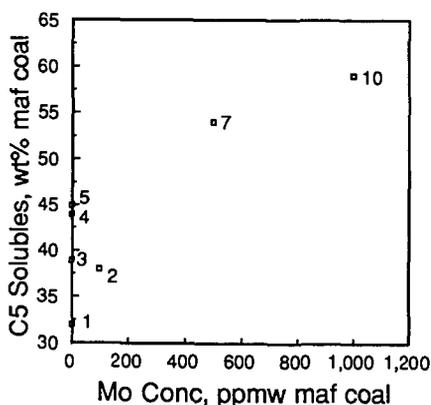


Figure 3. Distillate Oil Yield

