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Low Severity Coal Liquefaction Promoted by Cyclic Olefins

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MASTER

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Abstract

The goal of this research is to develop a methodology for analyzing the reactivity of cyclic olefins in situ in a high temperature and high pressure infrared cell. The reactivities of naphthalene, decalin, tetralin, isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene have been studied at 230 °C under ambient pressure and under 500 psig blankets of both nitrogen and hydrogen.

Executive Summary

The goal of this research is to develop a methodology for analyzing the reactivity of cyclic olefins in situ in a high temperature and high pressure infrared cell. The problem of loss of interferometer signal which plagued operation during Summer quarter, 1996 has been resolved. The reactivities of naphthalene, decalin, tetralin, isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene have been studied at 230 °C under ambient pressure and under 500 psig blankets of both nitrogen and hydrogen. Naphthalene, decalin, tetralin and 1,2-dihydronaphthalene have been shown to be stable under these conditions, whereas isotetralin and 1,4-dihydronaphthalene react. In future work, the stability studies will be extended to 350 °C using a perfluoroether obtained from DuPont.

High Temperature Infrared Analysis of Cyclic Olefins

FTIR at Combined Elevated Temperatures and Pressures

Introduction

The goal of this research is to develop a methodology for analyzing the reactivity of cyclic olefins in situ in a high temperature and high pressure infrared cell. Cyclic olefins, such as 1,4,5,8-tetrahydronaphthalene (isotetralin) and 1,4,5,8,9,10-hexahydroanthracene (HHA), are highly reactive donor compounds that readily donate their hydrogen to coal and model acceptors when heated to temperatures of 200 °C and above. These donors are active donors in the low severity liquefaction of coal at 350 °C as shown in the research performed in this project. The infrared studies are being performed in a high temperature infrared cell that was obtained from AABSPEC. Modifications to that cell have been made and have been reported in previous progress reports.

The useful temperature range of the high temperature infrared cell has been extended to 230 °C through the use of a high-boiling perfluorocarbon solvent. The solvent used was an Air Products and Chemicals Company proprietary product, trade named Multifluor APF-240. Solubilities of aromatics and cyclic olefins are quite low in APF-240, usually less than 0.1 wt% at room temperature, but were found to be a strong function of temperature, increasing markedly when the mixtures were heated to 65°C. High temperature infrared analyses have been performed using tetralin, isotetralin, decalin, naphthalene, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene. Stability studies have shown that naphthalene was quite stable at

temperatures up to 230 °C, as were tetralin, decalin and 1,2-dihydronaphthalene. High temperature FTIR analysis showed that isotetralin and 1,4-dihydronaphthalene reacted at elevated temperatures forming tetralin and 1,2-dihydronaphthalene, respectively.

The AABSPEC cell used in this research was modified to be able to handle atmospheres of 500 psig (at elevated temperatures) of N₂ and H₂. The research performed this quarter included high temperature and pressure studies using both nitrogen and hydrogen.

Results and Discussion

Resolution of the Interferometer Signal Loss Problem

The problem of loss of interferometer signal which plagued operation during Summer quarter, 1996 has been resolved. As noted previously, the interferometer was thought to be functioning properly, and the high temperature cell was thought to be the source of the problem. At the suggestion of the cell manufacturer, the cell was disassembled and inspected. A brown residue was observed on the sample window. The residue had been obscuring the optical path. This heavy tar-like precipitate was thought to be decomposition products from the high temperature reactions carried out in the cell. The cell window was cleaned and the cell reassembled. The interferometer signal rebounded and no further problems with loss of signal were encountered. Periodic cleaning of the window in contact with the sample is indicated. The extension of the current work to 350° C may necessitate even more frequent cleaning.

CURRENT WORK

With the loss of signal problem resolved, the stability studies were resumed. The work for the 230° C portion of this project was completed. The results of the ambient pressure studies, as well as the 500 psig nitrogen blanket studies for naphthalene and decalin were reported previously. The 500 psig nitrogen testing was extended to tetralin, isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene. 500 psig hydrogen blanket stability studies were conducted for naphthalene, decalin, tetralin, isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene. The results from these studies are presented in the following discussion and are illustrated with FTIR spectra taken at the specified temperatures with the specified gaseous atmospheres and pressures.

500 psig Nitrogen Blanket Tetralin Stability Study

Figures 1 and 2 present the initial scans for tetralin at 65° C and 230° C. Figure 3 presents the final scan at 230 °C. The peak height ratios in the three scans are virtually identical. The loss of absorbance strength at 230° C was thought to be caused by volatilization of the sample into the vapor space above the reactor.

500 psig Nitrogen Blanket Isotetralin Stability Study

Figures 4 and 5 present the initial scans for isotetralin at 65° C and 230° C, respectively. Figure 6 presents the final scan at 230° C. In the case of isotetralin, not only was there a loss of absorbance strength due to volatilization, but the peak height ratio changed as well. While these changes are thought to be caused by some reaction having taken place, a detailed spectral interpretation has not yet been performed.

500 psig Nitrogen Blanket Decalin Stability Study

The 500 psig nitrogen blanket cis-decalin stability study was repeated because of a peak which emerged around 3070 cm^{-1} in the previously reported test. Figures 7 and 8 present the initial scans for cis-decalin at 65°C and 230°C , respectively. Figure 9 presents the final scan at 230°C . No peak emerged around 3070 cm^{-1} in this test. The peak which emerged in the previous test was thought to be caused by an impurity.

500 psig Nitrogen Blanket 1,2-Dihydronaphthalene Stability Study

Figures 10 and 11 present the initial scans for 1,2-dihydronaphthalene at 65°C and 230°C , respectively. Figure 12 presents the final scan at 230°C . 1,2-Dihydronaphthalene appeared to be stable under these conditions.

500 psig Nitrogen Blanket 1,4-Dihydronaphthalene Stability Study

Figures 13 and 14 present the initial scans for 1,4-dihydronaphthalene at 65°C and 230°C , respectively. Figure 15 presents the final scan at 230°C . The peak height ratios were observed to change under these conditions.

500 psig Hydrogen Blanket Naphthalene Stability Study

Figures 16 and 17 present the initial scans for naphthalene at 65°C and 230°C , respectively. Figure 18 presents the final scan at 230°C . The two most prominent peaks merged at higher temperatures and there was some loss of definition in the shoulder peaks. These effects were noted earlier in the ambient pressure and 500 psig nitrogen blanket studies.

500 psig Hydrogen Blanket Decalin Stability Study

Figures 19 and 20 present the initial scans for cis-decalin at 65°C and 230°C . Figure 21 presents the final scan at 230°C . cis-Decalin appeared to be stable under these conditions.

500 psig Hydrogen Blanket Tetralin Stability Study

Figures 22 and 23 present the initial scans for tetralin at 65° C and 230° C, respectively. Figure 24 presents the final scan at 230° C. A loss of definition in the peak around 2890 cm⁻¹ and a change in the peak height ratios for the peaks at 2870 cm⁻¹ and 2850 cm⁻¹ were noted.

500 psig Hydrogen Blanket Isotetralin Stability Study

Figures 25 and 26 present the initial scans for isotetralin at 65° C and 230° C, respectively. Figure 27 presents the final scan at 230° C. The peak height ratios appeared to be changing, but most of the hydrocarbons vaporized out of the reactor.

500 psig Hydrogen Blanket 1,2-Dihydronaphthalene Stability Study

Figures 28 and 29 present the initial scans for 1,2-dihydronaphthalene at 65° C and 230° C, respectively. Figure 30 presents the final scan at 230° C. A change in the peaks above 3000 cm⁻¹ was observed, but those below 3000 cm⁻¹ appeared stable.

500 psig Hydrogen Blanket 1,4-Dihydronaphthalene Stability Study

Figures 31 and 32 present the initial scans for 1,4-dihydronaphthalene at 65° C and 230° C, respectively. Figure 33 presents the final scan at 230° C. Again, a loss of definition of the peaks was noticed. Some of this loss may have been caused by reaction, but the primary effect here appeared to be vaporization.

GC Analysis of Reaction Products

Since such a great effort was directed to trouble-shooting the AABSPEC cell and collecting data when it was functional, little time was left for GC methods development. Another problem which arose was the malfunctioning of the analytical balance used in the quantitative analyses. Our electronics support department repaired and calibrated the balance, but it still

appeared to be malfunctioning.

The 60 meter column was installed on the chromatograph. Although quantitative analyses could not be performed, some qualitative tests were conducted. The elution times of naphthalene, decalin, tetralin, isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene have been determined using the new column and the instrument parameters developed to date. Reaction products have been injected to determine whether they were mixtures or just unaltered reactants. Because the elution times of reactants and potential products are so close together, and because the concentration of hydrocarbons in the APF-240 are so low, it was not possible to tell if two peaks were emerging in the reaction products. Adjustments to the attenuation and sensitivity of the instrument improved the baseline separation, and it was hoped this and possible further refinements will allow for more accurate determinations.

Conclusion

FUTURE WORK

A large portion of Winter quarter, 1997 will be devoted to the preparation of a report for publication covering the work up to 230° C. Spectral interpretation will be necessary, as will quantitative GC work. A properly functioning analytical balance with an accuracy of 0.01 mg will be required for this work. The internal standard method for determining the concentrations of reactions products will be developed into a routine. In future research, the stability studies will be extended to 350° C using a perfluorether obtained from DuPont. The linear region of the absorbance vs. concentration curves will be determined. It may be necessary to use the least squares and/or deconvolution software packages in connection with this determination. The kinetics of the reaction of isotetralin at elevated temperatures and pressures will be determined.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17

Figure 18

Figure 19

Figure 20

Figure 21

Figure 22

Figure 23

Figure 24

Figure 25

Figure 26

Figure 27

Figure 28

Figure 29

Figure 30

Figure 31