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LOW SEVERITY COAL LIQUEFACTION PROMOTED BY CYCLIC OLEFINS

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Low Severity Coal Liquefaction Promoted by Cyclic Olefins

Introduction

Low severity coal liquefaction offers the opportunity to convert coal while minimizing undesirable side reactions. The research undertaken in this project is to promote low severity coal liquefaction by transferring hydrogen from highly reactive cyclic olefins which have been shown to release their hydrogen readily at low severity coal liquefaction conditions (Bedell and Curtis, 1991). The cyclic olefins used in this study are isotetralin or 1,4,5,8-tetrahydronaphthalene, and 1,4,5,8,9,10-hexahydroanthracene. These compounds are nonaromatic hydroaromatics with nonconjugated double bonds. Hexahydroanthracene will be used first in this study because it is commercially available whereas isotetralin must be synthesized in the laboratory using the Birch reduction method.

The initial work performed utilized naphthalene as a test compound. The reason for this choice was that the master's candidate needed to learn how to perform microtubular reactions at the temperatures and pressures of coal liquefaction. Naphthalene represents a relatively inexpensive and nontoxic compound to use in initial scoping experiments. A number of reactions were performed initially that are not reported herein. These experiments were performed to teach the graduate research assistant the mechanics of performing these reactions and to establish reproducibility.

A literature search of low severity coal liquefaction was also performed. An annotated bibliography of low severity coal liquefaction is provided in this quarterly report. Subsequent quarterly reports will contain further experimental work as well as additional bibliography and descriptive literature reviews of the most pertinent literature described in the annotated bibliography.

Experimental Methods and Results

Methods. A parametric evaluation of the hydrogenation of naphthalene was performed to establish reproducibility and evaluate the effect of the reaction parameters on the activity of the catalysts for naphthalene hydrogenation. These parameters will give a starting point for the anthracene and hexahydroanthracene hydrogenation studies to be performed next quarter.

The naphthalene hydrogenation reactions were performed thermally which yielded no hydrogenation of naphthalene and catalytically using Molyvan L and Molyvan 822. Both of these catalysts were obtained from Vanderbilt Chemical Company. Molyvan L is sulfurized oxymolybdenum dithiocarbamate and Molyvan 822 is organo molybdenum dithiocarbamate. The reactions were performed in stainless steel tubular microreactors at 400 and 350°C and hydrogen pressures of 1000 and 1250 psig introduced at ambient temperature. The catalyst precursors were introduced at 1500 ppm of Mo. The reactions were performed with and without sulfur. Sulfur was introduced as elemental sulfur at a 3 to 1 sulfur to molybdenum stoichiometric ratio. The reaction time was 30 min. The reaction products were analyzed using a Varian gas chromatograph Model 3700 with a DB-5 capillary column and flame ionization detection. Quantitation was performed using the internal standard method with p-xylene as the internal standard.

A short study was performed evaluating the effect of the agitation direction on the product distribution obtained from naphthalene hydrogenation. The two agitation directions used were vertical and horizontal. These reactions were performed using Molyvan L with and without sulfur.

The term percent hydrogenation (% HYD) is defined for ease of comparison of the results from one set of reaction conditions to another. Percent hydrogenation is the number of moles of hydrogen required to produce the liquid products as a percentage of the number of moles of hydrogen required to produce the most hydrogenated product. In the case of naphthalene, the most hydrogenated product is decalin.

Results. The naphthalene hydrogenation performed thermally at 350 and 400°C showed no reactivity of the naphthalene. The Molyvan L catalyst precursor promoted a small amount of hydrogenation of naphthalene at 400°C as shown in Table 1. Reaction at the higher initial pressure of 1250 psi resulted in slightly more conversion of naphthalene and a higher production of tetralin but no decalin was observed. The naphthalene hydrogenation reactions with Molyvan L without sulfur yielded a slightly higher % HYD of naphthalene than did the reactions with sulfur. Likewise, the reactions with an initial hydrogen pressure of 1250 psi yielded a higher % HYD of naphthalene than did the reaction with 1000 psi, regardless of whether sulfur was present.

The Molyvan 822 catalyst precursor was substantially more active at 400°C than at 350°C as presented in Table 2. The presence of sulfur also promoted the activity of Molyvan 822 as a catalyst. Tetralin was the product and was produced in substantial quantities at 400°C. Molyvan 822 was much more active for naphthalene hydrogenation than was Molyvan L under equivalent conditions. For example, at 400°C with sulfur the reactions with Molyvan 822 produced 33.5% HYD while Molyvan L yielded 1.8% HYD.

With Molyvan L, the less active catalyst, the effect the mode of agitation (vertical or horizontal) was minimal. These results are shown in Table 3. However, other systems that are

more active tend to show a greater effect of the mode of agitation. Hence, for this work, horizontal agitation was chosen as the standard.

Table 1. Naphthalene Hydrogenation Using Molyvan L

Reaction Conditions			Product Distribution (wt %)		
Catalyst	Temperature (°C)	Pressure (psi)	Naphthalene	Tetralin	%HYD
Molyvan L (1500 ppm) without Sulfur	400	1250	91.83 ± 1.83	8.17 ± 1.83	3.2
	400	1000	93.73 ± 0.70	6.27 ± 0.70	2.4
	350	1000	100.0 ± 0.0	0 ± 0	0
Molyvan L (1500 ppm) with Sulfur	400	1250	93.28 ± 2.98	6.72 ± 2.98	2.6
	400	1000	95.33 ± 0.11	4.67 ± 0.11	1.8
	350	1000	100.0 ± 0.00	0 ± 0	0

Reaction Conditions: 2 wt % naphthalene in hexadecane, 30 min.

% HYD = Percent hydrogenation.

Table 2. Naphthalene Hydrogenation Using Molyvan 822

Reaction Conditions			Product Distribution (wt %)		
Catalyst	Temperature (°C)	Pressure (psi)	Naphthalene	Tetralin	%HYD
Molyvan 822 (1500 ppm) without Sulfur	400	1000	29.12 ± 2.96	70.88 ± 2.96	28.1
	350	1000	70.50 ± 1.51	29.50 ± 1.51	11.6
Molyvan 822 (1500 ppm) with Sulfur	400	1000	15.94 ± 1.29	84.06 ± 1.29	33.4
	350	1000	62.33 ± 1.12	37.67 ± 1.12	14.8

Reaction Conditions: 2 wt % naphthalene in hexadecane, 30 min.

% HYD = Percent hydrogenation

Table 3. Comparison of Catalytic Naphthalene Hydrogenation With Different Agitation Directions

Reaction Conditions		Product Distribution (wt %)		%HYD
Catalyst	Agitation	Naphthalene	Tetralin	
Molyvan L (1500 ppm) Without Sulfur	Horizontal	91.83±1.83	8.17±1.83	3.2
	Vertical	96.21±0.27	3.79±0.27	1.5
Molyvan L (1500 ppm) With Sulfur	Horizontal	93.28±2.98	6.72±1.83	2.6
	Vertical	93.40±0.51	6.60±0.51	2.6

Reaction Conditions: 400°C, 1250 psi H_2 at ambient temperature, 30 min, 2 wt % naphthalene in hexadecane.

% HYD = Percent Hydrogenation

Annotated Bibliography of Low Severity Coal Liquefaction

Baldwin, R.M.; Kennar, D.R.; Nguanprasert, O.; Miller, R.L. "Liquefaction Reactivity Enhancement of Coal by Mild Alkylation and Solvent Swelling Techniques," Fuel, 70:429-433, 1991.

Mild alkylation and solvent swelling techniques were used to pretreat Illinois No. 6 hvB and Wyodak subbituminous coal from the Argonne Premium Coal Sample Bank. Liquefaction reactions were performed using dihydrophenanthrene as solvent for direct liquefaction reaction and Cold Lake resid for coprocessing. Alkylation was beneficial as a pretreatment step for low severity conditions (350°C, 5 min.) for low rank coals which were selectively O-methylated. Nonselective methylation was effective for high severity coprocessing using Illinois No. 6 coal but not for low rank Wyodak coal. Preswelling coal with acetone promoted coal conversion and increased the yield of hexane solubles. The measure of effectiveness for all reactions was conversion to THF solubles.

Stenberg, V.I.; Gutenkunst, V.; Nowok, J.; Sweeny, P.G. "Low Severity Lignite Liquefaction: Temperature Programming to 350°C in an Inorganic Solvent," Fuel, 68:133-135, 1989.

Temperature programming from 300 to 350°C and times up to 60 min. was used to achieve high liquefaction conversions of Indian Head lignite. The liquefaction medium was the inorganic solvent system of H_2S-H_2O with CO, H_2, and pyrrhotite. The temperature program was based on spin data from ESR as well as data from TGA and DSC in an attempt to match free-radical generation rate with hydrogen donation rate. Temperature programming yielded higher THF, toluene and cyclohexane soluble yields compared to the corresponding isothermal experiments.

Lalvani, S.B.; Muchmore, C.B.; Koropchak, J.A.; Akash, B.; Chavez, C.; Rajagopal. "Coal Liquefaction in Lignin-Derived Liquids Under Low Severity Conditions," Fuel, 70:1433-1438, 1991.

Lignin-derived liquids reacted with coal at low severity conditions (375°C, 2.17×10^6 - 3.55×10^6 Nm^{-1}) increased the coal depolymerization rate by up to 30%. A significant amount of pentane soluble fraction was present in the product. The hypothesis was made that the rate of enhancement of depolymerization involved a reaction pathway with intermediates formed from lignin-derived liquids. A mathematical model was developed along with computed rate constants.

Smith, J.E.; Johnson, S.D. "Low Severity Coal Liquefaction Using Intermetallic Hydrides as Both Catalysts and Hydrogen Distribution Agents," ACS Fuel Chemistry Division Preprints, 35(1):23-30, 1990.

Intermetallic alloys that form reversible hydrides by storing atomic hydrogen within their matrices were evaluated as hydrogen transport and distribution agents as well as catalysts in liquefaction of Alabama Black Creek coal. The catalytic activity of these alloys ranked as $CaNi_5$ = $LaNi_5$ > FeTi > Mg_2Cu > Mg_2Ni under the conditions of 316, 371, and 427°C and a pressure of 4.83 MPa. Increased reaction temperature resulted in higher conversion to preasphaltenes and oils.

Miller, R.L.; Baldwin, R.M.; Kennar, D.R. "Addition of Basic Nitrogen Promoters to Enhance Low Severity Two-Stage Coal Liquefaction and Coal/Oil Processing," ACS Fuel Chemistry Division Preprints, 35(1):9-16, 1990.

Low severity single-stage reactions using 1,2,3,4-tetrahydroquinoline (THQ) and dipropylamine showed increased coal dissolution and distillate yields without these nitrogen materials being incorporated into the product. In two-stage processing with a low severity first-

stage with THQ present followed by catalytic upgrading resulted in coal conversions and distillable yields comparable to high severity liquefaction. However, much lower hydrogen consumption and hydrocarbon gas make were obtained under low severity conditions.

Olson, E.S.; Diehl, J.W.; Sharma, R.K. "Hydrocracking with New Solid Acid Catalysts: Low Severity Liquefaction Products from Low Rank Coal," ACS Fuel Chemistry Div. Preprints, 35(2):563-569, 1990.

Solid acid catalysts, $ZnCl_2$ on silica gel and acid-exchanged montmorillonite, were evaluated with the first stage low severity products from Wyodak subbituminous coal. Catalytic hydrocracking of these low severity products resulted in substantial yields of distillates that exceeded those from hydrotreating catalysts under similar conditions.

Snape, C.E.; Derbyshire, F.J.; Stephens, H.P.; Kottenstette, R.J. "Influence of Organic Coal Structure on Liquefaction Behavior Under Low-Severity Conditions," ACS Fuel Chemistry Div. Preprints, 34(3):793-802, 1989.

The influence of coal structure on the products from thermolytic extraction with different hydrogen donor and nondonor solvents. Presoaking of coal with H-donors at 250°C increased coal conversions and hydrogen transfer in short contact time (SCT) reactions. Removing THF-extractable materials from a bituminous coal increased conversion in aromatic solvents. Oil yields correlated with decreasing rank when reacted with a hydrogen donor and dry catalytic hydrogenation; but neither coal conversion or oil yield correlated with rank in SCT tetralin extraction.

Miller, R.L.; Giacomelli, G.F.; Baldwin, R.M. "Low Severity Co-Processing Using Homogeneous Basic Nitrogen Promoters," ACS Fuel Div. Preprints, 33(1):154-82, 1988.

The nitrogen containing compounds, 1,2,3,4-tetrahydroquinoline and dipropylamine, improved coal conversion and distillable liquid yields in low severity coprocessing reactions. No significant nitrogen losses through adduction or thermal degradation were observed.

Burgess, Caroline E.; Artok, L.; Schobert, H.H. "Effect of Molybdenum Sulfide Catalyst on the Mechanism of Coal Liquefaction," ACS Fuel Chemistry Div. Preprints, 36(2):462-469, 1991.

The mechanism by which a molybdenum sulfide catalyst promotes liquefaction during temperature-staging and low-severity conditions of subbituminous coals was described: molybdenum sulfide provides the hydrogen to cap the radicals generated from the production of asphaltenes. For bituminous coal, the mechanism is different: molybdenum sulfide provides

atomic hydrogen to help crack asphaltenes to oils, serving as a hydrogenation catalyst. Repolymerization is reduced.

Miller R.L.; Shams, K.; Baldwin, R.M. "Mild Coal Pretreatment to Enhance Liquefaction Reactivity," ACS Fuel Chemistry Div. Preprints, 36(2):462-469, 1991.

Low severity coal liquefaction was evaluated by pretreating and reacting coal in the following sequence: (1) pretreatment of the coal with methanol and a trace of HCl; (2) low severity coal dissolution to obtain a residual product for upgrading; and (3) catalytic upgrading of the residual material. Pretreatment with methanol and HCl improved coal conversion to THF solubles by 30% at 350°C. The cause of the improvement may be leaching of detrimental minerals from the mineral matter or mild alkylation at oxygen sites in the coal's organic phase.

Rindt, J.R.; Hetland, M.D.; Sauer, R.S.; Sukalski, W.M.; Haug, L.W. "Preconversion Treatments of Low-Rank Coal," ACS Fuel Chemistry Div. Preprints, 36(1):83-90, 1991.

Low severity preconversion techniques were used to liquefy Indian Head lignite in first stage processing. The preconversion treatment consisted of heating with a solvent, anthracene oil, cresylic acid or tetralin for 60 min at 175 or 250°C followed by a 20 min at 410°C. The conversion of lignite was improved by using the preconversion solvent treatment. The cresylic acid was a more effective solvent than anthracene oil but tetralin was more effective for converting coal to soluble material.

Derbyshire, F.; David, A.; Lin, R. "Considerations of Physiochemical Phenomena in Coal Processing," Energy and Fuels, 3:431-437, 1989.

Changes in the physical and chemical nature of coal during liquefaction were reviewed in terms of coal oxidation and low severity catalytic hydrogenation. Low temperature modifications of the coal structure can directly influence high temperature behavior.

Future Work

Reactions will be performed with hexahydroanthracene thermally and with the three catalysts. After these reactions are completed, then reactions with coal will commence. A high temperature, high pressure infrared cell is currently being investigated. The equipment bid will go out shortly to the manufacturers.

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