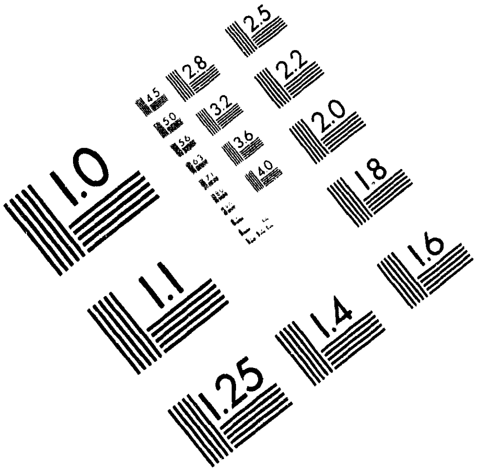

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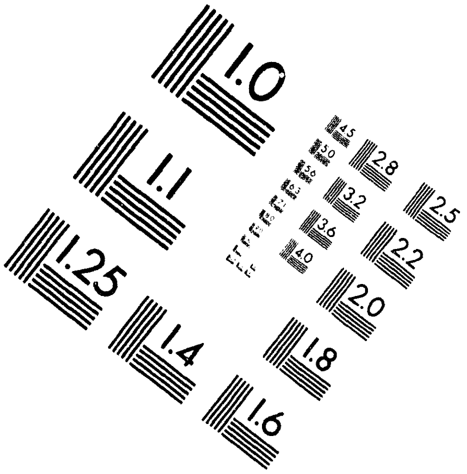

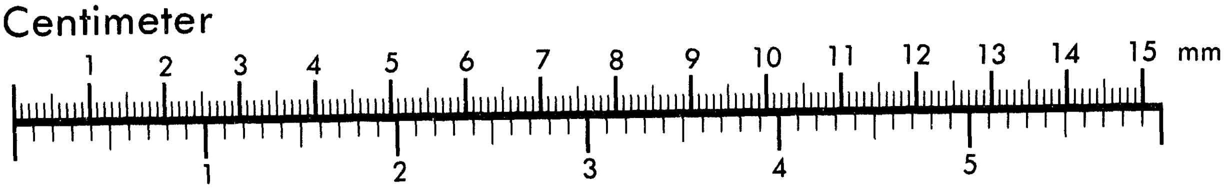

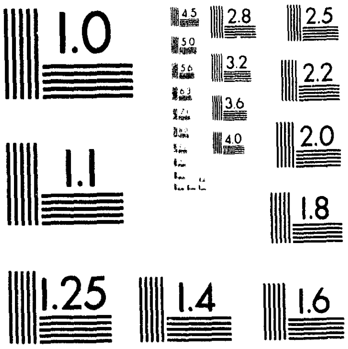

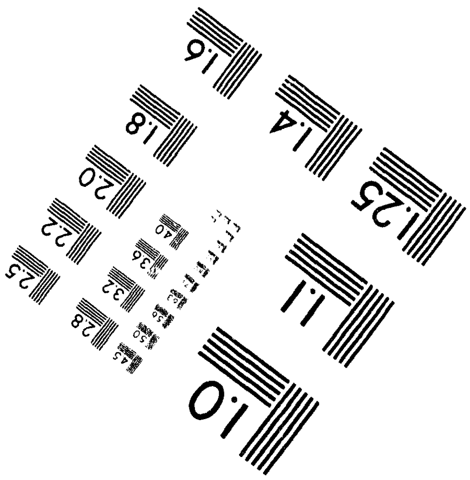

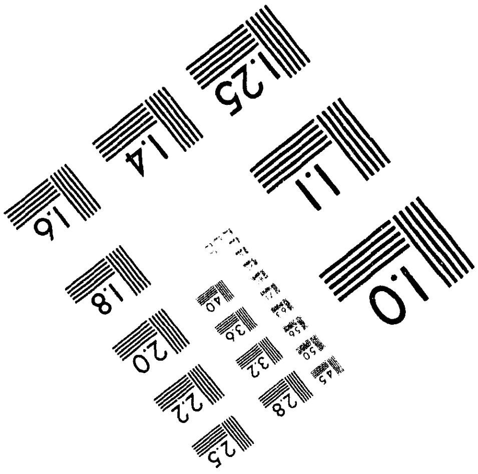

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Low Severity Coal Liquefaction Promoted by Cyclic Olefins

Grant No. DE-FG22-91PC-91281

Quarterly Report
January to March 1994

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Christine W. Curtis
Chemical Engineering Department
Auburn University, AL 36849

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Acknowledgments

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Table of Contents

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

Introduction

Achieving the goal of finding an economically feasible method to utilize coal resources in the production of transportation fuels continues to become more possible. Because of the vast number of avenues being discovered to better the entire process, progress is not only possible, it is probable. By finding different ways of preparing coal prior to liquefaction, of modifying the conditions of the liquefaction reaction and of upgrading the coal liquids from the reaction to a suitable fuel, the most ideal strategy will be found. This study will attempt to provide a valued addition to the fulfillment of this ambition.

Previous research has suggested that using a more effective hydrogen donor solvent in the low severity coal liquefaction reaction improves coal conversion. Bedell and Curtis (1991), as well as Huang and Curtis (1994), showed that cyclic olefins readily donate hydrogen to the low severity liquefaction reaction. Pretreatments of the feed coal both improve contact between coal and the solvent and remove cations that inhibit hydrogen transfer. Shams et al. (1992) used a mild acidic pretreatment to remove a large portion of the calcium in the coal. Hengel and Walker (1984) used an ammonium acetate (NAc) solution to remove the same cations. The effect of these pretreatments in conjunction with the use of cyclic olefins is central to this study.

In order to understand the results of these methods, both independently and combined, a factorial experiment was designed. A four-dimensional experimental matrix (Figure 1) was developed. Each triangular section of the diagram represents a different pretreatment and reaction combination.

Pretreating coal with hydrochloric and sulfurous acid solutions in both water and methanol is compared with pretreating coal using only methanol and with no pretreatment. The effects of these pretreatments on coal liquefaction behavior are contrasted with the ammonium acetate pretreatment. Within each of these, individual reactions are performed with the hydroaromatic 1,2,3,4-tetrahydronaphthalene (tetralin, TET) and the cyclic olefin 1,4,5,8-tetrahydronaphthalene (isotetralin, ISO). The final aspect of the factorial experiment is the comparison of Wyodak subbituminous coal (WY) from the Argonne Premium Sample Bank and Black Thunder subbituminous coal (BT) provided by Amoco. Lower rank coals are known to show greater improvements in coal conversion with pretreatment. Both coals are used for each of the different reactions.

In order to provide legitimacy for the results of the factorial experiment, the matrix is being completed as randomly as conditions will allow. Although two reactions are run simultaneously, no pair of reactors placed into the fluidized sandbath together ever contains the same reactants. This procedure ensures that each run of a specific reaction is a true replicate. At least three trials of each reaction in the matrix are being performed.

After the matrix is complete, the results will be analyzed. After some understanding of the results has been achieved, more reactions will then be attempted. Possible additional reaction conditions include: ammonium acetate pretreatment followed by mild acidic pretreatment, longer reaction times, increased levels of donable hydrogen and changes in reaction temperature and pressure. Changes in parameters that might improve the reaction conversion will be considered. An analysis of the kinetics of the reactions is also planned.

Experimental

Hydrochloric acid used in the pretreatment was provided by Fisher Scientific (37.1%, Reagent A.C.S. grade). Ammonium acetate was also provided by Fisher Scientific (98.1%, HPLC grade). The sulfurous acid was produced by bubbling anhydrous SO_2 through water according to the method and apparatus of Schien et al. (1984) (See Figure 2.). The sulfurous acid aqueous solution will be standardized using the titration method included in the same paper. Because of the delay in producing the sulfurous acid, some randomness in reaction order has been lost.

The mild acidic and ammonium acetate pretreatment methods were performed as detailed in previous reports. Ten grams of undried coal were used for the ammonium acetate pretreatment and five grams for the acid pretreatment. All coal samples both pretreated and untreated, unless otherwise specified, were dried at 22 inches of mercury vacuum for at least 12 hours until they are used. This procedure provides enough dry coal for at least three reactions, but no one pretreated sample was used for all three trials of a single reaction.

For each liquefaction reaction one gram of coal was loaded into a ~25 ml stainless steel tubing bomb microreactor. The reactor charge also included 1.33 g hexadecane (99% purity from Aldrich) and either 0.66 g TET (99% from Aldrich) or 0.66 g ISO (97% purity, recrystallized by M.W. Bedell) for a ratio that provided 1% donable hydrogen. All reactions in the matrix were reacted by agitating them at 350°C and 500 psi hydrogen for 30 minutes.

The coal liquids were then extracted with tetrahydrofuran (THF). The method is described in previous quarterly reports. Conversion is determined by comparing the amount of THF insolubles (insoluble organic matter, IOM) with the feed coal on a moisture and ash-free (maf) basis according to the following equation:

$$\%\ conversion = 1 - \left(\frac{IOM_{maf}}{Feed\ coal_{maf}}\right)$$

The THF was then driven off of the soluble matter, and the solvent-free liquids were weighed to determine recovery.

Results and Discussion

Half of the reactions in the matrix have now been completed. Due to the need to produce and standardize the sulfurous acid, none of the reactions involving sulfurous acid pretreatment have been run. The conversion results for the completed reactions can be seen in Tables 1 and 2. In all but one case, Black Thunder-HCl/H_2O, the ISO proved to be more reactive than TET. After the other four reactions using this combination are complete, the average conversion may be greater with the cyclic olefin. As expected, the best conversion for both coals occurred after HCl/CH_3OH pretreatment. The ammonium acetate pretreatment of the Wyodak coal improved conversion only slightly. Amoco has also provided an SO_2 pretreated Black Thunder. Reactions were performed with this to compare with the future sulfurous acid reactions; 18.4% conversion was achieved for TET and 33.7% for ISO. As the matrix nears completion, more conclusions may be drawn.

The previous problem with recovery has been alleviated. While the range of results are as low as 68.8% and as high as 113.4%, the average recovery has been 90.9%. For those reactions with an unusually low recovery, a fourth reaction will be run, and a reason found for such low recovery.

Summary

With the exception of the sulfurous acid reactions being delayed, every effort has been made to perform a true, random, factorial experiment with each reaction a true replicate of the other two identical to it. By doing so, the effect of each variant should be clearly seen, and methodical errors avoided.

After the initial matrix is completed and the data analyzed, it is likely that new smaller matrices may be developed to observe some of the additional reactions mentioned. The greatest conversion achieved with Wyodak was only 28.5% and for Black Thunder 39.5%. Sulfurous acid pretreatment may prove very effective. If not, other courses of action will be tried to increase conversion. If the sulfurous acid is better than the hydrochloric, this would be quite favorable, since HCl is such a difficult material to use industrially due to the corrosiveness of chlorine.

Select reactions will also be chosen from the matrix to perform a kinetics analysis. This may reveal further information on what factors would increase conversion. It is hoped that these attempts at improving coal conversion may be successful.

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Schein, Daniel B.; Lee, Tracy L.; Hokama, Jane and Zeitlin, Harry "Inexpensive Apparatus for Generating, Standardizing, and Dispensing Sulfurous Acid," *Review of Scientific Instruments*, 988-990, 55(6), 1984.

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Table 1. Coal Conversion for Wyodak Subbituminous From Matrix Reactions

Wyodak									
No Pretreatment		HCl/H_2O only		CH_3OH only		HCl/CH_3OH		NAc Pretreatment	
TET	ISO	TET	ISO	TET	ISO	TET	ISO	TET	ISO
18.7	24.0				21.9	18.8	27.4	15.2	26.6
13.9	22.6				23.9	21.3	28.1	21.8	25.1
16.3	23.5						30.1	20.4	24.3
16.3	**23.4**				**22.9**	**20.1**	**28.5**	**19.1**	**25.3**

Table 2. Coal Conversion for Black Thunder Subbituminous From Matrix Reactions

Black Thunder									
No Pretreatment		HCl/H_2O only		CH_3OH only		HCl/CH_3OH		NAc Pretreatment	
TET	ISO	TET	ISO	TET	ISO	TET	ISO	TET	ISO
17.8	24.1	31.3	27.1	23.0	28.4	15.8	43.9		
17.8	23.7			20.5	23.4	16.5	44.9		
21.7	22.3					14.7	29.7		
19.1	**23.4**	**31.3**	**27.1**	**21.8**	**25.9**	**15.7**	**39.5**		

Figure 1. Four-Dimensional Matrix to Observe Effects of Pretreatment and Cyclic Olefins on Coal Conversion.

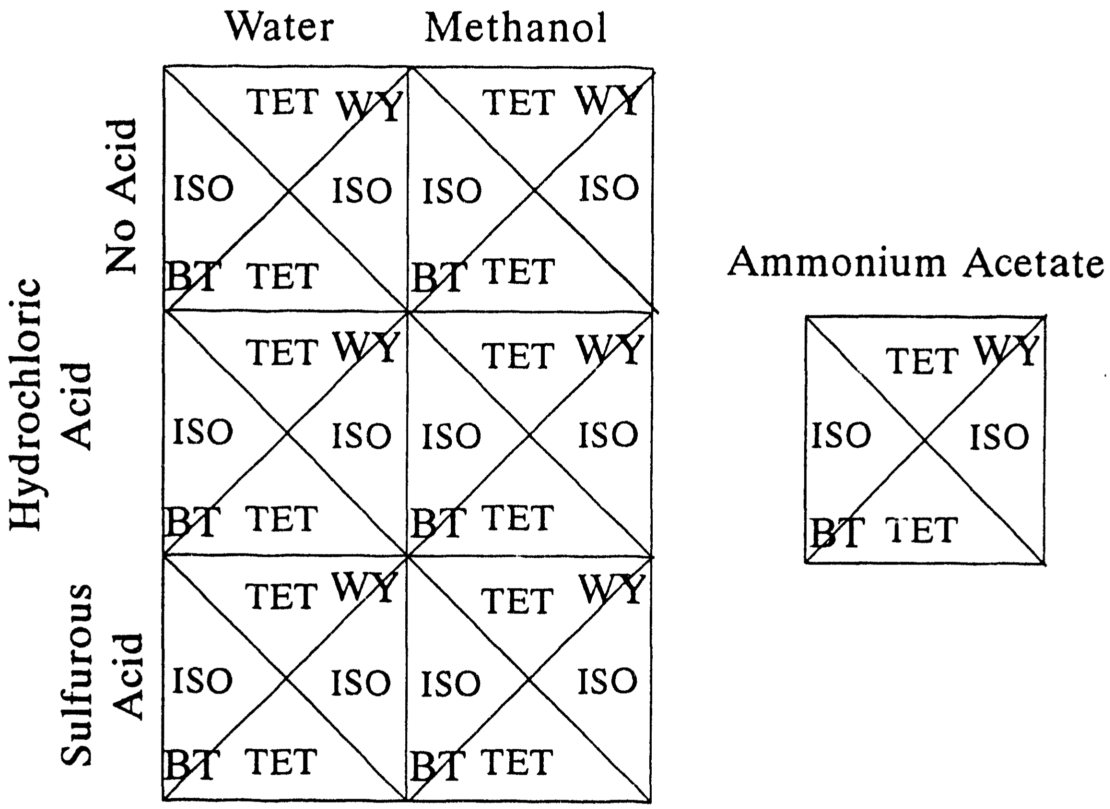
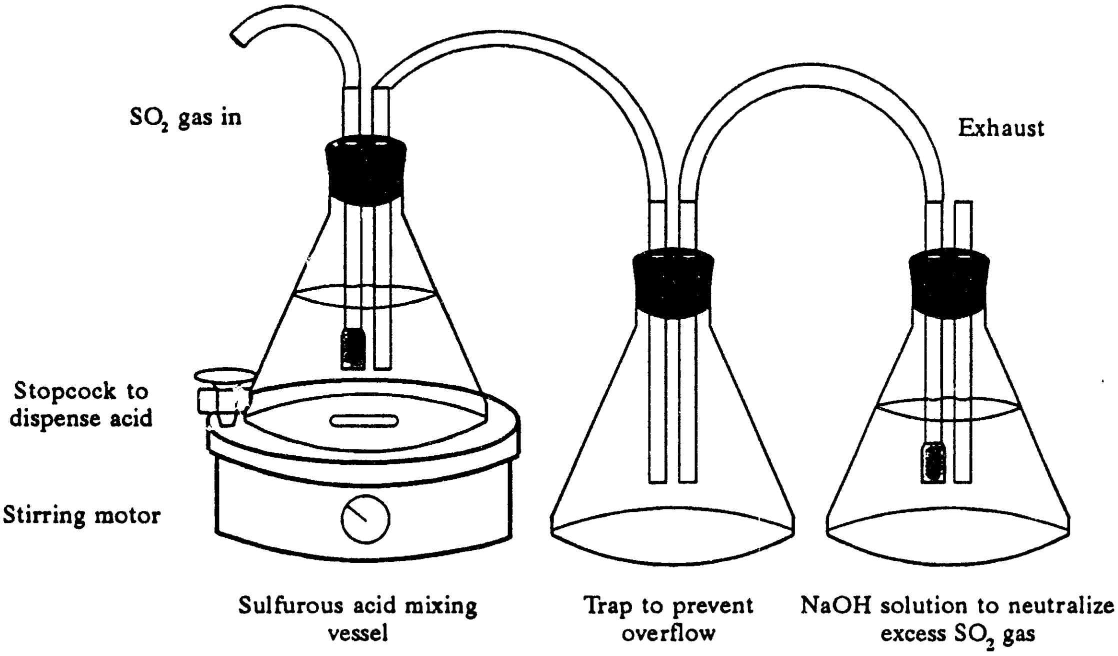


Figure 2. Apparatus for Production of Sulfurous Acid.



APPENDIX A

Calculations

TET and ISO both can give 4 hydrogen atoms. Percent donable hydrogen (%DH) for the solvent is found by solving the equation.

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

M.W. ISO and TET = 132.2

M.W. DH = 4.0

Coal conversion is calculated using the following equation:

$$\%\ conversion = 1 - \frac{(grams\ THF\ insolubles - grams\ ash)}{(grams\ coal\ charged - grams\ H_2O_{in\ coal} - grams\ ash_{in\ coal})}$$

grams ash = 0.0631(Total weight of coal) [for Wyodak]

0.0540(Total weight of coal) [for Black Thunder]

grams $H_2O_{in\ coal}$ = 0 [for feed coal *dried* in the vacuum oven]

APPENDIX B

Procedure for Production of Sulfurous Acid

1. Prepare apparatus, as shown in Figure 2, utilizing three Erlenmeyer flasks. The flask used for holding the sulfurous acid should have a stopcock attached to bottom of it.
2. Fill the flask with the sample vent with distilled water. (400 ml was used for this experiment.) Prepare concentrated NaOH solution (here, 400 ml of 2M) to neutralize excess SO_2 gas.
3. Connect hose from the SO_2 source to a tube with a sintered glass frit immersed in distilled water. Another sintered gas frit is used to bubble the exhaust gas through concentrated NaOH. Only these two should be immersed. All other glass tubes should be above the liquid level.
4. Place the flask with the sample vent on a stirrer.
5. Open the SO_2 valve to about 5 psi and allow the gas flow to continue for an hour, stirring it continuously in order for it to reach equilibrium. Be aware of overpressure in the system. Unless stoppers are clamped down, they may pop off.
6. After equilibrium has been reached, a sample may be drawn off and standardized. This standardization procedure will be detailed in the next report.

Part II.

Fourier Transform Infrared Spectroscopy
Current Work

Research has progressed in the area of Fourier Transform infrared spectroscopy during this quarter. The objective of this work is to determine the kinetics of reaction of isotetralin at high temperatures and pressures. To this end, techniques must be developed to analyze individual products produced which are present in the reaction product mixture. Spectral subtraction is the method of choice. This quarter combinations of three products typically produced from isotetralin were used in spectral subtraction.

When isotetralin reacts at elevated temperature, isotetralin quickly converts to tetralin and naphthalene when a nitrogen atmosphere is present, and to tetralin, naphthalene and decalin when a hydrogen atmosphere is present. The partially saturated dihyronaphthalenes, either 1,2 or 1,4, are produced when the appropriate temperature is used. Each of these compounds has some unique spectral characteristic although substantial overlap occurs among most of the compounds.

The experimental difficulties experienced last quarter with the spectral gaps have been solved as has the leaking cell. This quarter preparation has begun for utilization of the AABSPEC high temperature cell. The high temperature cell holder has been installed. Its use will not interfere with the routine operation of the spectrometer. The cooling bath required for use with the high temperature cell has been tested with water to 4°C. Carbon tetrachloride has replaced carbon disulfide as the solvent of choice for evaluating the hydroaromatics and cyclic olefins at room temperature.

Experimental

The first experimental work was to determine individual spectra of tetralin, isotetralin, decalin and naphthalene. These spectra of three volume percent reactant were used to assign the peaks which were unique to the individual compounds. Then mixture spectra of tetralin, decalin and naphthalene were obtained first in pairs and then as a tertiary mixture. The peaks coming from the individual components were identified in the mixture. Then spectral subtraction was used to determine the contribution of the individual components to the absorbances of the mixture. The subtraction routine provided by the Nicolet 5SXC was utilized.

Qualitatively, the binary mixtures showed increased absorbances where the two component absorbances overlapped. However, the initial attempts at quantitation indicated that absorbance peak heights did not add linearly. The areas under the individual component peaks did not sum to the area under the mixture peaks.

Nicolet indicated that with structurally similar chemical species, peak heights typically do not add linearly because of spectral interferences. However, the difference between the sum of the individual peak heights and that of the mixture was substantially different, indicating that perhaps an error in experimentation may have occurred. A series of individual solutions was prepared to verify the result. This work is currently in progress.

Future Work

As the high temperature cell requires a cooling medium at a temperature of -20°C, the cooling system will be tested for lower temperature operation using a commercial automotive antifreeze preparation. It is proposed to evaluate a quantitation software package from the instrument vendor for use in absorbance peak analysis. The current work with mixtures will be extended to 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, and possibly hexahydronaphthalene and octahydronaphthalene.

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