

OPTIONS FOR IRON-CATALYZED LIQUEFACTION OF LOW-RANK COALS

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Key Words: Coal liquefaction, iron catalysts, ion exchange

ABSTRACT

Liquefaction of low-rank coals is impeded by the mineral content of the coal. Inorganic constituents such as calcium are a major factor in deposits in the process equipment, but they also disrupt the functioning of the catalyst by blocking pores, deactivating sites, or causing sintering or aggregation. A series of liquefaction tests was performed that compared ion-exchanged Wyodak coal with the as-received coal. The catalysts were impregnated iron or iron dispersed on acidic supports. Highest conversions to heptane solubles were obtained with iron impregnated (PETC method) into acid-washed Wyodak. Alternatively, solubilization of as-received Wyodak with CO/water (uncatalyzed) gave an ash-free intermediate that produced high conversions to heptane-soluble product in the subsequent catalyzed liquefaction reaction.

INTRODUCTION

The high calcium content of low-rank coals has been recognized for some time as a potential problem in processing these coals to useful products. Operational difficulties were experienced at the Wilsonville Advanced Coal Liquefaction Research and Development Facility during the runs with Black Thunder (Wyoming) subbituminous coal due to substantial solids deposition (1). These deposits contained large amounts of calcium carbonate. In batch and continuous unit tests conducted at PETC (2), dispersed iron catalysts prepared by the PETC method exhibited poorer activities with subbituminous coals than previously obtained with bituminous coals. Swanson (3) recently reported that deposits of calcium coated the dispersed catalyst particles during tests with Black Thunder coal. Joseph and Forrai (4) examined the adverse effects of exchangeable cations (Na, K, Ca) on liquefaction of low-rank coals by ion-exchanging additional ions into the coals. The evidence cited in these reports implies that calcium deposits can rapidly deactivate the catalyst by blocking pores and active sites in the fine particles or could cause the particles to aggregate. Loss of catalytic activity for the activation of hydrogen then leads to condensation and retrograde reactions that form carbonaceous deposits and low oil yields.

Replacement of the alkaline earth cations with hydrogen ions is a possible solution. However, previous studies at EERC (5) demonstrated that noncatalytic thermal liquefaction of acid-washed lignite gave lower

conversions than the as-received coals. The lower yields were attributed to condensation reactions catalyzed by the highly acidic clays generated during the exchange process. Recently the conversions of coals washed with methanolic HCl were examined (6). This pretreatment significantly increased the conversion to THF-solubles in noncatalytic reactions. The significant increase in conversion to oils for ammonium-exchanged lignite (4) also demonstrates the potential for metal cation removal but may not be feasible for catalytic processing because of release of the ammonia. The behavior of acid-exchanged and other demineralized low-rank coal materials in liquefaction with various types of dispersed catalysts requires extensive investigation and elucidation.

This paper reports our investigations on the catalytic liquefaction of low-rank coal that was pretreated by ion exchange with aqueous acid and by thermal solubilization to a mineral-free product. A series of tests with ion-exchanged Wyodak subbituminous coal (IEW) was conducted to determine the effectiveness of various dispersed iron catalysts without the complications of the exchangeable cationic components. A second objective was to examine an alternative liquefaction scheme that produces mineral-free low-severity intermediate in a noncatalytic thermal pretreatment stage, that is subsequently liquefied with various dispersed iron catalysts in hydrogen.

EXPERIMENTAL

Preparation of Ion-Exchanged Coals

Acid-washed Wyodak (IEW) coal was prepared by stirring 7 g of ARW in 100 ml 1N nitric acid for one hour at ambient temperature. The acid-treated coal was separated by centrifugation and washing with water.

Coal Liquefaction

As-received Wyodak-Clovis Point (ARW) and IEW coals were pretreated using several different techniques prior to liquefaction. The PETC-method (7) was used for both ARW and IEW. Procedures reported by Ziolo and coworkers (9) were modified to prepare Fe_2O_3 dispersed on the coals. A slurry consisting of 7.0 g of ARW coal or product coal obtained from pretreatment of 7.0 g ARW, 10 wt% of catalyst (if required), 0.1 g of elemental sulfur, and 14 g of tetralin (solvent) were placed in a 70-ml Parr reactor. The reactor was evacuated and charged with 1000 psi (initial) of hydrogen gas. The reactor was heated to 425°C in a rocking autoclave (initial heatup time = 15 minutes) and left at this temperature for 60 minutes. At the end of the reaction, the reactor was cooled to room temperature, and the gases were removed. The product slurry was extracted with tetrahydrofuran (THF). The THF-insoluble product was dried under vacuum and weighed. A 4 ml aliquot of the THF-soluble was mixed with one ml solution of internal standard (a mixture of 2,2,4-trimethylpentane and n-octadecane in dichloromethane) and analyzed by GC. The remaining THF-solubles were evaporated to remove THF, and the dark oil was added to a large excess of heptane and stirred. The heptane-insoluble product was separated by centrifugation, washed with heptane, dried in vacuo at 50°C and weighed. The percent conversion was calculated on the basis of the coal (maf) that did not appear in the THF-insoluble fraction. Heptane-soluble yields were obtained by difference (100% - %THF-insolubles - %heptane-insolubles).

RESULTS AND DISCUSSION

Wyodak subbituminous coal was treated with nitric acid to remove by ion-exchange the metal cations bound to the coal matrix. Initial thermal (noncatalytic) tests were carried out to provide a basis for comparison with the catalytic tests. These tests required heating the coal/tetralin slurry in a rocking microtube reactor for 1 hr at 425 °C with 1000 psi (cold pressure) of hydrogen. Conversion and yield data are given in table 1. The thermal reaction of as-received Wyodak coal (ARW) gave a very high conversion (89%) to THF-soluble products. These data are consistent with earlier results for low-rank coals in thermal (noncatalytic) reactions in hydrogen or carbon monoxide (5). Carbon monoxide works as well as hydrogen in the noncatalytic reactions. The conversion for the (IEW) test (86%) was lower than that for the ARW coal on a maf basis. The lower conversion is also consistent with earlier work with low-rank coals that demonstrated that acid-washing lowers the conversion. This effect was attributed to the generation of highly acidic sites on clay minerals in the coal that catalyze carbonium ion reactions that often result in condensations to higher molecular weight and less soluble products. The amounts of heptane-soluble products formed in the two thermal reactions were similar (48%). The heptane-soluble yields are obtained by difference (100% - %THF-I - %heptane-I) and include major amounts of the gaseous products (CO₂, H₂O, etc.) in addition to the heptane-soluble oils.

The ion-exchanged coal was then reacted in catalytic liquefaction tests with several dispersed iron catalysts, and these results were compared with similar catalytic reactions carried out with the ARW in order to determine the effect of the inorganic cations on the catalytic activity. The PETC method (7) for impregnating iron as the iron hydroxyoxide on the coal surface was utilized for preparing the dispersed iron catalyst for liquefaction of both ARW and IEW coals. Addition of iron hydroxyoxide to ARW via the PETC method resulted in a conversion to THF solubles similar to those found in the thermal reactions (88%), but the yield of heptane-solubles was substantially higher (52%). Thus the catalytic effect is demonstrated principally in the oil yield. Generation of iron hydroxyoxide on the IEW significantly improved the conversion THF-solubles as well as heptane-solubles (56%). The significant increase in yields for the IEW can be attributed to less deactivation of the catalyst by the inorganic matter.

Alternative methods for generating dispersed iron on the coal surface were also examined. Previous work at Universal Fuel Development Associates, Inc. (8) demonstrated that clay-supported iron catalysts with high concentrations of maghemite fine particles were much more catalytically active than those with hematite. Ziolo and coworkers (9) reported that maghemite fine particles can be generated on ion-exchange resins by reducing ferric ions with hydrazine and sodium hydroxide or by treating ferrous ions with hydrogen peroxide and ammonium hydroxide. Since sodium hydroxide dissolves humic acids from the low-rank coal, ammonium hydroxide was utilized instead of sodium hydroxide to prepare the maghemite fine particles on the coal surface. Treatment of the coal with ferrous chloride/ammonium hydroxide to maximize maghemite formation did not improve conversions for IEW, 92% to THF-solubles, 47% heptane-solubles. Likewise treatment with ferric nitrate/hydrazine did not improve conversions, 91% THF-solubles, 46% heptane-solubles. A reaction carried out with this same pretreated coal but

Table 1
Catalytic Liquefaction with Dispersed Iron

Reaction Temp. = 425°C, Reaction Time = 1 hr, H ₂ = 1000 Psi (cold) Wyodak (AR) coal = 7.0 g., Coal/Tetralin = 0.5, Sulfur = 0.15 g.				
Pretreatment	Conv. (%)	THF-I (%)	Heptane-I (%)	Heptane-S (%)
None*	89	11	41	48
Acid washed*	86	13	40	47
Fe(NO ₃) ₃ + NH ₄ OH ^a	88	12	36	52
1 Acid washed 2 Fe(NO ₃) ₃ + NH ₄ OH ^a	91	9	36	56
1 Acid washed* 2 Fe(NO ₃) ₃ + N ₂ H ₄ + NH ₄ OH ^b	88	12	43	45
1 Acid washed 2 Fe(NO ₃) ₃ + N ₂ H ₄ + NH ₄ OH ^b	91	9	45	46
1 Acid washed 2 FeCl ₂ + NH ₄ OH + H ₂ O ₂ ^b	92	8	45	47

* = No sulfur was added to the reaction mixture.

a = PETC method.

b = Modified Ziolo method.

without addition of sulfur gave a similar conversion, indicating that the iron dispersed by this method is inherently inactive.

Previous work in this project was concerned with the preparation of fine iron sulfide particles supported on an acidic clay, and a preliminary report of mixed iron/alumina-pillared montmorillonite catalysis was presented (8). Catalytic liquefaction reactions of ARW and IEW were performed in tetralin using conditions similar to those above. Reactions were carried out using 10 wt% of the clay catalysts (sulfided in situ using small amount of elemental sulfur) at 425°C for one hour in 1000 psi of initial hydrogen pressure. The reaction conditions and yields data are given in table 1.

With the most active of the mixed iron/alumina-pillared clay catalysts in the presence of sulfur, the conversion of the ARW was 91% to THF-solubles with 53% heptane solubles. In the absence of sulfur required for sulfidation of the oxyiron catalyst, the conversion was substantially less, 87% to THF-solubles, with only 33% heptane-solubles. This large reduction in oil yield is attributed to the presence of the highly acidic clay and absence of any good hydrogen activation capability. The reaction of IEW coal with the active sulfided clay catalyst gave a significantly higher conversion to THF solubles, and excellent conversion to heptane-solubles (54%).

Although significant improvements in oil yields were obtained as a result of pretreating the Wyodak to remove metal cations, the economics of an ion-exchange process and subsequent disposal of the acidic waste water may not compensate for the increase in conversion and operability. An alternative liquefaction process has been utilized for many years at the Energy and Environmental Research Laboratories. This processing involves a noncatalytic thermal pretreatment under carbon monoxide atmosphere to break down the cross-links in the coal to give a high molecular weight THF-soluble intermediate in 95% yield. Mineral matter is conveniently removed from the coal solution. This cation-free low-severity intermediate is then used in catalytic liquefaction tests with hydrogen.

Several reactions of a mineral-free low-severity intermediate from Wyodak coal (LSW) were carried out with dispersed iron catalysts. A THF-soluble intermediate was obtained by thermal liquefaction in CO and was separated from heptane-soluble products and solvent(tetralin)-derived materials by solvent (heptane) precipitation to give the high molecular weight LSW intermediate for these tests. The LSW is a low-density solid at ambient temperature, but melts easily. A thermal (noncatalytic) reaction of the LSW in tetralin at 425 °C for 1 hr in 1000 psi hydrogen gave 15% conversion to heptane-solubles (Table 3). The conversions obtained for the LSW substrate cannot be directly compared with the coal conversions above, because the substrates are quite different. The 15% value for the LSW substrate represents a conversion of preasphaltenes and asphaltenes to heptane-soluble oils, whereas the 48 to 54% yields of heptane-solubles given above for coal substrates include both the more easily cleaved oil products as well as the gaseous products of liquefaction, such as significant amounts of carbon dioxide and water.

The liquefaction reaction of the LSW in tetralin with the dispersed iron/alumina-pillared clay catalyst (in situ sulfided) gave 30% conversion to heptane-solubles under the same conditions. The two-fold increase in conversion to oils for catalytic versus thermal reactions with the LSW substrate thus compares favorably with the increase of 6% (48 to 54%) found in the experiments with ion-exchanged coal described above.

The LSW intermediate was also subjected to the PETC iron dispersion treatment by stirring the low-density solid LSW with ferric nitrate solution and adding ammonium hydroxide to generate the surface-bound iron hydroxyoxide. The conversion of this material under conditions identical to those above with in situ sulfidation gave 15% heptane-solubles, the same as the thermal reaction. It is not known yet whether the iron sulfide that forms in the reaction with LSW is able to activate hydrogen, or whether some acidic component is required at this stage of liquefaction. This result may have very important implications for selecting conditions and coals for application of the PETC method to low-rank coals.

A variation of the PETC method was attempted to generate the dispersed iron catalyst on the LSW. Ethanol was used to obtain a colloidal dispersion of the LSW, which was then mixed with the ferric nitrate solution in ethanol and the ammonium hydroxide. After removal of the ethanol, the liquefaction was carried out in tetralin under conditions similar to those used above. When the dispersed iron obtained by this method was utilized, a 28% yield of heptane-soluble oils was obtained. It is now obvious that there are critical interactions between the iron and the coal surface that need to be

further elucidated and evaluated for designing a viable coal liquefaction method.

CONCLUSIONS

In coal liquefaction reactions that utilize dispersed iron catalysts, the catalytic activity was significantly improved by ion-exchange of cations present in the low-rank coals by aqueous acid-washing. Higher conversions to heptane-solubles were obtained with ion-exchanged Wyodak when dispersed iron catalyst was prepared by the PETC method. The ion-exchange pretreatment also improved the activity of the dispersed iron/alumina-pillared montmorillonite catalyst. A thermal pretreatment was also used to eliminate mineral matter, and the iron/alumina-pillared clay and one of the dispersed iron catalyst preparations were catalytically active.

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Table 2
Catalytic Liquefaction with Iron/Alumina Pillared Clay

Reaction Temp. = 425°C, Reaction Time = 1 hr, H ₂ = 1000 psi (cold) Coal/tetralin = 0.5, Catalysts = 10 wt%						
Coal (g)	Catalyst (wt. %)	Sulfur (g)	Conv. (g)	THF-I	Heptane-I	Heptane-S
Wyodak (AR) (7.0)	None	None	89	11	41	48
Wyodak (AR) (7.0)	APC-Fe ₃ (10)	None	87	13	54	33
Wyodak (AR) (7.0)	APC-Fe ₃ (10)	0.10	91	9	38	53
Wyodak (IEW) (5.34)	APC-Fe ₃ (10)	0.10	95	5	41	54

AR = as received Wyodak
IEW = 7.0 g AR coal was acid washed and dried

Table 3
Catalytic Liquefaction of LSW Intermediate

Reaction Temp. = 425°C, Reaction Time = 1 hr, H ₂ = 1000 psi (cold) Coal/tetralin = 0.5, Catalysts = 10 wt%					
Substrate (g)	Catalyst (wt. %)	Sulfur (g)	THF-I	Heptane-I	Heptane-S
LSW (1.0)	None	None	0	85	15
LSW (1.0)	APC-Fe ₃ (10)	0.1	0	70	30
LSW (1.0)	PETC METHOD	0.10	0	73	28