

USE OF DISPERSED CATALYSTS FOR DIRECT COAL LIQUEFACTION

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INTRODUCTION

With dwindling supplies of petroleum products, efforts to utilize alternative energy feedstocks such as coal, is essential. Several areas in coal conversion technology have been identified that, if improved, could make coal liquefaction more cost competitive with petroleum.¹⁻⁴ The objectives of this project are to address possible improvements in the economics by utilizing low-rank coals, new precursors to dispersed catalysts, and processing variations such as using syngas atmospheres. The purpose of the dispersed catalysts is to better control retrogressive reactions and avoid char formation, while the purpose of the carbon monoxide atmosphere is to improve the economics by simplifying or totally eliminating a separate water-gas-shift step, and perhaps help remove oxygen in the product slate. These possible improvements are being examined and evaluated for potential use in a 2-stage liquefaction process with the goal of converting coal to distillable liquids at a cost competitive to petroleum of \$25/bbl.

To evaluate our catalysts and process conditions, we used three types of laboratory-scale operations. In the first operation, we compared the reaction chemistry of various ranks of coals and catalysts in synthetic solvents such as hexadecane. This method allowed us to better compare our catalysts without the complications of solvent initiated chemistry. Once the catalysts were tested in this manner, they were examined for the conversions of a Black Thunder subbituminous coal using a recycle vehicle derived from the same coal as the solvent. Finally, we upgraded selected first-stage conversion products using a conventional hydrotreating catalyst to compare with recent results in two-stage coal liquefaction development. The results were evaluated for economic feasibility through a subcontract with Bechtel Corp.

EXPERIMENTAL

Catalysts: MolyVanL and iron oxide were received from the Wilsonville liquefaction facility. Pentacarbonyl iron was obtained from Aldrich, and the sulfur-containing iron cluster, $(\mu-S)_2Fe_2(CO)_6$, referred to as Fe_2S_2 , was prepared by the method of Bogan et al.⁵ Ammonium tetrathiomolybdate, (MoS_4) , was obtained from Alfa Chemicals. The organometallic molybdenum catalyst was $(C_5H_5)_2Mo_2(\mu-SH)_2(\mu-S)_2$, referred to as $Mo(OM)$, and was prepared by modification of the method of Dubois et al.⁶ Nickel biscyclooctadiene $[Ni(COD)_2]$ was obtained from Strem Inc. The hydrotreating catalyst Shell 317, obtained courtesy of Criterion Chemical Company, was presulfided under flowing 10% H_2S/H_2 before use.

Coal conversions in synthetic solvents: The model coal liquefaction experiments were conducted in a 300 mL Autoclave Engineers (AE) stirred reactor using 5.0 g of coal, 3 mmol of catalyst, 30 g of solvent, and 500 psig (cold) hydrogen. Reaction temperatures were held at either 400°C or 425°C for 20 minutes.

Black thunder studies: The screening experiments were conducted in a 300 mL autoclave with conversions being run at 425°C for 1 hour. Two autoclaves were used, referred to as autoclave A and B. The properties of autoclave B are such that for a high viscosity medium the conversions are lower in autoclave B than in A. The molybdenum based catalysts were first screened in autoclave B, and then selected reactions were repeated in autoclave A for comparison. The feedstock consisted of 2.5 parts by weight of recycle vehicle (50g) from Wilsonville run #263 to 1 part Black Thunder coal (20g). The total gas charge was up to 1000 psi (cold), and contained 3% H_2S . Carbon monoxide concentrations ranged from 20% to 50%. The simulated 2-stage liquefaction experiments were conducted in a 1 liter autoclave (AE) equipped with an injection port.

RESULTS AND DISCUSSION

Coal conversions using synthetic solvents: The comparison of model coal conversions using various catalysts for a hexadecane solvent system is presented in Table 1. The first three liquefaction experiments listed in Table 1, were conducted at 400°C. They include a noncatalyzed conversion, and conversions using molybdenum (MoS_4 and $Mo(OM)$) catalysts on an Illinois #6 coal. The fourth liquefaction experiment was conducted in tetralin, for comparison. Most of the conversions are quite low, as expected. For instance, in the absence of catalyst, the Illinois #6 coal was converted to 25% toluene-soluble material.

However, in the presence of the molybdenum catalysts, the conversions were greatly enhanced. For instance, the coal impregnated with $(\text{NH}_4)_2\text{MoS}_4$ gave a conversion of 41% toluene-soluble material, compared to 54% for the organometallic molybdenum-impregnation [Mo(OM)].

The remaining five experiments, conducted at 425°C using an Argonne lignite coal, compare various soluble iron-, molybdenum-, and nickel-based catalysts. Both the soluble organometallic iron complexes, $\text{Fe}(\text{CO})_5$ and $\text{Fe}_2\text{S}_2(\text{CO})_6$, are effective for the low rank coals, giving toluene-soluble conversions in the range of 40% (carbon-based yields). In previous work we found that these catalysts gave only nominal conversions for the Illinois #6 coal. X-ray analyses of the residues show that both catalysts were converted into pyrrhotite; however, the iron carbonyl also appeared to have been converted into elemental iron and other iron-based products. The Mo(OM) catalyzed reaction gave a higher conversion of 49% for this lignite, consistent with the better efficacy of Mo catalysts over Fe catalysts. Considering the organic chemistry of carboxylates, we also decided to investigate nickel as a potential catalyst for low rank coals. Since iron has a tendency to form dimers during decarboxylation of organic acids,^{7,8} and nickel tends to promote decarboxylation without dimerization we speculated that nickel may be a better catalyst for oxygenated coals.⁸ Consistent with this premise, the conversion using a Ni-based catalyst $[\text{Ni}(\text{COD})_2]$ shows that the lignite conversion increased from 40% with the iron catalyst to 60% with the nickel catalyst.

Black Thunder screening tests. The iron oxide catalysts were found to give poorer liquefaction yields than either the iron carbonyl and thiolato iron carbonyl. For instance, under hydrogen atmospheres, the iron oxides gave THF-soluble conversions in the range of 75% compared to over 90% for the iron carbonyl and thiolato iron carbonyl. However, in the presence of syngas, the iron carbonyl gave significantly lower yields than the thiolato iron carbonyl catalyst. Thus the latter catalyst appears to be superior for concepts that take advantage of the carbon monoxide chemistry, and no evidence of methanation was observed.

In a similar manner, Figure 1 illustrates the relative abilities of the MolyVanL and the thiolato Mo catalyst for conversions of the Black Thunder coal. In this case the conversions were conducted in Reactor B, which gives lower conversions than in Reactor A. The molybdenum content in all cases was 500 ppm of Mo. As seen in Figure 2, the MolyVanL gave relatively low conversions in Reactor B, but they were about the same (50%) whether in hydrogen atmospheres or syngas atmospheres. Thus the molybdenum catalyst appears to be able to use the carbon monoxide atmospheres. In the presence of the thiolato molybdenum catalyst, however, the conversion increased from 50% with the MolyVanL catalyst to over 75% conversion showing that the organometallic molybdenum catalyst is a far superior catalyst.

Table 2 compares the conversions using various catalysts in Reactor A. This table lists the best iron-catalyzed conversions described above as well as results from a series of MolyVanL conversions that were repeated in Reactor A for comparison. Prompted by the high conversions obtained for the $\text{Ni}(\text{COD})_2$ -catalyzed lignite conversions, we also conducted conversions on Black Thunder coal with this catalyst. We investigated both hydrogen atmospheres and syngas atmospheres containing 50% CO; these results are also included in Table 2. The last column of Table 2 lists the coal conversions based on conversions to THF-soluble materials and allows for contributions from the recycle solvent. The nickel-catalyzed reactions both under hydrogen and under 50% carbon monoxide gave very high conversions to THF-soluble material, with overall coal conversions in excess of 90%.

Simulated Two-Stage Conversion. A base-line run was also conducted to simulate a two-stage liquefaction conversion process. For this simulated conversion we used the MolyVanL catalyst in hydrogen atmospheres, and for comparison, in syngas atmospheres. We decided to use this catalyst as a baseline case for comparison with other work that has recently used this commercially available oil-soluble molybdenum compound. Note, however, we have identified other catalysts that are more active than MolyVanL. For instance our thiolato molybdenum catalyst was found to give coal conversions of over 25% greater than that found for the MolyVanL catalyst under mild coal conversion conditions (reactor B). Thus we expect a significant improvement using this catalyst over these base-line conditions.

Tables 3 and 4 list the distillation yields and elemental analyses for the hydrogen atmosphere and syngas atmosphere conversions, respectively. The conversions using the two systems were similar, with the syngas conversion giving a slightly lighter product (C5-650°F product contents were 47.6%) than the hydrogen conversion products (C5-650°F product contents were 40.8%). Furthermore, the amounts of the 1000°F+ fractions were similar, at 25% for the hydrogen conversion and 28% for the syngas conversion. Although there was not enough data using the batch results to obtain a complete economic analysis without a significant amount of approximations, we were able to deduce some effects of the use of syngas in the first stage of the coal conversion. For instance, we found that more value-added products are produced (mainly phenols), the CO shift requirement is reduced, and there is an added effort in the purification of hydrogen for the second stage reactor. The preliminary results suggest that the benefits of syngas in the first stage slightly outweigh the disadvantages.

FUTURE WORK

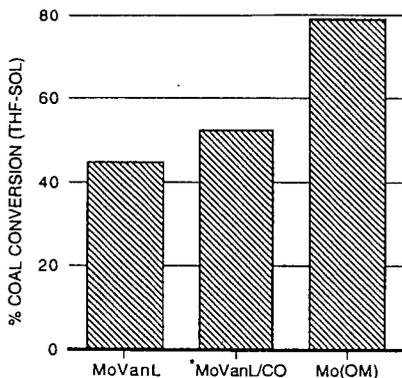
These preliminary results are encouraging, but economics need to be conducted on the best catalysts. Additionally, we have only used hydrogen in the second stage upgrading step, and thus not achieved the full economic benefits of syngas atmospheres. However, we feel that with proper catalyst and process development, our methods may significantly improve the final product quality and economics during coal liquefaction.

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*Conversions conducted using 50% CO/H₂ atmosphere for MoVanL catalyst.

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Figure 1. Effect of molybdenum catalysts for Black Thunder coal conversions in Reactor B.

Table 1

CONVERSION TO TOLUENE-SOLUBLE PRODUCTS IN HEXADECANE^a

Catalyst	Coal	T(°C)	% TS ^b
None	Illinois # 6	400	25
MoS ₄	Illinois #6	400	41
Mo(OM)	Illinois #6	400	54
Mo(OM) ^c	Illinois #6	400	61
None	Lignite	425	24
Fe(CO) ₅	Lignite	425	41
Fe ₂ S ₂	Lignite	425	39
Mo(OM)	Lignite	425	49
Ni(COD) ₂	Lignite	425	60

^aReaction conducted in a 300-mL autoclave with 5 g coal, 3 mmol catalyst, 30 g solvent and 500 psi H₂ for 20 min at temperature.

^bYields calculated on daf basis for Illinois #6 coal and on carbon basis for the lignite.

^cReaction run in tetralin under identical conditions.

Table 2

DAF YIELDS OF USING VARIOUS METAL CATALYSTS IN REACTOR A^a

Catalyst	Atmosphere ^c	THF Insol	Preasphaltene	Asphaltene	Oils	% Conv
Recycle	As received	8.7	7.5	60.9	23.2	-
Recycle	1000 psi H ₂	6.7	4.4	51.3	29.7	-
Fe(CO) ₅	1000 psi H ₂	5.8	7.5	54.9	21.7	96.5
Fe(CO) ₅	50% CO	14.9	18.7	34.8	25.4	64.7
Fe ₂ S ₂ (CO) ₆	1000 psi H ₂	7.6	11.8	37.5	24.4	90.2
Fe ₂ S ₂ (CO) ₆	50% CO	10.7	11.2	35.4	23.9	79.4
MolyVanL ^b	1000 psi H ₂	5.1	10.0	40.2	28.8	98.9
Ni(COD) ₂ ^b	1000 psi H ₂	7.2	11.6	41.8	20.7	91.6
Ni(COD) ₂ ^b	50% CO	7.4	11.8	46.3	23.3	90.9

^aReaction conducted in a 300-mL autoclave for 1 hr with 20 g Black Thunder Wyodak coal, 2% iron metal in catalyst, 50 g recycle solvent and at 425°C. Atmosphere contained 3% H₂S in H₂.

^b500 ppm metal added.

^cTotal pressure 1000 psi.

Table 3
ANALYSES OF DISTILLATION PRODUCTS FOR
H₂/H₂ TWO-STAGE COAL CONVERSION^a

Fraction °F	Wt. %	C	H	N	S	H/C
C5-350	4.3	83.63	16.37	b	b	2.332
350-650	21.6	86.24	10.13	0.68	0.17	1.398
650-850	14.9	87.91	9.91	0.64	0.30	1.344
850-1000	15.9	88.48	9.02	0.70	0.49	1.215
1000+	25.0	89.60 ^c	6.12 ^c	0.97 ^c	ND	0.812
Ash	8.5					
H ₂ O	5.5					

^a425°C, 30 minutes first-stage, 400°C, 30 minutes second-stage.

^bToo low for accurate N and S determination.

^cCalculated on an ash-free basis.

Table 4
ANALYSES OF DISTILLATION PRODUCTS FOR CO/H₂ 1ST STAGE, H₂ 2ND
STAGE TWO-STAGE COAL CONVERSION^a

Fraction °F	Wt. %	C	H	N	S	H/C
C5-350	3.5	85.10	14.34	0.5	0.07	2.008
350-650	20.9	85.05	10.61	0.52	0.05	1.449
650-850	23.2	88.55	9.06	0.60	0.14	1.219
850-1000	8.9	89.87	7.92	0.71	0.24	1.049
1000+	28.3	68.33 ^a	4.46 ^a	0.87 ^a	ND	0.778
Ash	9.6 ^b					

^a425°C, 30 minutes first-stage, 400°C, 30 minutes second-stage.

^bCalculated on an ash-free basis.