ELSEVIER

Catalysis Today 50 (1999) 141–148

CATALYSIS TODAY

Liquefaction catalysis of Wyodak coal impregnated with water soluble iron and molybdenum precursors

Xiaodong Zhan*, Edwin N. Givens

Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511-8410, USA

Abstract

A matrix of Fe and Mo impregnated coals were prepared by adding aqueous solutions of ammonium heptamolybdate (AHM) and ferrous sulfate (FS) to black thunder Wyodak coal (BT). These impregnated coals were liquefied in two different BT-derived solvents that contained a sizable concentration of solids-free 565°C+ resid. Reactions were run at 440°C for 30 min in microautoclaves pressured to 7.0 MPa (ambient) with H_2 containing 3 vol% H_2S. Coals impregnated with various Fe and Mo combinations, at Fe concentrations from 0.1 to 1.0 wt% Fe_2O_3 and Mo concentrations from 100 to 500 ppm Mo, based on dry coal, were systematically investigated. The activity of the catalysts generated from the impregnated metal precursors was related to solubilization of coal in tetrahydrofuran (THF) and conversion of 565°C+ reactants to lighter products. All of the impregnated coals gave higher conversions than metal-free BT coal. Coals containing at least 300 ppm Mo fell into a narrow range of THF and resid conversions, of which none was clearly superior to the others. Five of the impregnated coals, including all of the coals containing Fe concentrations up to an equivalent of 1.0 wt% Fe_2O_3 and Mo concentrations from 0 to 100 ppm failed to give high conversions consistently. For the active impregnated coals, no difference was observed for coal liquefaction in two different solvents. However, a difference in resid conversion of 10% between the same two solvents was observed. This provides evidence that in the presence of an active catalyst, solvent can influence conversion of residual materials to distillate products. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Liquefaction catalysis; Iron and molybdenum precursors; Black thunder Wyodak coal

1. Introduction

Although coal dissolves quite readily producing residual products that boil at temperatures greater than 565°C, further conversion to distillate requires the use of a catalyst. Pilot plant studies at the Wilsonville Advance Coal Liquefaction Facility in Wilsonville, AL showed that excellent distillate yields could be produced from Wyodak subbituminous coal in a thermal-catalytic two-stage process. The best results were obtained in a run in 1992. In this run a first stage catalyst was used that comprised a dispersed Fe_2O_3 (1 wt% on coal) and an oil-soluble Mo alkyl thiophosphate (100 ppm Mo on coal). A Ni–Mo extrudate catalyst was used in the second stage [1]. Unfortunately, the high catalyst cost for this combination was driven by the cost of the oil-soluble Mo compound and the second-stage extrudate catalyst. An economic study showed that using a water-soluble Mo salt in lieu of an oil-soluble Mo compound would decrease the cost of the Mo catalyst close to that of the Fe

---

*Corresponding author. Tel.: +1-6062570323; fax: +1-6062570302; e-mail: zhan@caer.uky.edu

0920-5861/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(98)00471-4

catalyst [2]. Also, by eliminating the need for the second-stage extrudate catalyst the overall catalyst cost could be reduced quite significantly. This requires that dispersed catalysts be developed that can provide the activity necessary to achieve a comparable level of conversion to that observed in the thermal-catalyst two-stage process so as not to increase the overall capital cost of the plant.

The chemical and structural forms of dispersed catalysts and the specific reactions that they catalyze are still almost completely unknown. Both Fe and Mo are effective catalysts, especially in their sulfided forms, which are thermally stable at reaction conditions [3]. Past work has shown that the more highly dispersed the metals are in the reaction system the more active the catalyst [4]. Finely divided catalysts are generated by introducing water or oil-soluble metal precursors into the reaction system by impregnating them onto coal [5,6]. The highly dispersed catalyst provides effective contact with the coal-solvent slurries at low catalyst concentrations, reducing intraparticle diffusion limitations.

The effectiveness of dispersed Mo catalysts formed from water-soluble precursors impregnated onto coal was determined compared with the catalyst derived from an oil-soluble Mo compound. The concentrations of Mo that were studied are consistent with those that would be present in a process unit when operating at a Mo concentration that would be economically viable. Because of the significant contribution of the Fe catalyst to the overall cost of the dispersed catalyst, the effect of dispersed Fe catalysts on the activity of low-concentration Mo catalysts was investigated using a water soluble Fe precursor. The ultimate objective was to decide whether the Fe concentration could be significantly reduced below the 1–2 wt% Fe_2O_3 levels used in pilot operations in the past [7,8]. A further objective was to test these catalysts under conditions that would achieve conversion in an all-slurry mode equivalent to the conversion achieved in the thermal-catalytic configuration [9].

2. Experimental

2.1. Materials

Wyodak coal (BT), obtained from the Black Thunder Mine in Wright, Wyoming, was ground (90%-200 mesh), riffled and stored under nitrogen at 4°C. Proximate and ultimate analyses of the coal are presented in Table 1. The plant derived solvents used in this study were prepared by combining distillate and resid fractions produced at Wilsonville when processing BT coal. These include an IBP-565°C distillate from Run 258 (**I-D**), an IBP-565°C distillate from Run 262 (**II-D**), and two solids-free 565°C+ materials from Runs 258 (**I-R**) and 262 (**II-R**) [7,10]. The solids-free resids were produced from a proprietary residuum oil supercritical extraction-solids rejection unit (ROSE-SR) that was developed by the Kerr-McGee. Solvents **I** and **II**, which comprise 33 wt% heavy distillate and 67 wt% solids-free resid, were prepared using Run 258 and Run 262 derived materials, respectively. The compositions of the solvents are shown in Table 2. Molyvan L, which is molybdenum di(2-ethylhexyl)phosphorodithioate dissolved in a petroleum process oil (Mo, 8.1%; P, 6.4%), was supplied by R.T. Vanderbilt. Ammonium heptamolybdate (AHM), ACS reagent, and ferrous sulfate (FS), ACS reagent, were obtained from Aldrich. Coals were prepared by impregnating BT coal with an aqueous solution containing AHM and FS at the level of 0.5 g solution/g coal to achieve the desired metal loadings.

Table 1
Black thunder wyodak coal analysis

Proximate analysis	wt%	Ultimate analysis	wt%	Sulfur Type	wt%
Moisture	8.89	Carbon	70.62	Total	0.50
Ash	5.76	Hydrogen	5.03	Pyritic	0.08
Volatile matter	39.88	Nitrogen	1.13	Sulfate	0.08
Fixed carbon	45.47	Sulfur	0.52	Organic	0.34
		Oxygen (diff)	16.38		
		Ash	6.32		
		Ash, SO_3-free	5.46		

Table 2
Properties of feed solvents

	Distillate **I-D**	Resid **I-R**	Combined solvent[a] **I**	Distillate **II-D**	Resid **II-R**	Combined solvent[a] **II**
565°C−distillate (wt%)	96.6	19.3	45.0	96.9	14.7	42.1
565°C+ resid (wt%)	3.4	80.6	54.9	3.1	84.5	57.4
THF insolubles (wt%)	0	0	0	0	0.01	0
Ash (wt%)	0	0.1	0.1	0	0.73	0.49
Composition (wt%)						
C	89.25	90.01	89.76	88.86	89.79	89.48
H	9.72	6.47	7.55	9.91	7.26	8.14
N	0.55	1.2	0.98	0.44	0.86	0.72
S	n.a.[b]	n.a.[b]	–	<0.03	0.03	0.03
O (diff)				0.79	1.33	1.14
Ash	0	0.11	0.07		0.73	0.49
Mo (mg/kg)	n.a.[b]	n.a.[b]	–	2	6	4.7

[a] Combined solvent consists of 67% resid and 33% distillate. Elemental composition calculated from composition of resid and distillate fraction.

[b] n.a. not available.

The resulting coal paste was dried at 16 kPa and 100°C for two days. In several cases, the coal paste was partially dried to examine the effect of moisture content. A matrix of impregnated coals, in which metal loadings are reported as mg Mo per kg dry coal (ppm Mo) and wt% Fe_2O_3 on dry coal, were prepared which had up to 500 ppm Mo and 1.0 wt% Fe_2O_3.

2.2. *Liquefaction reaction procedures*

In a typical experiment, 3.0 g of dry coal and 5.4 g of solvent were added to a 50 ml microautoclave and pressurized to 7.0 MPa at room temperature with H_2 containing 3 vol% H_2S. The reactors were submerged in a fluidized sand bath maintained at 440°C and agitated at a rate of 400 rpm. After 30 min the reactor was removed from the sand bath and quenched in ice water. Gaseous products were collected and analyzed by gas chromatography and the liquid and solid products were removed from the reactor in THF and subjected to Soxhlet extraction for 18 h. THF insoluble organic matter (IOM) and mineral matter remained in the thimble. The THF soluble material was distilled at 0.1 kPa to an atmospheric equivalent cut point of 565°C according to ASTM method D-1160. Simulated distillation was performed on a HP 6890 gas chromatograph calibrated against an ASTM Method D2887 extended boiling point reference. Curves were generated using software developed by AC Analytical Controls and Hewlett Packard that extends the final boiling range to 750°C and corrects for partially-eluting samples. Experiments were replicated at least twice to assure reproducibility. Net product yields are calculated by subtracting the amount of each fraction in the feed from the corresponding amount of each in the product. The total net product equals the amount of moisture and ash free (maf) coal in the feed and reflects the net make of each of the fractions. The calculation of the yield of each product fraction is illustrated for resid in Eq. (1).

$$\text{Yield resid} = ([\text{Resid}]_{\text{Products}} - [\text{Resid}]_{\text{Feed}}) / \text{Coal(maf)} \times 100. \qquad (1)$$

Estimates of the water yields were calculated based upon the following assumptions: the oxygen concentrations in the distillate and resid fractions of the feed and product are the same; the oxygen concentration in the IOM is the same as in the starting coal; the oxygen concentration in the mineral matter is assumed to be unchanged. Any experimental error and error in estimating the yield of water are included in the value for the distillate fraction. Conversion of maf coal to THF soluble material was calculated by Eq. (2).

$$\text{Coal conversion} = 100 \times \left(1 - \frac{[\text{IOM}]_{\text{product}}}{\text{Coal(maf)}}\right). \qquad (2)$$

Resid conversion was calculated by Eq. (3).

$$\text{Resid conversion} = 100 \times \left(\frac{[\text{Coal(maf)}+\text{Resid}]_{\text{feed}} - [\text{IOM} + \text{Resid}]_{\text{product}}}{\text{Coal(maf)}}\right). \quad (3)$$

Standard deviations in the percent yields for each the following were: IOM, 0.7; C_1–C_6 hydrocarbon gases, 0.9; CO+CO_2, 0.4; resid, 2.7.

3. Results and discussion

The metal impregnated coals were prepared by adding aqueous solutions containing the requisite amount of AHM and FS to the coal and evaporating to dryness. Although iron molybdates are insoluble, within the time needed to impregnate the solution onto the coal, no indication of a precipitate was observed from the freshly prepared solutions. The impregnated coal pastes were then usually dried at 16 kPa and 100°C to remove water before reaction. A series of runs were made to decide if coal moisture affected coal dissolution and conversion to distillate. Residual moisture has been reported to both improve coal reactivity [11–13] and have a deleterious effect [14,15] on liquefaction. Moisture may affect the activity of the Fe catalyst through promoting conversion of the Fe precursors into inactive catalysts [14]. It has been suggested that repeated oxidation–reduction in the presence of moisture can lead to particle agglomeration in the case of high-surface area iron catalysts [16]. Water has been reported to have both a promoting and a deactivating effect on the activity of Mo catalysts. Song and Saini [13] reported that the activity of impregnated Mo catalysts significantly improved at 350°C in the presence of water. At 400°C, however, they found that the catalyst activity decreased significantly. Adding water when processing petroleum derived vacuum tower bottoms and FCC decant oil with dispersed Mo catalysts in the presence of H_2S gave higher conversion [17] and improved the sulfiding of the oxide catalysts [18]. On the other hand, the presence of water has been reported to deactivate Mo catalysts through loss of sulfur [19].

To determine the effect of moisture on impregnated coals, a series of runs was made in solvents **I** and **II**. A coal impregnated with Fe to a level of 1.0 wt% Fe_2O_3 and Mo at 100 ppm was dried to varying moisture contents up to 59 wt% (based on dry coal). Over the range of moisture concentrations in these coals, the estimated steam pressures at reaction conditions ranged from approximately 1.8 MPa (250 psi) for dry coal up to 10.4 MPa (1500 psi) for the coal containing 59% moisture. The estimated hydrogen pressure in these experiments remained constant at 16.6 MPa (2400 psi). The estimate of steam pressure includes the contribution made by the conversion of a portion of the combined oxygen in the coal (10 wt% of dry coal) to water. The bulk of the remaining combined oxygen that is converted produces CO+CO_2. The results from this series of runs shown in Fig. 1 suggest that conversion of coal into THF soluble products was unaffected by the very wide range of steam pressures. Resid conversion, however, decreased as moisture content of the coals increased. Although an active catalyst was apparently generated from the impregnated coal, the drier system gave better resid conversions. Therefore, the bulk of the catalyst testing was done on impregnated coals that had been completely dried to a constant weight at reduced pressure and 100°C.

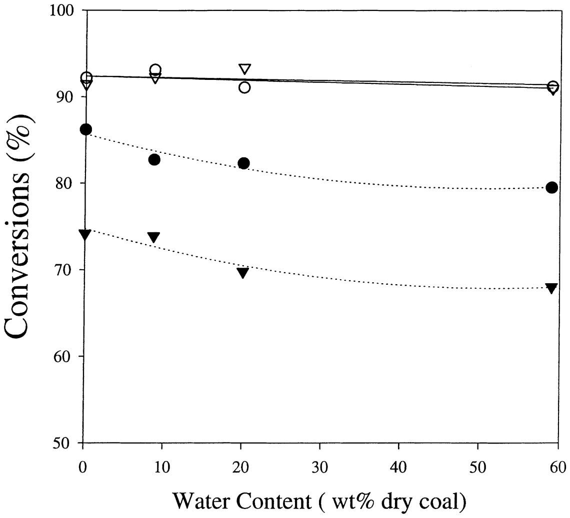

Fig. 1. Effect of moisture on conversion. THF conversion: solvent **I** (▽), solvent **II** (○). Resid conversion: solvent **I** (▼), solvent II (●).

The two solvents used in this study were prepared by blending heavy distillates and deashed resids

Table 3
Liquefaction of Mo and Fe impregnated coals in **I**

Mo (mg/kg dry coal)	0			100			300		
Fe_2O_3 (wt% dry coal)	0	0.5	1.0	0	0.5	1.0	0	0.5	1.0
Products (wt% maf coal)									
$CO+CO_2$	7.4	4.9	7.9	7.5	7.9	8.0	7.0	8.1	7.9
C_1–C_6	6.5	6.5	7.3	8.2	8.3	8.4	8.0	10.6	12.9
H_2O (estimated)	7.3	12.8	11.2	11.0	11.0	11.1	11.5	11.4	11.5
565°C−distillate	31.7	38.0	43.0	36.7	44.5	46.6	48.1	44.0	44.6
565°C+ resid	7.8	26.1	23.3	26.5	18.7	17.3	15.0	19.3	16.1
IOM	39.3	11.7	7.2	10.1	9.6	8.5	10.2	6.7	7.1
THF coal conversion (%)	60.7	88.3	92.8	89.9	90.4	91.5	89.8	93.3	92.9
Resid conversion (% maf coal)	52.9	62.2	69.5	63.4	71.6	74.2	74.7	74.0	76.8

produced in the Wilsonville pilot plant. The two solvents differed in hydrogen and nitrogen concentrations with the hydrogen content in **II** being higher and the nitrogen concentration being lower. The 565°C+ resid fraction in **II-R** was 4.6% higher which makes the 565°C+ fraction in **II** higher by 2.5%. This makes the concentration of the resid fraction in the experiments higher. **II** also contains 6 ppm of Mo, which is a carryover of dispersed Mo catalyst used in the Wilsonville Run 262 into the ROSE SR deashed product. This very small concentration should not affect the overall results.

The results from liquefaction of the metal impregnated coals in **I** and **II** are shown in Tables 3 and 4, respectively. The small differences in yields of gaseous products in these runs indicate a lack of sensitivity either to the impregnated catalysts or the solvents used in the runs. THF coal conversions were surprisingly constant for most of the impregnated coals that were tested. In **I**, all of the impregnated coals had conversions between 88% and 93% with an average of 91.4% with a standard deviation of 1.7 (n=24). The small differences in these values relative to standard deviations suggests the conversions of these coals are the same. This is still a sizable increase over the 60.7% THF conversion for metal-free BT coal indicating significant catalysis by the impregnated metal precursors. The corresponding THF conversions in **II** were also tightly grouped except for three of the 13 impregnated coals that were tested. All of the Mo impregnated coals, except one impregnated with 100 ppm Mo without any added Fe, fell into this tight group. The average THF conversion for this group of 10 impregnated coals was 92.2% with a standard deviation of 1.4 (n=22). Of the Mo-free coals, only the one that contained Fe at a concentration of

Table 4
Liquefaction of Mo and Fe impregnated coals in **II**

Mo (mg/kg dry coal)	0				100			300				500		
Fe_2O_3 wt% dry coal	0	0.1	0.5	1.0	0	0.5	1.0	0	0.1	0.5	1.0	0	0.5	1.0
Products (wt% maf coal)														
$CO+CO_2$	10.2	8.1		7.8	8.3	8.0	7.7	7.4	7.7	7.5	8.1	6.3	7.9	7.4
C_1–C_6	10.8	10.4		8.9	11.3	9.4	8.9	9.9	9.5	8.6	9.2	7.7	8.2	7.9
H_2O (estimated)	8.8	11.0		14.5	13.0	14.3	14.4	13.8	14.0	14.2	14.0	15.4	14.4	14.8
565°C−distillate	27.5	30.1		52.4	40.9	50.8	55.2	49.1	50.5	52.5	57.0	52.2	55.7	58.5
565°C+ resid	12.0	13.2	14.5	8.1	12.0	10.1	6.0	10.3	10.5	9.8	2.2	10.8	7.2	5.4
IOM	30.7	27.2	13.4	8.3	14.4	7.3	7.8	9.4	7.8	7.5	9.5	7.5	6.6	5.5
THF Coal conversion (%)	69.3	72.8	86.6	91.7	85.6	92.7	92.2	90.6	92.2	92.5	90.5	92.5	93.4	94.5
Resid conversion (% maf coal)	57.2	59.6	72.2	83.6	73.6	82.6	86.2	80.3	81.7	82.8	88.3	81.8	86.2	89.1

1.0 wt% Fe_2O_3 fell into this high THF conversion group. THF conversion of the Fe impregnated coal loaded at 0.5 wt% Fe_2O_3 was 5.6% below the average observed in **II**.

The variation in resid conversion for these impregnated coals followed a similar pattern with an increase being observed for all the coals onto which Mo or Fe had been impregnated. In **I**, five of the eight impregnated coals that were tested fell within a narrow range of resid conversions having an average value of 75.6% with a standard deviation of 3.7 (n=14). Three coals fell below this conversion range including two Mo-free coals and the Fe-free coal that contained 100 ppm Mo. However, the Mo-free Fe-containing (1.0 wt% Fe_2O_3) impregnated coal was only 6.1% below this group. In **II**, 10 of the 13 coals gave resid conversions having an average value of 85.2% with a standard deviation of 5.0 (n=22). Interestingly, the same three impregnated coals that fell below this resid conversion range in **II** also gave THF conversions in this solvent that were below the average THF conversion for this group. Note, however, that the larger value of the standard deviation calculated by grouping this set of 10 coals suggests that the higher resid conversions observed for the coals impregnated with 300 and 500 ppm Mo in the presence of Fe loaded at 1.0 wt% Fe_2O_3 may be statistically significant relative to the Fe-free coals impregnated with 300 and 500 ppm Mo.

In the set of impregnated coals, the majority gave nearly equivalent THF and resid conversions with none of them being higher than the others. Only four of the coals failed to give high conversion consistently. These include the Fe-free 100 ppm Mo impregnated coal and all of the Mo-free Fe-impregnated coals. The Fe-free 100 ppm Mo-impregnated coal gave low THF conversion in **II** and low resid conversion in both solvents. The impregnated coals loaded with Fe at 0.1 and 0.5 wt% equivalent Fe_2O_3 gave low resid conversions in both solvents and low THF conversion in **II**. The Fe impregnated coal with the equivalent of 1.0 wt% Fe_2O_3 gave low resid conversion in **I** although it gave high THF and resid conversions in **II**.

Overall, results from this test show that higher conversions were consistently obtained for BT coal impregnated with at least 300 ppm Mo. They also show that adding Fe or increasing the concentration of Mo provided, at most, only slightly higher resid conversion. However, a significant difference was observed in resid conversion between the two solvents. The difference of 10% in average resid conversions between solvents **I** and **II** was observed for impregnated coals assigned to the high activity groups. Except for the solvents, the runs were made under identical conditions indicating that the difference in reactivity of the impregnated coals can be attributed to the solvents.

The compositions of the two solvents are different. **II** contains 2.5% more 565°C+ material than **I** (see Table 2) making the concentration of the reactive material greater in the **II**, which can increase resid conversion (see Eq. (3)). Recent continuous bench-scale processing runs with Mo and Fe impregnated coals showed that product could be correlated to the concentration of coal and recycled resid in the feed [20]. Regression analysis on data from these runs predicted that 74% conversion of the reactive coal and 39% conversion of the resid accounted for the product. Assuming the same conversion, the 2.5% greater 565°C+ material in II could increase resid conversion by 2%. The bulk of the increased conversion must be attributed to other factors related to the solvent.

The hydrogen concentrations in the two solvents are different. The combined solvent **II** contains approximately 0.6 wt% higher hydrogen concentration, which is distributed equally between the distillate and resid fractions (see Table 2). The higher hydrogen concentration in **II-R** suggests the presence of material richer in hydrogen, which may convert more easily to distillate. The boiling distributions of the two solvents are essentially the same since the simulated distillation curves are nearly identical (see Fig. 2). The lower nitrogen concentration in **II-R** also supports the suggestion that this resid is already more highly converted. The lower nitrogen content in **II** would not likely have any further depressing effect on catalyst activity since the number of nitrogen atoms in both solvents is approximately 1000 times greater than the number of Mo atoms present on the impregnated coal.

The higher hydrogen concentration in **II-D**, which suggests a higher H-donor capacity, does not affect the initial dissolution of the coal since THF conversion is the same in both solvents. A similar result was reported by Guin et al. [21] who observed higher oil yields at essentially the same THF conversions

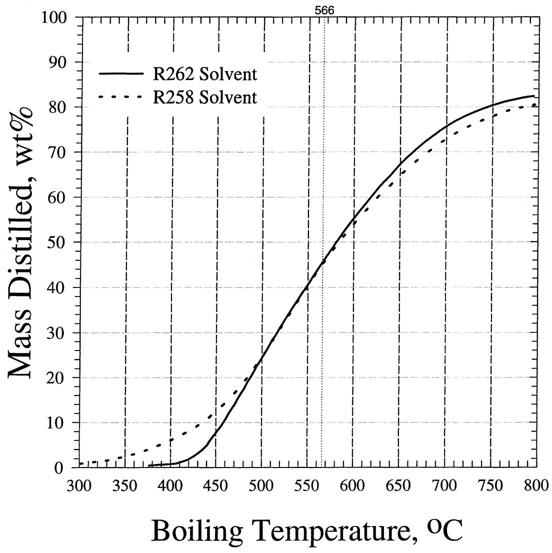

Fig. 2. Simulated distillation of solvents.

when better H-donor solvents were used in liquefaction of Blind Canyon coal in the presence of Fe catalysts. It is generally accepted that the most important role of the H-donors in the liquefaction reaction is the stabilization of free radicals generated during the initial solubilization of the coal, even in the presence of catalyst and H_2 [22]. Although this function is important, McMillen et al. [23] proposed a mechanism by which H-donors can influence liquefaction yields through promoting the cracking of aromatics. In their mechanism, lower molecular weight products result from cleavage of alkyl-aromatic bonds in *ipso* $H^{\bullet}$ substituted benzyl aromatic intermediates formed via H-atom transfer from donor solvent. This provides a plausible explanation of how the higher donor capacity of **II** can lead to increased resid conversion. The overall increased resid conversion may, in fact, result from the combined effect of higher donor capacity, higher resid concentration in the starting reaction mixture, and the higher reactivity of the resid fraction of **II**. Further work will be necessary to resolve this question.

Since the objective of this work was to provide a Mo-based catalyst system that could replace the use of more expensive oil-soluble organomolybdenum materials, comparative tests were performed on Molyvan L. Runs were made with BT coal in **II** under the same conditions used for the impregnated coals with Molyvan L added at a concentration of 300 ppm Mo on dry coal. The THF and resid conversions for these runs, which were 91.1% and 82.8%, respectively, were essentially the same as obtained for the high activity group of impregnated coals. Therefore, based upon lab-scale screening studies, AHM impregnated coals are as active as the high-activity organic soluble precursors used at Wilsonville.

4. Conclusions

Significant catalysis is observed for liquefaction of Wyodak coal impregnated with aqueous solutions of Fe and Mo salts. The concentration of residual water remaining on the coals after impregnation did not affect THF conversion but the drier system gave slightly better resid conversions. Coals impregnated with AHM to a concentration of at least 300 ppm Mo gave both high THF and resid conversions, of which none were clearly superior to the others. The presence of Fe, loaded to a concentration of up to 1.0 wt% Fe_2O_3, had only a slight influence on the activity of the Mo catalyst. Resid conversions were significantly higher in one of the recycle solvents (**II**), although THF conversions in both solvents were the same. The increased resid conversions in **II** may be related to higher H-donor capacity in the distillate fraction or a more reactive resid fraction that converts more easily into distillate product. Gaseous products were relatively constant in these runs and were unaffected by the impregnated catalysts or the solvent used in the runs. The AHM impregnated coals are as active as and much less expensive than the high-activity organic soluble precursors that have been successfully tested in larger-scale pilot plant runs.

Acknowledgements

This work was supported by the US Department of Energy under contract No. DE-AC22-91PC91040.

References

[1] Southern Electric International, Inc., Run 263 with Black Thunder Mine subbituminous coal and dispersed molybde-

num catalyst, US Department of Energy Report DOE/PC/90033-23, Wilsonville, AL.

[2] University of Kentucky, et al., Advanced Direct Liquefaction Concepts for PETC Generic Units; Phase I Final Report, US Department of Energy Report DOE/PC/91040-55, Section 3, Lexington, KY 1995.

[3] O. Weisser, S. Landa, Sulphide Catalysts, Their Properties and Applications, Pergamon Press, New York, 1973, pp. 46-49.

[4] A.V. Cugini, D. Krastman, D.V. Martello, G.D. Holder, Prep. Pap. Am. Chem. Soc., Div. Fuel Chem. 38(1) (1993) 99.

[5] S.W. Weller, Catalysis in the liquid-phase hydrogenation of coal and tar, in: P.H. Emmett (Ed.), Catalysis, vol. 4, Reinhold, New York, 1956, p. 513.

[6] C.O. Hawk, R.W. Hiteshue, Hydrogenation of coal in the batch autoclave, US Bureau of Mines Bull. 622 (1965).

[7] Southern Electric International, Inc., Run 258 with subbituminous coal, US Department of Energy Report No. DOE/PC/50041-130, Wilsonville, AL, 1991.

[8] R.A. Winschel, G.A. Robbins, J. Hu, Oil agglomeration at low pH as a pretreatment for liquefaction of Wyoming (USA) subbituminous coal, Paper presented to the International Conference on Coal Science, Essen, Germany, 1997.

[9] T. Rantell, R.K. Anderson, E.N. Givens, Prep. Pap. Am. Chem. Soc., Div. Fuel Chem. 41(3) (1996) 993.

[10] Southern Electric International, Inc., Run 262 with Black Thunder subbituminous coal, US Department of Energy Report No. DOE/PC/90033-22, Wilsonville, AL, 1992.

[11] University of Wyoming, Integrated two-stage coal liquefaction studies, EPRI Report AP-4193, Laramie, WY, 1985, pp. 3–91.

[12] Catalytic, Inc., The Wilsonville Advanced Coal Liquefaction Research and Development Facility, Technical Progress Report: Run 249 with Wyodak Coal, US Department of Energy Report No. DOE/PC/50041-75, Wilsonville, AL, 1986, p. 14.

[13] C. Song, A.K. Saini, Energy Fuels 9 (1995) 188.

[14] Y. Kamiya, T. Nobusawa, S. Futamura, Fuel Process. Technol. 18 (1988) 1–10.

[15] M.A. Serio, P.R. Solomon, E. Kroo, R. Bassilakis, R. Malhotra, D. McMillen, Prep. Pap. Am. Chem. Soc., Div. Fuel Chem. 35(1) (1990) 61.

[16] N. Pernicone, F. Traina, Catalyst activation by reduction, in: B. Delmon et al. (Eds.), Preparation of Catalysts II, Proceedings of the Second International Symposium, 1978, p. 321.

[17] J. Lopez, J.D. McKinney, E.A. Pasek, Heavy oil processing, US Patent 4 557 821 (1985).

[18] P. Arnoldy, J.A.M. van den Heukant, G.D. de Bok, J.A. Moulijn, J. Catal. 92 (1985) 35.

[19] J. Lopez, E.A. Pasek, Process for preparing heavy oil hydroprocessing slurry catalyst, US Patent 4 710 486 (1987).

[20] E.N. Givens et al., Bench-scale testing of advanced concepts for direct coal liquefaction: evaluation of dispersed Mo catalysts, Paper presented to the 1997 Coal Liquefaction and Solid Fuels Contractors Review Conference, Pittsburgh, PA. 4 September 1997.

[21] J.A. Guin, X. Zhan, R.S. Linhart, Energy Fuels 8(1) (1994) 105.

[22] D.C. Cronauer, D.M. Jewell, Y.T. Shah, R.J. Modi, Ind. Eng. Chem. Fundam. 18(2) (1979) 153.

[23] D.F. McMillan, R. Malhotra, D.S. Tse, Prep. Pap. Am. Chem. Soc., Div. Fuel Chem. 36(1) (1991) 498.