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Mild Acidic Pretreatment to Enhance Low Severity Coal Liquefaction Promoted By Cyclic Olefins

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Introduction

The research performed this quarter involved revising a manuscript after review. The manuscript was entitled "Mild Acidic Pretreatment to Enhance Low Severity Coal Liquefaction Promoted By Cyclic Olefins" by Thomas A. Beasley, Christine W. Curtis and James N. Hool. The manuscript has recently been accepted by *Energy and Fuels*.

Research using high temperature infrared of cyclic olefins progressed well during this quarter. Several fluorinated solvents were found that provide a high temperature medium for isotetralin and its aromatic and aliphatic analogues.

High Temperature Infrared Analysis of Cyclic Olefins

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.¹⁻³ 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.

During this quarter 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 were 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. Spectra have been obtained of n-hexadecane and naphthalene at temperatures of 65, 100, 125, 150, 175, 200 and 230 °C. This demonstration of the safe operation of the high temperature IR cell and the acquisition of spectra at elevated temperatures paves the way for kinetic studies of the hydrogen donor capability of isotetralin. A perfluoroether has been obtained from Dupont which should extend the useful temperature range of the high temperature IR cell to 350 °C.

Research Performed During this Quarter

The quarter began with a continuation in training the graduate student working on this project in the use of Windows and the new software packages that had been purchased for the FTIR. The training in basic operations is virtually complete and the day-to-day operations of the spectrometer are now a matter of routine. Concurrently, the search for a suitable solvent to extend the useful temperature range of the high temperature IR cell continued.

Perfluorocarbon Liquids. Dr. W.E. Hill of Auburn University's Chemistry Department suggested the use of perfluorocarbon solvent. A U.S. manufacturer of perfluorocarbon solvents was located. Dr. Frank Schweighardt of Air Products and Chemical company provided a sample of Multifluor APF-240, a perfluorocarbon liquid with a boiling point of 240 °C. Scans of the neat liquid at room temperature, 50, 100, 150, 200 and 230 °C showed good IR transparency throughout the region of interest (3100 to 2700 cm^{-1}) in this study. A high operational temperature of 230 °C allows a margin of safety of 10 °C below the boiling point and has thus been taken as the upper temperature limit for work with this solvent. The scans also revealed the presence of residual hydrocarbons in the sample cell. Flushing the cell several times with carbon

tetrachloride and rescanning indicated in the daily procedure, a description of which can be found in the appendix. Dr. Schweighardt also cautioned about the low solubility of hydrocarbons in perfluorocarbon solvents.

Solubility Tests. Room temperature solubility test confirmed very low solubilities for naphthalene, decalin and tetralin with each being less than 0.1 wt% soluble in APF-240. The naphthalene/APF-240 mixture was heated on a hot plate and naphthalene was observed to evaporate out of the mixture. It was not noted whether the naphthalene crystal dissolved. The mixture was injected into the sample cell. No peaks were detectable upon scanning. A more careful heating experiment was devised to observe the solubility of naphthalene in APF-240. A closely monitored careful heating of a naphthalene crystal (0.1 wt%) in APF-240 showed that the solubility was a strong function of temperature. The crystal dissolved at about 60 °C. When allowed to cool to room temperature, the naphthalene crystallized out of solution. If the solution was placed in an oven at 65 °C, however, the naphthalene remained in solution. For this reason, 65 °C was taken as the lower temperature limit for this work.

It was thought that a chlorinated hydrocarbon might exhibit greater solubility in APF-240. A 0.1 wt% mixture of trichloroethane in APF-240 was prepared. No C-H peaks were detectable for this mixture. Increasing the concentration of 1 wt% gave some weak peaks. Increasing the concentration of 10 wt% gave peaks of sufficient strength to be readily observable; however, this concentration was outside the normal concentration range for this study. It was reasoned that n-hexadecane might give noticeable hydrocarbon peaks at lower concentration. A 0.1 wt% mixture of n-hexadecane and APF-240 was prepared. Scanning over the temperature range of 65 to 230 °C demonstrated observable C-H peaks within the working concentrations. At that point, the

focus was shifted back to naphthalene. Figures I and II present the spectra of n-hexadecane at 65 °C and 230 °C, respectively.

Spectra of Naphthalene at Elevated Temperatures. A 0.1 wt% solution of naphthalene in APF-240 was prepared. The solution was scanned at 65, 100, 125, 150, 175, 200 and 230 °C. The scan at 230 °C was quite similar in appearance to that at 65 °C, confirming the thermal stability of naphthalene over this temperature range. Two spectral features were worthy of note, however. One was the near disappearance of the shoulder at 3096 cm^{-1} with increasing temperature. The merging of the peaks at 3072 and 3058 cm^{-1} , which are distinct at 65 °C but merged into one peak at about 3062 cm^{-1} at 230 °C, as shown in Figures III and IV. The interpretation of these spectral changes is currently on going. It is noted at this time that this was a temperature effect rather than a reaction because when the sample was returned to room temperature, the shape of the spectra generated returned to that of Figure III.

Future Work

The demonstration of the safe operation of the FTIR and the acquisition of spectra at elevated temperature marked a major advance towards the realization of kinetic studies of cyclic olefin hydrogen donors. Fall quarter work will begin with stability studies which will be conducted on naphthalene, tetralin, isotetralin and decalin. The linear region of the absorbance versus concentration curves at elevated temperatures will be determined. It may be necessary to use the least squares and/or deconvolution software packages in connection with this determination. Some effort will be directed to increasing the signal to noise ratio in the spectra. It may be possible to post-process the noise with the existing software.

Additionally, the sample cell will be mounted in a holder which can be secured to the bench reproducibly to insure that the optical path remains the same from sample to sample. A sample of a perfluoroether has been obtained from Dupont which should extend the useful temperature range of the high temperature IR cell to 350 °C.

References

1. Bedell, M.W., Curtis, C.W., 1991, "The Chemistry and Reactivity of Cyclic Olefins as Donors in Coal Liquefaction," *Energy and Fuels*, 5, 469.
2. Bedell, M.W.; Curtis, C.W.; Hool, J.N., 1993, Comparison of Hydrogen Transfer from Cyclic Olefins and Hydroaromatic Donors Under Thermal and Catalytic Liquefaction Conditions," *Energy and Fuels*, 7, 200.
3. Bedell, M.W.; Curtis, C.W.; Hool J.N., 1994, "Reactivity of Argonne Coals in the Presence of Cyclic Olefins and Other Donors," *Fuel Processing Technology*, 34, 1.
4. Beasley, T.A., Curtis, C.W.; Hool, J.N., 1995, "Mild Acidic Pretreatment to Enhance Low Severity Coal Liquefaction Promoted By Cyclic Olefins," in press *Energy and Fuels*.

APPENDIX

A Routine for Obtaining High Temperature Spectra

1. Check IR source coolant and nitrogen purge flows.
2. Scan empty spectrometer as background.
3. Scan empty spectrometer as sample. This should give a straight line.
4. Flush cell thoroughly with carbon tetrachloride, trichloroethane, perchloroethylene or similar solvent.
5. Mount cell and attach coolant lines, power cord and thermocouple.
6. Scan empty cell as sample. This provides a check for residual hydrocarbons.
7. Scan empty cell as background.

8. Scan empty cell as sample. This should give a straight line.
9. Fill cell with neat solvent and remount as in Step 4.
10. Scan neat solvent as sample. This is a check for impurities.
11. Scan neat solvent as background.
12. Scan neat solvent as sample. This should give a straight line.
13. Place cell in oven at 65 °C.
14. Place a glass pipette in the oven at 65 °C.
15. Sample preparation
 - a. Solid sample handling (naphthalene, isotetralin)
 - i. Weigh the appropriate amount of solid.
 - ii. Pipette the appropriate amount of solvent.
 - iii. Reweigh to determine the mass of solvent used.
 - iv. Keep in the oven at 65 °C until ready to use
 - v. Shaking may be necessary to achieve dissolution.
 - b. Liquid sample handling (tetralin, decalin)
 - i. Pipette the appropriate amount of solvent.
 - ii. Weigh the solvent.
 - iii. Inject fractions of a microliter quantities of liquid sample into the bottle containing the solvent.
 - iv. Reweigh to determine the mass of liquid sample used.
 - v. Keep in the oven at 65 °C until ready to use.
 - vi. Shaking may be necessary to achieve dissolution.

16. Remove cell, pipette and sample from the oven.
17. Fill the cell with sample solution using the hot pipette.
18. Mount cell as the Step 5.
19. Scan sample using neat solvent as background.

Figure I. IR Spectrum of n-Hexadecane at 65 °C

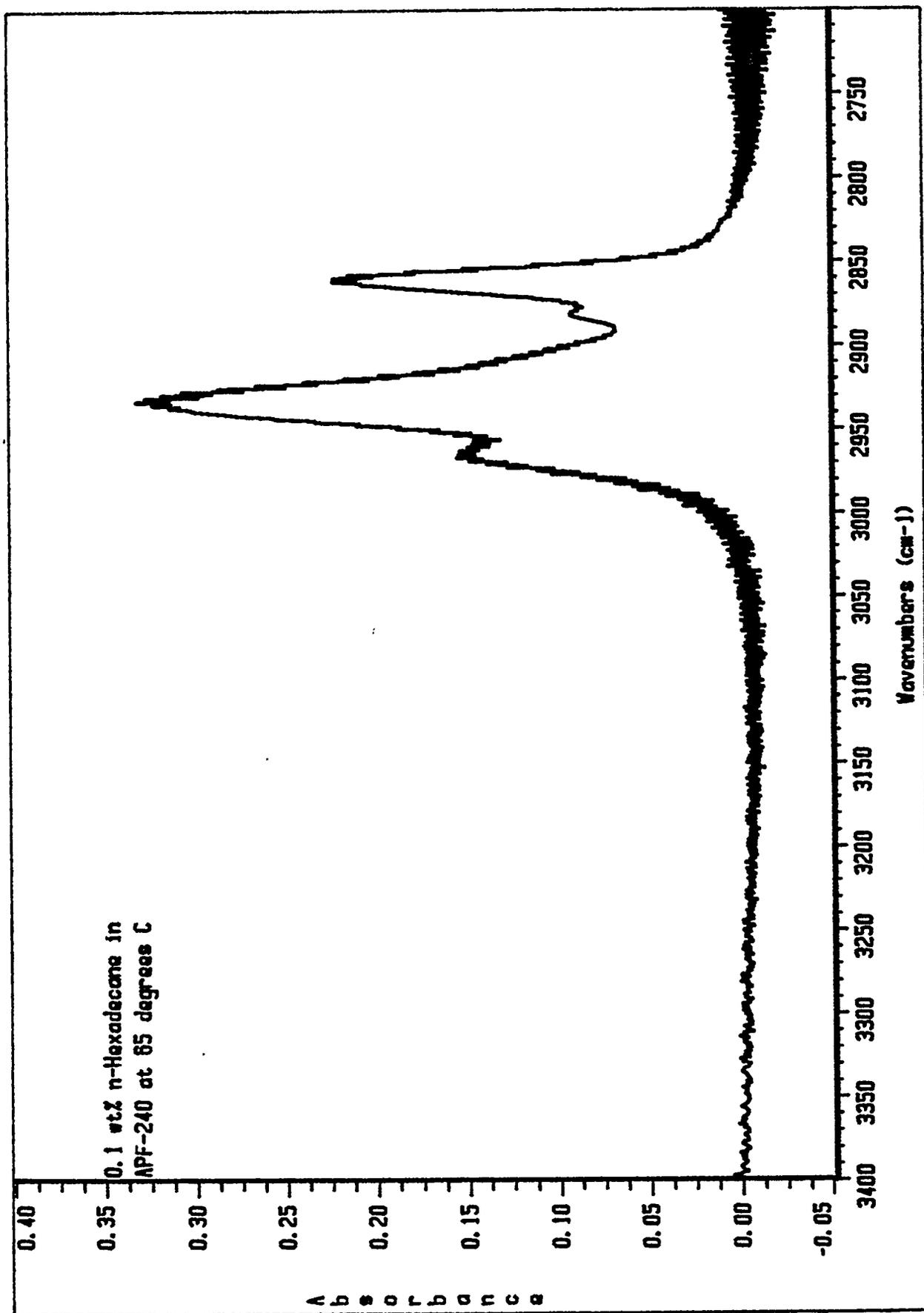


Figure II. IR Spectrum of n-Hexadecane at 230 °C

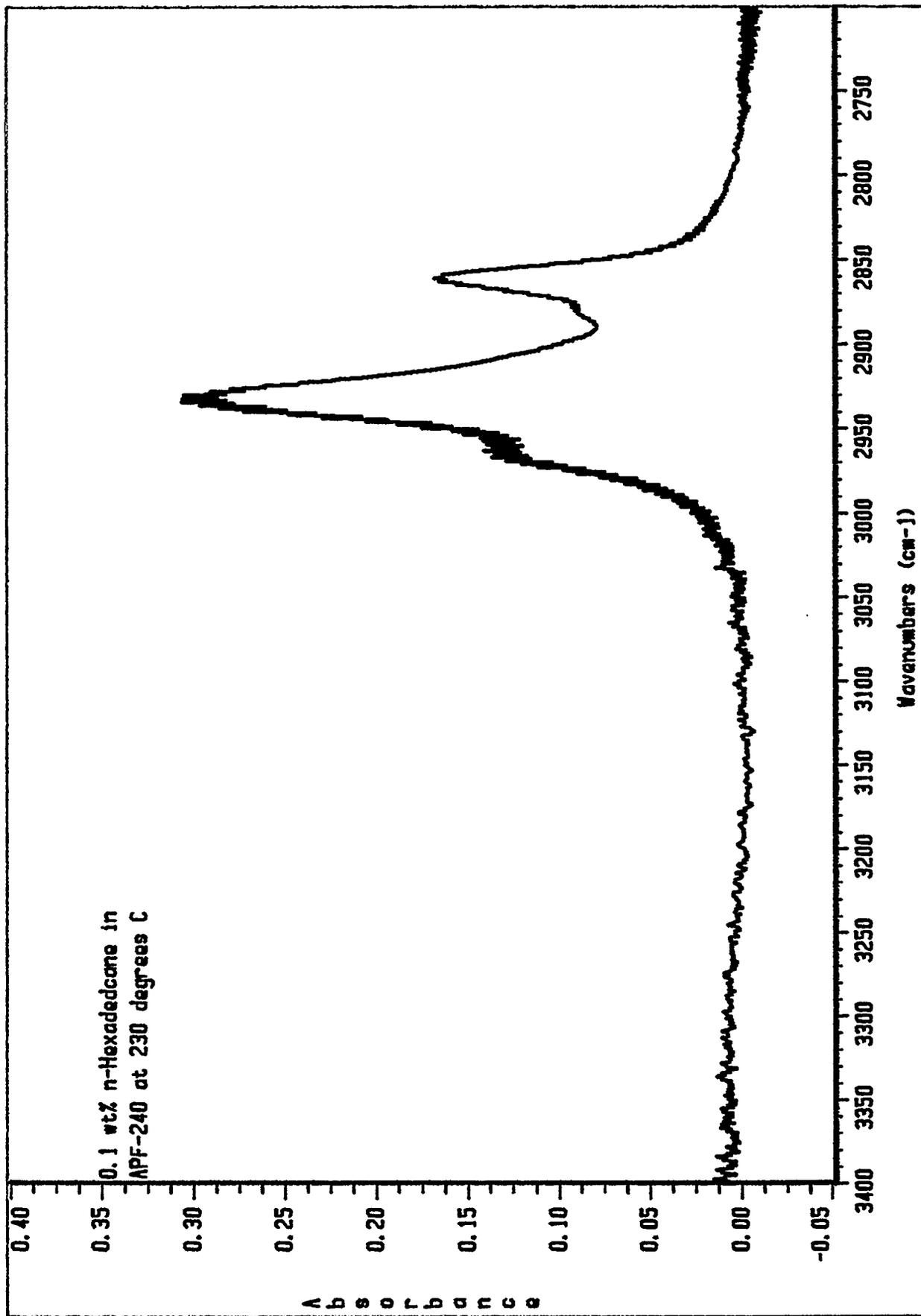


Figure III. IR Spectrum of Naphthalene at 65 °C

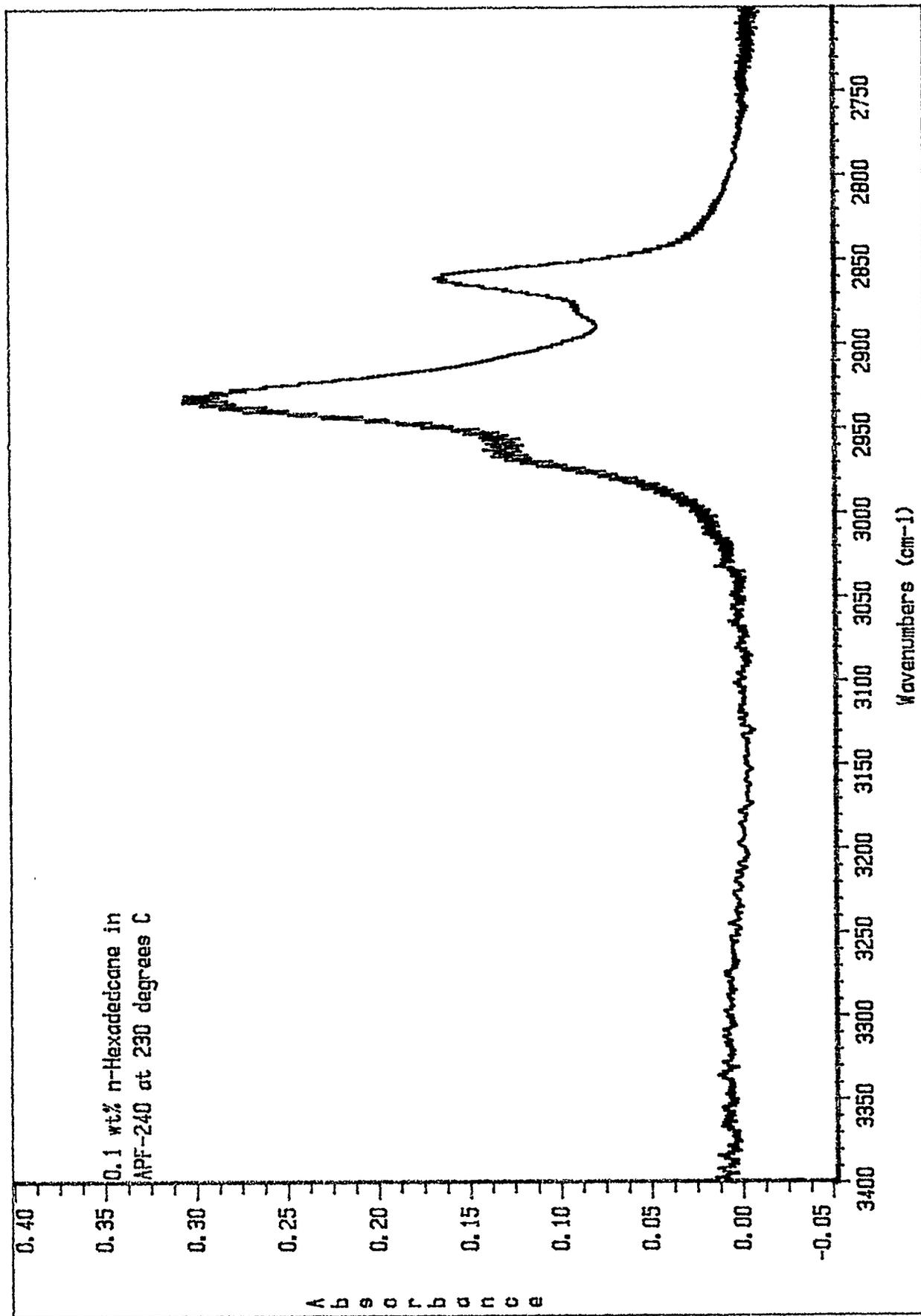


Figure IV. IR Spectrum of Naphthalene at 230 °C

