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Low Severity Coal Liquefaction Promoted by Cyclic Olefins

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PART I

MILD ACIDIC PRETREATMENT TO ENHANCE LOW SEVERITY LIQUEFACTION PROMOTED BY CYCLIC OLEFINS

Introduction

In the continuing effort to improve low severity coal liquefaction technology, much of the work has been directed toward one goal, increasing the amount of hydrogen transferred to the coal. Transfer of hydrogen to coal is important for making coal into a liquid fuel. Liquefying coal is also the purpose of this study, with the added proviso that the liquefaction be conducted at low severity conditions.

One must consider what is necessary to achieve a greater transfer of hydrogen. One of the variables that can be positively influenced is the availability of donable hydrogen in the reaction. Simply put, if there is more hydrogen available in the liquid phase, more hydrogen can be transferred yielding greater conversion. Bedell and Curtis (1991) showed that cyclic olefins, under low severity conditions, donated their hydrogen readily, even more so than their hydroaromatic analogues. These results were affirmed by Huang and Curtis (1993) in their work with the cyclic olefin, 1,4,5,8,9,10-hexahydroanthracene (HHA).

Providing more hydrogen improves one aspect of the liquefaction process. Unfortunately, inorganic sodium, potassium and calcium cations inhibit coal reactivity and the acceptance of hydrogen by coal through hydrogen transfer. In order to achieve efficient hydrogen transfer, the effect of these cations on coal reactivity must be countered. This task can be accomplished by various pretreatment methods. One such pretreatment uses a mild acidic solution to wash the coal (Shams et al., 1991). The acid destroys ionic bridges and reduces the coordination between oxygen containing functional groups, allowing better contact between coal and solvent. More

importantly, acid pretreatment removes those alkaline metal and alkaline earth cations which inhibit coal reactivity and hydrogen transfer. Shams et al. (1992) found that through this pretreatment a large portion of the calcium present in coal was removed. Hydrochloric acid was used in that study, but sulfurous acid, if similar results are achieved, would be a much more suitable acid for processing. Another pretreatment method to remove these cations is one using ammonium acetate (Hengel and Walker, 1984).

This study will evaluate the effect of combining these two principles, acid pretreatment of coal and rapid hydrogen transfer, for improving hydrogen transfer under low severity conditions. The acid pretreatment methods showed more success with low rank, subbituminous coals and lignite. Therefore, Wyodak subbituminous coal (WY) from the Argonne Premium Sample Bank and Black Thunder subbituminous coal (BT) from Amoco are being used and compared in this study. The cyclic olefin, 1,4,5,8-tetrahydronaphthalene (isotetralin, ISO) and its analogue, 1,2,3,4-tetrahydronaphthalene (tetralin, TET), will also be used and compared in this study. The efficacy of the two-ringed ISO can then be compared with the previously studied three-ringed HHA.

Dr. James Hool, Professor of Industrial Engineering and an expert in statistics and experimental design, assisted in formulating the four-dimensional experimental matrix found in Figure 1. It is through this parametric analysis that the effect of each factor in this pretreatment and low severity liquefaction system will be determined.

Experimental

In order to be more statistically accurate, the reactions with various conditions monitored in the matrix will be performed randomly. Each reaction will also be done three times to preserve statistical soundness of the results. Because of this experimental design, both pretreated

and untreated coals, are being held at 22 inches of mercury vacuum until they are used. Often, this storage under vacuum could last for several days.

Since the Argonne Wyodak coal is ground to -100 mesh and the Black Thunder is not nearly so fine, the Black Thunder must be ground in order to compare the results. The Black Thunder is ground in a Fritsch Pulverisette Type 22.101, an electric mortar and pestle grinder, for approximately 10 min until its particle size compares to that of the Wyodak.

Pretreatment of the coal with the hydrochloric and sulfurous acids is performed according to Shams' method (1991) which is described in the previous quarterly report. Amoco has also provided a Black Thunder coal which had already been pretreated with sulfurous acid. This previously pretreated coal will be compared with coal pretreated following Shams' method. Finally, pretreatment with ammonium acetate solution is performed according to the method of Hengel and Walker (1984) and is detailed in the appendix.

All of the coal will be reacted under low severity conditions in a ~25 ml stainless steel tubular microreactor. Each reactor will be loaded with 1 g of coal and 2 g of solvent. This solvent is comprised of approximately 1.33 g of hexadecane (99% purity from Aldrich) and either 0.66 g TET (99% purity from Aldrich) or 0.66 g ISO (97% purity, recrystallized by M.W. Bedell). This ratio provides 1% donable hydrogen. After the reactor is sealed, it is placed under 500 psi of hydrogen and agitated in a sandbath at 350°C for 30 min.

The reaction products are compared using conversion to tetrahydrofuran (THF) soluble products. This is a common method for determining the effectiveness of coal liquefaction. It is defined by

$$\% \text{ conversion} = 1 - \left(\frac{\text{IOM}_{\text{maf}}}{\text{Feed coal}_{\text{maf}}} \right)$$

where, IOM = insoluble organic matter (THF insolubles)

maf = on a moisture and ash-free basis.

The method for the separation of THF solubles from THF insolubles follows the procedure from the previous quarterly report, with one exception. Because the volatility of the reaction products of TET and ISO, the filtered solution of THF solubles is placed in the Büchi RE 121 Rotavapor for 1 hr and 45 min at approximately 45°C. This lower temperature which requires longer evaporation time helps to prevent anything but THF from being driven out of the solution, and solves an earlier problem with low recovery, caused by loss of ISO and TET reaction products.

Results and Discussion

Before entering the experimental matrix, it was necessary to verify some assumptions and review some background information. Since the HHA proved to be more effective as a donor than the hydroaromatic dihydroanthracene, it would seem that the ISO would be more effective than TET. It was necessary to compare the ISO and TET initially to be certain.

Fortunately, untreated coal falls into the first square of the matrix. Pretreatment with no acid and water is the same as no pretreatment at all. The coal was only dried for 12 hr. Conversion for the untreated Wyodak coal, when reacted with TET, was 15.1%. This amount is compared with a conversion of 23.0% for coal using ISO as the donor solvent. For all of the reactions, the recovery was $100\% \pm 10\%$. These results show that there is indeed a significant improvement when ISO is used instead of TET.

Another observation to be made concerned the importance of drying the coal. When calculating conversion an maf basis is used. If the coal has previously been dried, only ash must

be taken into consideration. Lignite and subbituminous coals have a high moisture content (WY: 28.09% and BT: 11.2%). It was necessary to see whether or not moisture had any effect on the reaction. If it did not, when the moisture was included in the calculations, the conversion would end up the same. Experimentation showed that the moisture in the coal did affect more than just the final calculations. When the reactions were run with Wyodak coal, as received, a coal conversion of 3.7% was found for TET and 16.4% for ISO. Clearly, the presence of moisture caused a reduction of hydrogen transfer with liquefaction under low severity conditions.

The matrix may now be completed using each of the dry pretreated coals. By performing each reaction three times, there will be at least 84 reactions to be completed. If time permits other variables may be added to increase the matrix to find the most ideal pretreatment method.

Summary

A large portion of this study involved perfecting the methods to be used and defining exactly what is to be done. Performing the specified experiments should now go smoothly. Many problems that had been encountered earlier have been overcome.

By reviewing what has succeeded in the past, the experimental matrix developed of different combinations of pretreatment and hydrogen donors should complement each other. It now remains to be seen which combination provides the best conversion.

Gas chromatography will be used to analyze the THF soluble products of these reactions also. It is hoped that this will offer some information on the mechanics of the dehydrogenation of both the TET and ISO. Perhaps knowing this, an even better hydrogen donor can be found.

All of this research continues to lead to the same goal, allowing more hydrogen to be transferred to the coal. By doing so, process of coal liquefaction can further approach the realm of economic feasibility. Due to oil politics and increasing environmental restrictions,

dependence on petroleum must be relieved and alternate fuel sources explored. Since coal is an abundant resource, better and more productive uses for coal can help to accomplish this goal.

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APPENDIX A

Procedure for Ammonium Acetate Pretreatment of Coal

1. Prepare at least one liter of 1.5 M NAc (Ammonium Acetate).
2. Using standard weighing paper, weigh out 10 g of coal to be pretreated. Place this into a nalgene centrifuge bottle. To this add 125 ml of 1.5 M NAc solution using a pipet or other accurate measuring vessel.
3. Then place bottle onto a stirrer or an orbit shaker and stir vigorously at room temperature for 1 hr.
4. To prevent losses while decanting and for final washing, a vacuum filtration system similar to the one used for acid pretreatment (see previous quarterly reports) should be set up.
5. Centrifuge slurry and decant liquid over filter paper. Wash coal with three 50 ml aliquots of NAc solution centrifuging after each washing.
6. After the final washing, add 125 ml of NAc solution and stir slurry again for 2 hr.
7. Centrifuge slurry and decant liquid over filter paper.
8. Add 125 ml of NAc solution and stir slurry for 3 hr.
9. Pour slurry directly onto filter paper to collect the pretreated coal. Then again wash with three 50 ml aliquots of NAc solution.
10. Wash coal with three 50 ml aliquots of distilled water to rinse the NAc solution off of the coal.
11. Remove the filter paper and place it on a large petri dish. Place it in a vacuum oven at room temperature for at least 12 hr before use.

APPENDIX B

Calculations

TET and ISO both can donate four hydrogen atoms. Percent donable hydrogen (%DH) for the solvent is found by solving the equation.

$$\frac{\text{M.W. ISO or TET}}{\text{M.W. DH}} = \frac{\text{ISO or TET charge}}{(\% \text{DH})(\text{Total solvent charge})}$$

$$\text{M.W. ISO and TET} = 132.2$$

$$\text{M.W. DH} = 4.0$$

Coal conversion is calculated using the following equation:

$$\% \text{ conversion} = 1 - \frac{(\text{grams THF insolubles} - \text{grams ash})}{(\text{grams coal charged} - \text{grams H}_2\text{O}_{\text{in coal}} - \text{grams ash}_{\text{in coal}})}$$

$$\text{grams ash} = 0.0631 (\text{Total weight of coal}) [\text{for Wyodak}]$$

$$0.0540 (\text{Total weight of coal}) [\text{for Black Thunder}]$$

$$\text{grams H}_2\text{O}_{\text{in coal}} = 0 [\text{for feed coal dried in the vacuum oven}]$$

Figure 1. Four-Dimensional Experimental Matrix for Mild Acidic Pretreatment to Enhance Low-Severity Coal Liquefaction Promoted by Cyclic Olefins.

PART II

Fourier Transform Infrared Spectroscopy for Cyclic Olefins

Current Work

Several quarters ago, data were reported concerning the infrared spectra of cyclic olefins using Fourier transform infrared (FTIR) spectroscopy. Infrared spectra of decalin, tetralin, isotetralin, naphthalene, and dihydronaphthalenes were obtained at room temperature using fluorolube as the infrared medium. The spectra of the three-ring system, anthracene, dihydroanthracene, hexahydroanthracene, and octahydroanthracene was also analyzed using fluorolube. The conclusions obtained from this study were that the infrared spectra of the cyclic olefins and their reaction products were sufficiently unique that if reacted using a high temperature infrared cell that their spectra would be sufficiently unique to determine the types and estimate the quantities of materials present. The work on the infrared analysis stopped at that point because the individual working on the project left the University.

The work using FTIR spectroscopy and cyclic olefins was commenced again in October 1993. The researcher undertaking this task is Jeff Snelling who has a background in chemistry and industrial processing and who is currently a student in chemical engineering.

This quarter was spent teaching Jeff Snelling the operation of the FTIR spectrometer and how to prepare liquid samples using solvents such as carbon disulfide and carbon tetrachloride. Several problems arose such as leaking cells and gaps in the spectral display. The leaking cell was abandoned and the gaps in the spectral display were subsequently remedied.

Future Work

The research planned for next quarter is to develop further the analysis of the solution spectra of the cyclic olefins. The two-ring system using isotetralin and its reaction products will be used. Spectral subtraction will be employed to isolate the different products: tetralin, isotetralin, naphthalene, 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, decalin, and possibly hexahydronaphthalene and octahydronaphthalene. Spectra of mixtures of these compounds will be obtained with a view toward identifying the respective peaks for each compounds out of the mixture. The mixtures will be built from simple mixtures of two components to complex mixtures of five or more components.

The operation and use of a high temperature cell from AABSPEC will be investigated. The cell will first be operated at room temperature and then will be heated and used a higher operating temperatures. Auxiliary equipment needed for operation of the AABSPEC will be put into operating condition.

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