DE-AC22-91PC91042-F1

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DOE/PC/91042--T5-Vol.1

EFFECTS OF LOW-TEMPERATURE CATALYTIC PRETREATMENTS ON COAL STRUCTURE AND REACTIVITY IN LIQUEFACTION

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Vol. 1: Effects of Solvents, Catalysts and Temperature Conditions on Conversion and Structural Changes of Low-Rank Coals

Lili Huang, Harold H. Schobert and Chunshan Song

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Department of Materials Science and Engineering
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University Park, Pennsylvania, PA 16802

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ACKNOWLEDGEMENTS

This project was supported by the U.S. Department of Energy, Pittsburgh Energy Technology Center, in Advanced Coal Research Program. Dr. M.A. Nowak is DOE/PETC Project Manager; Dr. M. J. Baird was the project manager during the first three quarterly periods. Dr. H.H. Schobert, Dr. C. Song and Dr. P.G. Hatcher are the Co-Principal Investigators at The Pennsylvania State University.

The principal investigators and the authors wish to express their appreciation to U.S. DOE for financial support, to Drs. M.A. Nowak, M. J. Baird, S. Lee, and E. B. Klunder of DOE/PETC for their support and helpful discussion. The authors would also like to thank Dr. A. Davis and Mr. D. Glick of PSU for providing coal samples and data from DOE/Penn State Coal Sample Bank, Mr. J. McConnie for assistance in some liquefaction experiments, Dr. L. Hou for assistance in solid-state NMR analysis, and Mr. R.M. Copenhaver for the fabrication of tubing bomb reactors.

ABSTRACT

The main objectives of this project were to study the effects of low-temperature pretreatments on coal structure and their impacts on subsequent liquefaction. The effects of pretreatment temperatures, catalyst type, coal rank, and influence of solvent were examined. Specific objectives were to identify the basic changes in coal structure induced by catalytic and thermal pretreatments, and to determine the reactivity of the catalytically and thermally treated coals for liquefaction.

In the original project management plan it was indicated that six coals would be used for the study. These were to include two each of bituminous, subbituminous, and lignite rank. For convenience in executing the experimental work, two parallel efforts were conducted. The first involved the two lignites and one subbituminous coal; and the second, the two bituminous coals and the remaining subbituminous coal. This Volume presents the results of the first portion of the work, studies on two lignites and one subbituminous coal. The remaining work accomplished under this project will be described and discussed in Volume 2 of this report.

The objective of this portion of the project was to determine and compare the effects of solvents, catalysts and reaction conditions on coal liquefaction. Specifically, the improvements of reaction conversion, product distribution, as well as the structural changes in the coals and coal-derived products were examined. This study targeted at promoting hydrogenation of the coal-derived radicals, generated during thermal cleavage of chemical bonds, by using a good hydrogen donor-solvent and an effective catalyst. Attempts were also made in efforts to match the formation and hydrogenation of the free radicals and thus to prevent retrogressive reaction.

The low-rank coals investigated were a Texas subbituminous C, a Montana subbituminous B and a North Dakota lignitic coal. Tetralin, decalin, 1-methylnaphthalene, and Wilsonville middle distillate (WIMD) were used as reaction solvents. Ammonium tetrathiomolybdate (ATTM) was the catalyst precursor. Liquefaction was conducted in microautoclaves at temperatures ranging from 250°C to 450°C under single-staged, temperature-staged and temperature-programmed conditions. The reaction time was found to be optimum at 30 minutes.

The study of reaction conditions found that the temperature-staged and temperature-programmed conditions, which are designed to balance the formation and hydrogenation of free radicals, were advantageous over the single-staged condition, especially for the coals that were less reactive. The beneficial effects of these two conditions relied on both physical processes and chemical processes related to solvents and catalysts. For a more reactive coal, such as the Texas subbituminous, the single-staged condition was sufficient.

In-depth investigations of the effects of solvents and catalyst revealed some intriguing findings. Catalyst impregnation methods were examined for improved catalyst performance. However, it was seen that the effectiveness of the catalyst is not quite sensitive to the impregnation methods, which were swelling, incipient wetness and slurrying. In other words, the liquefaction conversion was not profoundly affected by the method used to load the catalyst on the coals.

In the absence of the catalyst, the donor solvent appeared to be quite efficient in terms of obtaining high conversions and desirable product distributions, particularly at temperatures of 350°C and higher. In the reaction of the Texas subbituminous coal, over

90% conversion can be achieved with tetralin, compared with 50% when no solvent was used. The non-donor solvent also showed a slightly beneficial effect on the conversion, which may be related to its ability to dissolve free radicals and thus to reduce retrogressive reactions. In the presence of the ATTM-derived catalyst, however, the solvent (including donor-solvent and non-donor solvent) effects were diminished for the Texas subbituminous coal at temperatures of 400°C and lower, suggesting that the catalyst has a much stronger effect on the liquefaction. However, for the Montana subbituminous and North Dakota lignitic coals, which were less convertible, the solvent provided extra conversions in the catalytic reactions. It should be emphasized that, at 450°C, retrogressive reactions took place. The catalyst can reduce them, but only to a small extent. The best approach is to employ a donor solvent, which can almost prevent them.

Liquefaction products, such as gases, oil, asphaltene and preasphaltene, as well as reaction residues, were characterized by gas chromatography, gas chromatography/mass spectrometry, solid-state ^{13}C NMR and FTIR. The total gas produced was found to be a function of temperature. Neither the solvents nor the catalyst has any remarkable influences on it. The oils were determined to contain mainly long-chain aliphatics unless a donor solvent or a catalyst was added, when a pronounced amount of aromatic compounds were observed in the chromatograms. Analysis of the residues, asphaltenes and preasphaltenes by NMR and FTIR suggested that the removal of aliphatic carbons from a coal was relatively easy. It may be fulfilled by conducting liquefaction at a proper temperature. The solvents and the catalyst did not show strong effects on it. However, the removal of the aromatic carbons from a coal matrix highly depended on the use of solvent and catalyst. In non-catalytic reactions, the donor solvent is indispensable in order to remove a decent amount of aromatic carbons. Whereas in catalytic reactions, the solvent can be replaced by the catalyst for a coal which is easy to convert, but not for a coal which is difficult to convert. In the characterization of products and residues, retrogressive reactions were again observed at 450°C, and the best way to prevent them was to use a donor solvent.

Comparing the effects of solvents, catalyst, catalyst impregnation methods, and reaction conditions, it is concluded that the inherent characteristics of a coal determine the extent of liquefaction. The employment of a donor solvent or a catalyst can significantly improve conversions and product distributions. Proper reaction conditions, meaning single-staged, temperature-staged and temperature-programmed, can also enhance conversions, but only to limited extents. The impregnation methods, compared with others, seem to have trivial effects on the performance of the catalyst as well as the conversions.

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ACKNOWLEDGEMENTS

I would like to gratefully thank my advisor, Dr. Harold H. Schobert, for his constant support, encouragement and extremely beneficial guidance during the entire course of my Ph.D. study. It has been very enjoyable and fruitful working for him in the past three-and-one-half years. I would also like to acknowledge my Ph.D. committee members, Drs. André Boehman, Semih Eser, Ian R. Harrison, Ljubisa Radovic and Peter Walsh, for their very useful guidance and advice.

I am pleased to acknowledge Dr. Chunshan Song for the very fruitful and stimulating discussions throughout the course of this study. I also wish to thank my good friend Mr. Ron Copenhaver for helping me with tubing bomb problems as well as other problems in experiments. My thanks also go to my fellow graduate student and research associate, Drs. Caroline Burgess, and Weichuan Lai, in Fuel Science. I have learned a lot from them, and I treasure their friendship.

I am indebted to my parents for their encouragement and support throughout my life. I especially intend to thank my husband, Xinglong Liang, for his love, encouragement, especially for his patience in my many late working days. My thanks also go to my wonderful daughter, Victoria. Her sweetness and her big smiles made life colorful even in the days while I wrote this thesis.

Finally, I wish to acknowledge the financial support from the United States Department of Energy. I am particularly grateful for many interesting discussions with Drs. Michael J. Baird and Michael A. Nowak.

CHAPTER 1

INTRODUCTION

The world's petroleum reserves are declining and eventually will be depleted [Derbyshire, 1990]. Coal, because of its abundance in the United States, is an attractive source for providing alternative liquid fuels. There are several approaches to produce liquid fuels from coal: solvent extraction, pyrolysis, hydropyrolysis, direct liquefaction and indirect liquefaction. One of the oldest commercial processes is direct liquefaction, discovered by the German scientist Friedrich Bergius in the 1920s. Since then coal liquefaction has been studied intensively. After years of research, it is no longer a major problem to have a high conversion and high oil yield, at least on a research scale. However coal-derived fuel still can not replace petroleum fuel. One of the major disadvantages of liquefaction is the high cost of coal-derived liquids compared to crude oil In addition, particularly in characterization of coal and coal-derived products. These problems create challenges in coal liquefaction even seventy years after its discovery.

Coal consists of complex macromolecules which are built primarily of carbon and hydrogen but also contain significant amounts of oxygen, sulfur and nitrogen. The constituent units tend to be mostly substituted aromatics or hydroaromatics, and the degree of condensation increases as the coal matures, that is, as the coal rank increases. Because coal has a hydrogen-to-carbon ratio significantly lower than that of petroleum, converting coal to liquid transportation fuels requires either the addition of substantial amounts of hydrogen or the removal of excess carbon [Lumpkin, 1988]. Development of a low-severity catalytic liquefaction process has great potential to improve overall process efficiency and to reduce operating costs for producing transportation fuels from coal. The present work is a fundamental study of the effects of solvents and catalysts, as well as of reaction conditions, that might lead to successful low-severity liquefaction. The overall objectives of this work were to conduct research that will provide the basis for an improved liquefaction process and facilitate our understanding of those processes that occur when coals are initially dissolved.

Liquefaction is a process including two steps: the break-up of coal macromolecules into fragment radicals and hydrogenation of these radicals. If the coal-derived free radicals are indeed hydrogenated, smaller molecules are produced and thus liquefaction is successful; while if the free radicals recombine and form more crosslinked and more condensed materials (a process referred to as retrogressive reactions), liquefaction has failed. It is assumed that for low-rank coals, bond breaking and free-radical formation can be done well by thermal energy, based on earlier studies [Derbyshire et al., 1986; Song et al. 1986 and 1991], i. e. by use of a proper reaction temperature. Therefore a task of this research is to enhance hydrogenation of the coal-derived free radicals by several approaches. To some extent, hydrogenation can be done by internal hydrogen donation from some hydroaromatic structures in the coal. However, external hydrogen must be introduced to the coal in order to have a significant conversion.

There are several approaches to enhance the hydrogenation and to prevent retrogressive reactions. As mentioned, an external hydrogen source must be introduced to the reaction system. Two most common sources are hydrogen donor solvents and gaseous H_2. The latter is usually accompanied by a catalyst to promote its performance. In addition to providing a hydrogen source to the system, there is another way to maximize hydrogenation and to minimize retrogressive reactions, which is to adjust reaction conditions to match the formation and hydrogenation of the free radicals. In liquefaction reactions, three conditions are often seen. They are single-staged, temperature-staged and temperature-programmed conditions. The latter two are usually targeted at low-rank coals whose macromolecules are readily broken down at relatively low temperatures.

The main objectives of this work are to study the effects of low-temperature pretreatments on coal structure and their impacts on subsequent liquefaction. The effects of pretreatment temperatures, catalyst type, and influence of solvent will be examined. The specific objectives are to identify the basic changes in coal structure induced by catalytic and thermal pretreatments using spectroscopic, thermochemical, and chemical techniques; and to determine the reactivity of catalytically and thermally treated coals for liquefaction. A remarkable amount of work can be found in the literature on determining good donor solvents, effective catalysts or the optimum reaction conditions. It was not our intention to repeat that work Instead, comparative studies were carried out targeting at how these factors influence liquefaction and to what extent they can enhance conversion, and especially how they affect product characteristics. Some well-known solvents, catalysts and reaction conditions were used, based on the studies in literature. The liquefaction products were analyzed using techniques such as NMR, FTIR and gas chromatography.

Three low-rank coals were used in this portion of the project. As originally detailed in the project management plan, it was intended to use two bituminous, two subbituminous, and two lignitic coals. For convenience in executing the work, the investigations were divided into two portions. One was to focus on primarily on the low-rank coals, involving two lignites and a subbituminous coal. Those results are reported in this volume. The results from the remainder of the project will be reported in a companion volume. The coals used in the present are DECS-1 (Texas subbituminous C), DECS-9 (Montana subbituminous B) and DECS-11 (North Dakota lignite) coals. (DECS-1 is a Big Brown coal from Texas, which appears to be at the lignite/subbituminous boundary. Other samples of this coal have been ranked as lignites.) The coals were characterized by solid-state ^{13}C NMR and FTIR; the results are reported in Chapter 3. To establish some standard conditions for the research, experiments were carried out to seek the optimum reaction time and to test whether the coal samples should be dried. Three reaction conditions, single-staged, temperature-staged and temperature-programmed, were compared at temperatures from 200°C to 450°C, using different solvents. The results are reported in Chapter 4.

Because a catalyst and a solvent are often used simultaneously in a reaction, and the effectiveness of a catalyst can be strongly influenced by the presence and composition of a solvent (and vice versa), it is necessary to discuss their effects together (Chapter 5). The catalyst precursor was ammonium tetrathiomolybdate. The solvents used were tetralin (a donor solvent), decalin (non-donor solvent), 1-methylnaphthalene (non-donor solvent), and Wilsonville middle distillate (liquefaction recycle solvent). For each coal, at least six sets of experiments were performed: non-catalytic reactions with no solvent, with a donor-solvent and with a non-donor solvent; and catalytic reactions with no solvent, with a donor-solvent and with non-donor solvent. Other experiments were also done, for example, using additional solvents. The reactions were performed at temperatures from 250°C to 450°C to test the activities of the catalyst and the solvents. The effects of solvents and the catalyst were first investigated in terms of conversion and product distribution. The reaction residues and products, such as gas, oil, asphaltene and preasphaltene, were characterized using gas chromatography, gas chromatography/mass spectrometry, solid-state ^{13}C NMR and FTIR. The results were compared and the effects of the catalyst and solvents on the structural changes of the coal and product were analyzed.

Finally, in the chapter on conclusions, the effects of reaction conditions, solvents and catalysts on liquefaction are comprehensively compared.

CHAPTER 2

LITERATURE REVIEW

Liquefaction is a process to produce liquid fuels from coal. It involves reactions of coal with a reducing gas (usually H_2) in a solvent vehicle at high temperature and pressure. Liquefaction consists of two loosely defined stages: coal dissolution into solvent-soluble materials; and upgrading of the solubilized materials. The desirable products from liquefaction of coal are transportation fuels, including gasoline, diesel and jet fuels [Song et al., 1990]. In order to understand the mechanism of coal liquefaction and further to design a proper process for maximum conversion, knowledge about coal structure and key factors in the reactions is required. In this chapter, studies on structure of coals, especially of low-rank coals, and the techniques which we can use to investigate coal structure will be reviewed. In terms of liquefaction, some controlling aspects, including reaction solvent, catalyst and temperature condition, will be discussed.

2.1 Coal Structure and Techniques to Study Coal Structure

2.1.1 Coal Structure

Coal is a physically and chemically heterogeneous rock composed of fossilized plant remains called macerals and also of mineralized inclusions. The macerals are differentiated into three major classes: vitrinite, exinite (or liptinite) and inertinite. Vitrinite occurs most often in coals and is believed to be derived from woody plant materials (mainly lignin) [Mackowsky, 1975], and the exinite from lipids and waxy plant substances. The inertinite is possibly produced from charcoal formed by prehistoric pyrolysis processes. As a result of its origin, coal is an almost non-volatile, insoluble, non-crystalline, extremely complex mixture of organic molecules with various sizes and structures.

Before discussing coal structure, it is necessary to have a brief overview on the elemental composition of coals and how coals are classified into various ranks. The major elements in coals are carbon, hydrogen, oxygen, nitrogen and sulfur. Their abundances may vary dramatically with different coals but all fall into the ranges of 65-95%, 2-6%, 2-30%, ~2% and 1-13% respectively. Based on their elemental compositions and their combustion behaviors when being used as fuels, coals are classified into four ranks from high to low: anthracitic, bituminous, subbituminous, and lignitic coal. Table 2.1 shows the classification. In coal research, carbon and hydrogen are usually considered as the "main" elements while oxygen, nitrogen and sulfur are usually called heteroatoms. As we know, the petroleum-derived fuels mainly contain carbon and hydrogen and the atomic ratio of H/C is close to 2; while in coal, the average H/C is about 0.8. Therefore a major task to make liquid transportation fuel from a solid coal is to add hydrogen while liquefying it. An earlier study by Artok et al.[1993] shows that in order to attain 100% conversion of the low-rank coals, about 4.5% hydrogen on dry and mineral-matter free basis is needed to be added to the coals.

There are two concepts often used in coal study. They are aromaticity and ring condensation. Aromaticity (f_a) is defined as "fraction of the total amount of carbon incorporated in aromatic structures", and ring condensation (R) is defined as "the average number of fused aromatic rings in a structure" [Schobert, 1990a]. For low-rank coals, the aromaticity is low and so is the ring condensation; while for high-rank coals, they are the

Table 2.1 ASTM rank classification of coals [reproduced from Schobert, 1990]

Class	Group	%FC$_{mmmf}$	%VM$_{mmmf}$	Calorific value, Btu/lb, m, mmf
Anthracitic				
	Metaanthracite	>98	<2	
	Anthacite	92-98	2-8	
	Semianthracite	86-92	8-14	
Bituminous				
	Low volatile	78-86	14-22	
	Medium volatile	69-78	22-31	
	High volatile A	<69	>31	
	High volatile B			>14,000
	High volatile C			13,000 - 14,000
Subbituminous				
	Subbituminous A			10,500 - 11,500
	Subbituminous B			9,500 - 10,500
	Subbituminous C			8,300-9,500
Lignitic				
	Lignite A			6,300 - 8,300
	Lignite B			<6,300

opposite. The higher the aromaticity and ring condensation, the lower the H/C ratio will be, and thus the more difficult it will be to liquefy coal because more aromatic ring clusters have to be broken and more aromatic carbons have to be hydrogenated. Therefore high-rank coals, such as anthracite and low volatile bituminous coals, are not good candidates for liquefaction. On the other hand, the lower the rank is, the higher the heteroatom contents will be, which means more efforts have to be made to remove them. Hence the very low-rank coals are not excellent liquefaction feedstocks either. Traditionally, it was believed that the medium-rank coals, such as bituminous, were the best choice for liquefaction, while some low-rank coals, e. g. subbituminous and lignite, were more difficult to deal with since they required higher temperatures [McLean et al., 1986; Whitehurst, 1979 and Longanbach, 1980]. However, some workers recently claimed that the low-rank coals can actually be liquefied at lower temperature than the medium-rank coals. The early observations made by McLean et al., Whitehurst and Longanbach are the results of retrogressive reactions caused by lack of precautions [Derbyshire et al., 1986; Wu and Storch, 1988 and Derbyshire and Stansberry, 1987]. In this study, three low-rank coals, two subbituminous and one lignite, were selected. Detailed research has been conducted to find the proper liquefaction temperature and reaction conditions (solvent, catalyst, etc.) for these three coals.

The heteroatoms exist in coals in various forms. By far the most important functional groups in low-rank coals, in terms of both the quantity and their effects on chemical and physical properties, are the various oxygen functional groups. On a weight basis, oxygen may exceed 20% of the coal. The oxygen is distributed among carboxyl, phenol, methoxyl, bridge ether, and carbonyl groups. Sulfur and nitrogen, on the other hand, may contribute only 1-2% each to the coal. The functional groups incorporating these heteroatoms are not well characterized; they are usually assumed to be heterocyclic

[Schobert, 1990b]. The existence of a heteroatom in a chemical bond may cause bond cleavage at a low temperature [Song, 1986; Song et al., 1991], and further lead to retrogressive reaction due to difficulties of hydrogenation at such a low temperature. In addition to that, the heteroatoms may also consume hydrogen and produce H_2O, NH_3 and H_2S during reactions and thus increase the cost of liquefaction. Therefore, the existence of heteroatoms in coals can almost be considered as a disadvantage in coal liquefaction.

2.1.2 Techniques to Study Coal and Coal Derived Product

Detailed structural characterization of coal has been found to be extremely difficult and that is why such research is pursued extensively. There are two major branches in the study of coal structure. One deals with the physical structure of a coal, such as surface area, porosity, and pore size distribution; the other one deals with the chemical structure of a coal, such as aromatic ring sizes, aliphatic chain length, and how the aromatic rings and aliphatic chains are connected.

Researches on physical structure of coals are targeted at determining the physical properties of coals, including solvent swelling, porosity, surface area, and density. To keep this thesis to a reasonable length, only the studies on first three properties will be briefly reviewed.

Solvent swelling is a characteristic property of a crosslinked macromolecular structure. Swelling can be described as that when a material is mixed with a solvent, the solvent molecules diffuse into the material and produce a swollen gel. Unlike a usual dissolving process, the swollen gel does not further dissolve into the solvent and form a true solution. As a macromolecule, coal possesses the swelling property to a certain degree based on the number of crosslinks it has. Lignites are highly crosslinked and show very little swelling in solvents. Bituminous coals, with fewer crosslinks, can swell to a much greater extent. While for anthracite, there are even fewer crosslinks. On the other hand there are strong π-π interactions between large ring systems. Therefore anthracites do not swell nearly as much as bituminous coals.

A coal is thus characterized by a highly porous structure and large surface area because the basic "unit" of a coal is aromatic ring clusters connected by aliphatic crosslinks, and these "units" are frequently found randomly packed. The porosity is the volume percentage occupied by the pores. It may be calculated from density measurements using helium and mercury as displacement fluids. Whereas helium is supposed to be capable of penetrating into the whole structure, mercury, at low pressure, does not penetrate at all. Pore size distribution can be obtained based on the fact that mercury can penetrate into pores under pressure. The higher the pressure, the smaller will be the minimum openings of the pores to which mercury has access. Surface area of a coal is usually measured by gas adsorption. It has been found that lignites have the highest surface area and highest porosity [Schobert, 1990]. Bituminous coals, because of their structure, have the lowest surface area as well as the lowest porosity. On the other hand, it has also been found that 90% of the surface area of lignite is in the internal surface of pores. This implies that in order to carry out coal reactions effectively, reaction sites have to be extended to the internal surface. In the case of catalytic reactions, the catalyst particles have to be deposited onto the internal surface of the numerous pores to achieve a high dispersion because a large proportion of the surface area is enclosed in the pores. This thought led to the development of a new catalyst impregnation technique, the swelling method (detailed in Chapter 5), in which the coal is swollen by a solvent containing the catalyst, in an attempt to open up the pores and load the catalyst onto the internal surface.

In the study of the chemical structure, it is desired to determine the functional groups (especially the functional groups containing heteroatoms), the aliphatic chain length, the aromatic ring sizes and the fashion in which aliphatic chains and aromatic rings connect. In principle, two approaches can be used. One attempts to degrade the coal macromolecules into representative fragments and to derive the original coal structure from the structures of the fragments. An example of this approach is pyrolysis-chromatography/mass spectrometry (GC/MS). The other approach attempts to use non-destructive techniques to investigate the coal structure. Such techniques include, for instance, infrared (IR), solid-state nuclear magnetic resonance (NMR), X-ray diffraction, small-angle-X-ray scattering and Mossbauer spectroscopy. In this work, solid-state NMR and Fourier transform infrared spectroscopy (FTIR) are the major techniques involved in investigating the structure of reacted and unreacted low-rank coals. Therefore, literature related to works using these two techniques will be reviewed.

2.1.2.1 Solid-State ^{13}C NMR

Van Krevelen in 1961 stated that "coal as a whole is strongly aromatic; its aromaticity increases more or less steadily with rank, reaching its maximum value of unity at about 94% carbon in vitrinites" [Van Krevelen, 1961]. Usually there are two important aromaticity values to be considered: the percentage of <u>hydrogen</u> atoms directly bonded to aromatic carbons and the percentage of aromatic <u>carbon</u> atoms. The latter is more important and will be discussed in this entire thesis unless otherwise mentioned. It is only in recent years that the carbon aromaticity could be measured by direct examination of the carbons in solid coals. This was mainly due to advances in nuclear magnetic resonance techniques. NMR is the resonance absorption of radio frequency (5-500 MHz) radiation by nuclei with non-zero spin in the presence of a static magnetic field. It enables chemists to look at the molecular environment of certain atoms that are sensitive to the magnetic field. Since there are isotopes of hydrogen, carbon, oxygen and nitrogen possessing non-zero nuclear spin, coal, containing these elements, is in principle a rich source of information via NMR. Because isotopic abundance is well known and transition probabilities may be arranged to be essentially unity, the intensity of the NMR signal may be used as a quantitative analysis for the nuclear species under measurement [Gerstein and Pembleton, 1977]. Proton (^1H) NMR is largely limited to coal liquids, and soluble products, while ^{13}C NMR is more suitable for obtaining information about aromaticity of solid coals.

In 1973, Retcofsky and Friedel first reported a study of ^{13}C magnetic resonance on coals using a "conventional" broad-line technique accompanied by signal averaging of spectra. The spectra obtained were very broad and lacked resolution, and thus were not of real quantitative significance. However, it did demonstrate that ^{13}C NMR was potentially useful and able to give valuable qualitative indications of aromaticity. Approximately at the same time, Pines and his associates [Pines et al., 1972 and 1973] demonstrated that high-resolution spectra of solids could be obtained and it was possible to resolve four functional types of carbons: simple aromatic, quaternary aromatic, oxygen-bonded aromatic and simple aliphatic. This method, now usually called cross-polarization (CP) ^{13}C NMR, has several advantages over the conventional one. The weak signals from the ^{13}C atoms (with abundance of 1.1%) are greatly enhanced by transferring polarization from protons to carbons and then decoupling the C-H coupling by irradiation with high-power radiofrequency (rf). This enables the use of short proton relaxation time, which is the decay time as excited nuclei return to their normal lower energy states, instead of the long ^{13}C relaxation time, as the waiting time between experiments. Therefore more scans can be obtained and averaged in a certain amount of time for a better spectrum.

In a coal sample, most carbon nuclei are in the close proximity of protons. The spin of these protons can be aligned with or against that of the nucleus under study. Thus each energy level of the nucleus is further split due to the spin of the adjacent proton, and the result is that more than one line is obtained from a particular nucleus. In a liquid, this multiplicity can be quite simple, but in a solid, the situation is much more complicated because of the various orientations of the proton with respect to the carbon nucleus and the lack of motion of the molecules. In addition, the energy levels are also split as a result of strong dipolar force across the C-H bond. This interaction is called dipolar coupling. There are two methods to remove the dipolar coupling. The first is called decoupling. It involves irradiating the protons in the sample so that rapid transition between energy levels of protons occurs and hence the carbons experience only the presence of a single averaged interaction with the attached proton spins. This increased resolution is sufficient to partly resolve aromatic from aliphatic carbons in a coal sample, but is insufficient for high resolution experiments. The second method of removing the dipolar interaction is rapid spinning, termed "magic-angle spinning" (MAS) [Andrew et al., 1958, 1959, and 1971; Low, 1959]. The magic angle, the angle between the magnetic field and internuclear vector, is 54.7° by calculation using classical physics. For a single crystal, the crystal can be aligned so that the angle is 54.7°. For an amorphous sample, such as a coal, this is impossible. Instead, the sample is spun rapidly about the magic angle which achieves the same effect, since on average each internuclear vector is at 54.7° [Wilson, 1987].

By combining cross-polarization (to enhance the signal/noise ratio) and magic-angle spinning (to remove chemical shift anisotropy, or in other words to increase resolution), sufficient resolution can be obtained in the spectra of coal samples to distinguish clearly the aromatic and aliphatic carbons and, in some favorable cases, further structure may be observed in the spectra and assigned to particular functional groups. Thus CP/MAS ^{13}C NMR has become a standard technique to measure aromaticity. There is a tremendous amount of work reported in the recent literature using this technique to study coal and other geochemical samples [Hatcher et al., 1981, 1982a &b, 1983; Wilson et al., 1981, 1983a, 1984; Zilm et al. 1981; Lambert and Frye, 1982; Preston and Ripmeester, 1982; Pugmire et al., 1982; Benzing-Purdie and Ripmeester, 1983; Skjemstad et al. 1983; Steelink et al., 1983; Thurman and Malcolm, 1983; Pfeffer et al. 1984]. Regarding the accuracy of aromaticity, caution should be taken when interpreting f_a's of materials containing considerable quantities of paramagnetic materials. For instance, in coals rich in inertinite, the association of mineral matter with inertinite rather than vitrinite and presence of pyrolytic fusinite may reduce the contribution of the carbon in the inertinite part of the sample to the observed spectrum.

The general quantitative reliability of aromaticity measured by CP/MAS has been evaluated by Dudley and Fyfe [1982], Wilson and Vassallo [1985] and Packer [1983]. It is postulated that at present there is no direct evidence that can be used to establish whether f_a's measured by CP/MAS are quantitatively accurate or not. Of course, it is possible to make comparisons with more traditional methods of determining f_a's [Van Krevelen, 1961], but those methods are also not definitive. Packer [1983] suggested that a way to check whether f_a's measured by CP/MAS were correct was to plot f_a versus H/C ratio. However, this suggestion is not quite practical because if correlation between H/C and "true" f_a's can be found, there is no need to undertake the NMR experiments since f_a could be determined from the H/C ratio. Despite the lack of an "ideal" technique which can accurately measure the "true" aromaticity and thus determine the quantitative reliability of f_a's measured by CP/MAS, Wilson et al. [1985] estimated that in 90% of cases, a simple CP/MAS experiment will give an accurate aromaticity data, while in other cases it may be necessary to check f_a's by using other techniques, such as electron irradiation and single pulse techniques.

Based on the above discussion, the purpose of measuring aromaticity of coals and reacted coals in this thesis is not to gain the absolute value of aromaticity. It is rather to use the f_a's obtained by CP/MAS as an approach to look at the structure and structural changes of coals during liquefaction reaction and thus to evaluate the benefits of condition (solvent, catalyst and temperature conditions) applied.

2.1.2.2 FTIR

Infrared spectroscopy is one of the physical techniques which can give detailed and valuable information about the constitution of organic materials, such as coals. Even though sometimes the spectra are too complicated for individual compound analysis, qualitative information about specific structural elements or functional groups can often be surmised [Painter, 1985].

Infrared spectroscopic studies of coal have been reported in many publications and attempts have been made to diagnose the functional groups and carbon skeleton of the coals or macerals in coals, Figure 2.1 [Painter, 1985]. From results in the literature, it is generally agreed that coal contains various aliphatic and aromatic carbon-carbon and

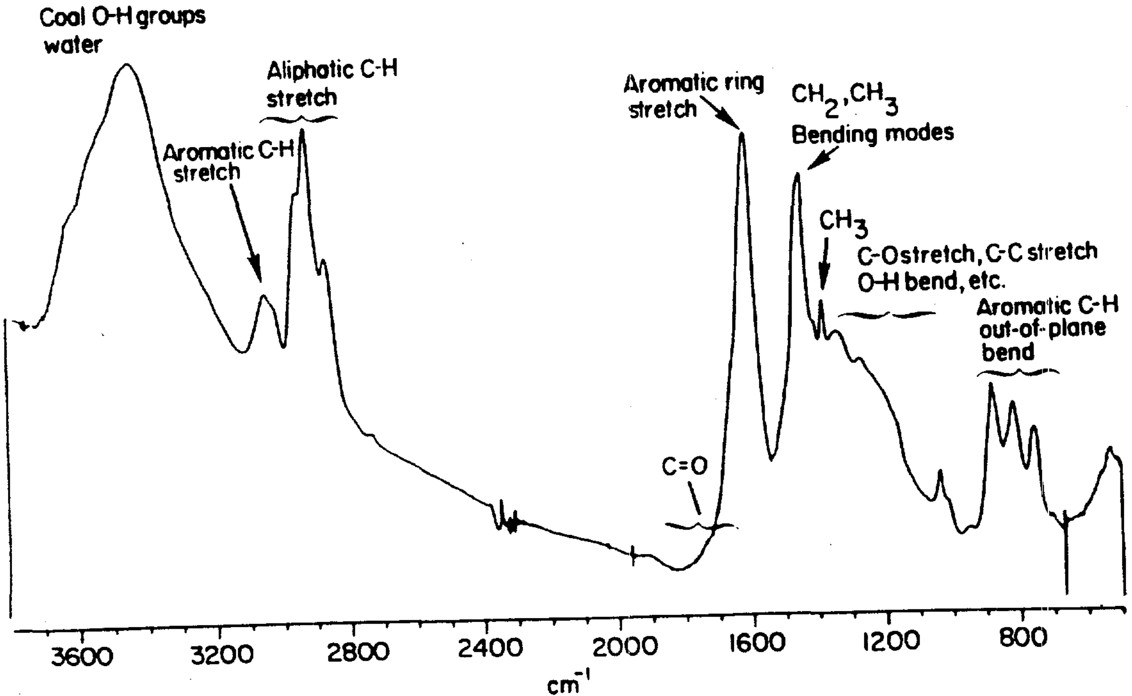
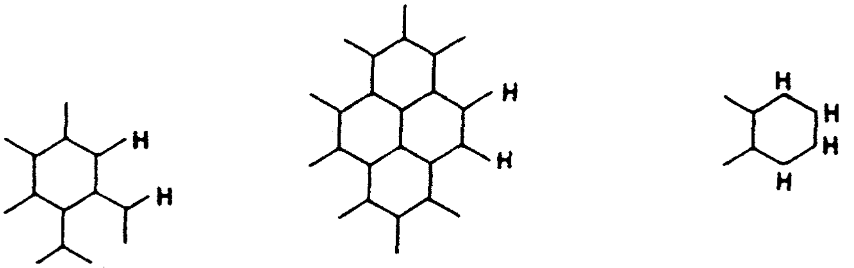


Figure 2.1 FTIR spectrum of a vitrinite concentrate (PSMC 52) [Painter et al., 1985]



Isolated CH groups

Two adjacent CH groups

Four adjacent CH groups

Figure 2.2 Three types of aromatic CH groups [Painter et al., 1985]

carbon-hydrogen bonds but few isolated C=C and C≡C bonds [Roy, 1965]. Brown [1965] studied infrared spectra from 650 to 4000 cm^{-1} for a variety of coals and noted that the ratio of aromatic hydrogen to total hydrogen increased (hydrogen aromaticity) with rank, which was also observed later by Kojima et al. and Osawa et al. [Kojima et al., 1956, Osawa et al., 1969]. The absorption band at 760 cm^{-1} has been assigned to an isolated aromatic CH group, the one at 814 cm^{-1} to two adjacent aromatic CH groups and the one at 870 cm^{-1} to four adjacent aromatic CH groups, Figure 2.2 [Gourlay, 1950; McMurry and Thornton, 1952; Hadzi, 1954; and Brown, 1955]. The relative intensities of these three bands have been suggested to give an indication of the degree of aromatic ring condensation. Table 2.2 summarizes the assignment of infrared bands of carbon-hydrogen absorption.

The assignments of absorptions in the infrared spectra to various oxygen functions have also received some attention. In fact, using infrared to study the oxygen functional

Table 2.2 Assignments for infrared absorption [reproduced from Van Krevelen, 1993]

Band position		
cm	µm	Assignment of spectral bands
4000-3400	2.5-3.0	H_2O (stretching)
3800-3600	2.6-2.8	H bond -OH (stretching)
3760-3620	2.5-3.0	4 *Kaolinite* and *Illite* bands
3625-3200	2.7-3.1	4 bands of hydrogen-bonded groups
3300	3.0	-OH stretching, -NH stretching
		phenolic -OH, O=, =NH, =N-, -OH hydroperoxide
3090-3030	3.24-3.30	7 bands of ArH, $(C\text{-}H)_{ar}$ (stretching)
3024-3019	3.3	C=C bond, $R_2C\text{=}CHR$, RCH=CHR
2992-2988	3.35-3.37	Undefined
2978-2960	3.4	Asymmetric R-CH
2946-2944	3.39-3.40	Asymmetric $Ar\text{-}CH_3$; Aliphatic C-H (stretching)
2931	3.4	$\text{-}CH_2\text{-}C\text{=}O$
2925-2918	3.41-3.42	Asymmetric R_2CH_2- (stretching)
2904-2888	3.44-3.48	$R_3C\text{-}H$ (stretching)
2870-2867	3.48-3.50	Symmetric RCH_3 (stretching)
2860	3.5	Aliphatic C-H (stretching)
2854	3.5	Symmetric $R\text{-}CH_2$- (stretching)
2853-2846	3.5	Symmetric $R\text{-}CH_2\text{-}R$ (stretching)
2837-2790	3.5-3.6	not identified
2728	3.7	RCHO; Ar_3CH (stretching)
2550-2410	3.9-4.1	-SH (stretching)
2400-2300	4.2-4.35	CO_2
1850-1775	5.4-5.6	-(C=O)-O-(C=O)-; -O-(C=O)-O-
		Acetylated phenolic -OH, Alkyl-OH
1745	5.4	Alkyl -OH
1734-1720	5.40-5.75	-(C=O)-O (ester)
1675-1500	6.0-6.7	NH
1671	6.0	Hydrogen-bonded quinone C=O
1660	6.0	Isolated C=C bond
1654	6.0	Conjugated -C=O
1635	6.1	Water

Band position		
cm	um	Assignment of spectral bands
1615-1590	6.2-6.3	-C=O; -OH
1615-1590	6.2-6.3	$(C-H)_{ar}$ (stretching); Polynuclear aromatic syst.
1500-1450	6.55-6.9	$(C-C)_{ar}$ (stretching)
1460-1450	6.9	$(C-H)_{al}$ (bending)
		$-CH_3$ asymmetric deformation (bending)
		$-CH_2-$ scissor deformation
1380	7.3	$-CH_2-$ symmetric deformation (bending)
		cyclic CH_2 deformation
1300-1000	7.7-10.0	phenolic and alcoholic C-O deformation (bending)
		$C_{ar}O-C_{ar}$; $C_{al}-O-C_{al}$; $C_{ar}-O-C_{al}$; (stretching)
1300-920	7.7-10.9	C-N (stretching)
925-700	10.8-14.3	N-H (rocking)
925-670	10.8-14.9	"Aromatic bonds"; $(C-H)_{ar}$ (out-of-plane bending)
893	11.2	H-atom in meso-position (anthracene)
884	11.3	Isolated CH_2
875	11.4	*Calcite*
873	11.4	Substituted benzene ring with 2 neighboring H atoms
864	11.6	Isolated CH_2
860-750	11.6-13.3	Aromatic HCC rocking (single and condensed rings)
834	12.0	Isolated CH_2
820	12.2	Angular condensed ring system
816	12.3	Subst. benzene ring with two neighboring H atoms
815	12.3	Isolated CH_2
801	12.5	Do.
785	12.7	Adjacent CH_2 groups (rocking)
758	13.2	o-Substituted benzene ring
		mono-substituted benzene ring
		condensed ring system
753-750	13.3	4-adjacent $(CH)_{ar}$ (out-of-plane bending)

groups in coals, especially in low-rank coals, attracts many coal scientists. The broad absorption band associated with oxygen-hydrogen stretching modes in the region between 3500 and 3100 cm^{-1} has been investigated and used by many workers to measure the hydroxyl contents in coals [Painter et al., 1981]. In the spectra of most coal samples, a band is usually observed at 3400 cm^{-1}, which has been assigned without much argument to the hydrogen-bonded water. Because of the interference of water absorption, it was further suggested to use the intensity at 3200 cm^{-1}, where the water absorption is expected to be weak, to determine the hydroxyl contents. Solomon and Carangelo [1982] demonstrated that this was an improvement in the accuracy of results. The 3200 cm^{-1} band has been assigned to hydroxyl groups of phenolic structure, carboxylic acids and alcohols. Further identification of the types of hydroxyl groups can be done by analyzing other absorption bands such as those around 1700 and 1600 cm^{-1}. For low-rank coals (subbituminous, lignite and brown coals) which are rich in oxygen, there are two prominent peaks centered approximately at 1720 and 1600 cm^{-1}. For higher-rank coals, with low oxygen contents, the absorption at 1720 cm^{-1} appears as a shoulder of that at 1600 cm^{-1}. By using curve-fitting method, four bands at about 1760, 1735, 1700 and 1670 cm^{-1} can be resolved for the broad band at 1720 cm^{-1}, and they are ascribed to carbonyl functional groups. Furthermore, a predominant functional group associated with the band at 1760 cm^{-1} is probably a phenolic ester (RCOOAr) while the absorption at 1735 cm^{-1} is ascribed mainly to aliphatic esters (RCOOR') and phenol esters of aromatic acids (ArCOOR). The absorption at 1700 cm^{-1} is assigned predominantly to carboxylic acids, but a contribution from alkyl esters of aromatic acids (ArCOOR) is also probable. The band at 1670 cm^{-1} is attributed to ketonic structure [Supaluknari et al., 1988].

Many research groups have focused their attentions on the assignment of the 1600 cm^{-1} band in the infrared spectra of petroleums, even in those with less than 1% oxygen contents [Speight, 1972]. The assignment has been a matter of controversy for more than 20 years. It was found that this band was not affected either by acetylation or by oxidation of fractions [Bergmann, et al., 1958]. Fujii et al. [1963a, 1963b, and 1970] performed some experiments of $LiAlH_4$ reduction of coals and their results indicated that this absorption is predominantly due to the presence of highly conjugated hydrogen-bonded carbonyl groups in coals. However, many other researchers disagreed with the carbonyl assignment, but believed that the 1600 cm^{-1} band is really attributable to aromatic ring stretching [Rao et al., 1962, Friedel et al., 1971, Painter et al., 1981, and Painter et al., 1983]. Recently Painter et al. [1983] demonstrated that the broad band at 1600 cm^{-1} can be curve-fitted to several peaks, Figure 2.3. The ones at 1614 and 1589 cm^{-1} are classic group frequencies for aromatic ring stretching modes [Colthup et al., 1975, Bellamy, 1975]. The 1589 cm^{-1} band can be assigned to a COO^- group and, as their early study showed, such groups can be readily identified by acid washing, when the band shifts to 1700 cm^{-1}. Since this shift was not observed in their sample, they therefore concluded that it was attributable to aromatic ring stretching. Other peaks around 1600 cm^{-1} can also be identified. The most important one is at 1656 cm^{-1} and it is believed to be due to highly conjugated carbonyl, most probably in quinone type structures [Colthup et al, 1975, Bellamy, 1975]. In a summary, the assignment of bands associated with oxygen functional groups are also listed in Table 2.2.

2.2 Coal Liquefaction

Generally speaking, coal liquefaction is a process involving two steps. The first step is the rupture of chemical bonds and formation of free radicals. The second step involves reactions of the free radicals. When the radicals are stabilized by hydrogenation,

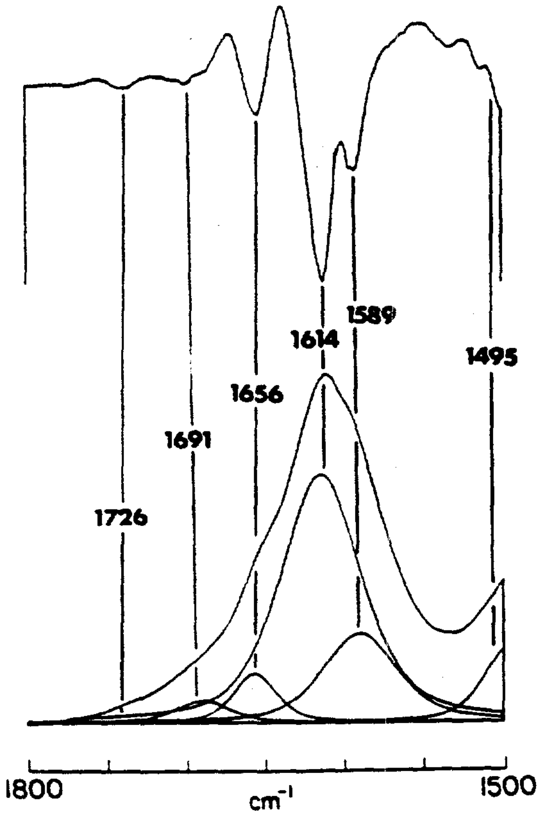


Figure 2.3 Bottom: infrared spectrum between 1800 and 1500 cm-1 of a vitrinite concentrate, PSMC 36 [84.3% carbon (dmmf)] with individual curve-resolved bands. Top: second derivative of spectrum. [Painter et al., 1985]

the liquefaction process is considered to undergo the desirable pathway, that is, molecular weight reduction is achieved. If hydrogenation is insufficient, the free radicals will have to undergo recombination reactions accompanied by hydrogen loss and aromatization, which is undesirable, and called retrogressive reaction. Therefore, in liquefaction, the main effort is to match the rate of hydrogenation and the rate of free-radical formation. To do that, there are three possible approaches. Usually bond breaking is a process governed by thermal energy and can be controlled by adjusting temperature, so the first approach is to find a proper temperature condition. The second and third approaches are to improve effectiveness of hydrogenation by using a hydrogen-donor solvent and a catalyst. In this section, the three approaches will be reviewed.

2.2.1 Solvent in Coal Liquefaction

Liquefaction solvents have two major beneficial roles in reaction. One is to stabilize reactive molecular fragments, which are coal-derived free radicals, during the degradation of the coal macromolecule. The other is to participate in the subsequent stage of liquefaction in which the initial products are upgraded by hydrogenation, by removal of heteroatoms and by reduction of their average molecular weight. A liquefaction solvent should have one or more of the following properties:

1) to act as a physical solvator,
2) to donate hydrogen during reaction (a hydrogen-donor solvent),
3) to transfer hydrogen atoms (a hydrogen shuttler),
4) to promote reaction, such as to induce bond cleavage (a real reactant).

2.2.1.1 Physical Solvator

The role of a physical solvator is to disperse or dissolve coal-derived free radicals, hydrogen atoms and liquefaction products. Firstly in coal liquefaction, one major problem is that the rate of free-radical formation and the rate of hydrogenation are often unmatched. In most cases involving low-rank coals, the coal matrix is broken down very quickly at relatively low temperatures and thus free radicals are produced at a high rate. However the rate of hydrogenation, on the other hand, is usually so low that it can not catch up with that of free-radical formation. In this case, there are excess free radicals in the reaction system, and there is a strong tendency that they will combine with each other, resulting in undesirable retrogressive reactions. Therefore, to prevent the retrogressive reactions, it is crucial to have a solvent acting as a solvator to disperse the free radicals so to reduce the local concentration of radicals. Secondly, the dissociation of hydrogen molecules to hydrogen atoms is a reversible reaction regardless of the use of a catalyst. From general knowledge of chemical kinetics, one way to enhance the reaction from hydrogen molecules to hydrogen atoms is to reduce the local concentration of H-atoms by dispersing and transferring them to the coal-derived free radicals where hydrogenation takes place. Thirdly, the majority of liquefaction products still possess large molecular weight. Therefore a solvator is needed to reduce viscosity.

A good solvation solvent is believed to be the coal-derived recycle solvent according to the basic rule in chemistry that "like dissolves like" [Bockrath, 1983]. These recycle solvents usually contain a high proportion of aromatic and highly condensed aromatic compounds. Work has been done showing the positive solvation effect of naphthalene in experiments of liquefaction of coals [Neavel, 1976] and vitrinite macerals [Shibaka, 1981a and 1981b].

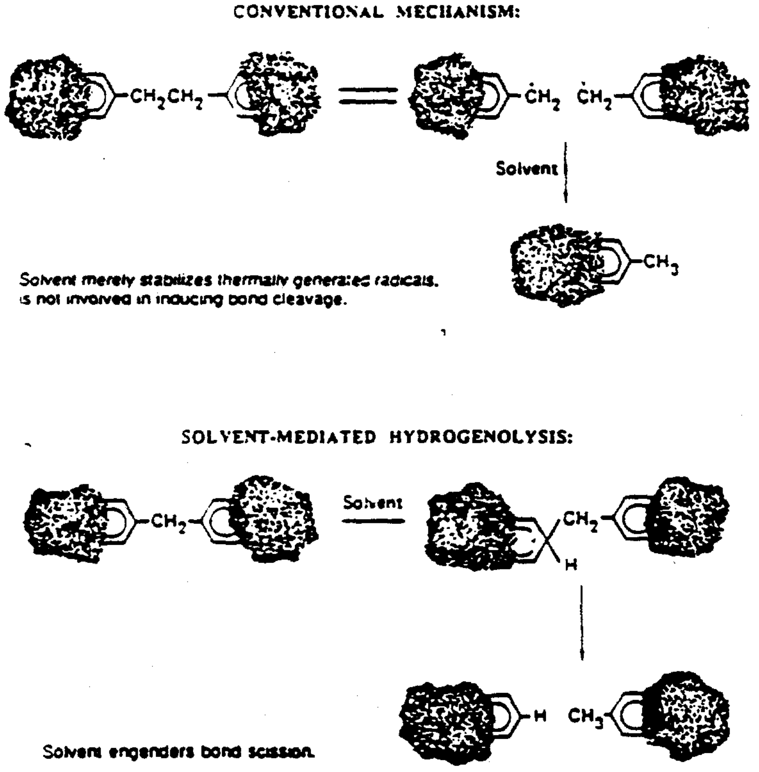
2.2.1.2 Hydrogen-Donor Solvent

A hydrogen-donor solvent has the ability to provide hydrogen atoms to the coal liquefaction reaction system even without the presence of hydrogen gas. Curran et al. [1967] were apparently the first investigators to describe the transfer of hydrogen from a reaction solvent (tetralin) to coal as a free-radical reaction involving thermal cleavage of the coal molecules. Later Neavel [1976] compared the influence of tetralin, naphthalene and dodecane on reaction. It was observed that an organic solvent without hydrogen-donating properties, e. g. naphthalene and dodecane, appeared to be as effective in terms of dispersing ability as a donor solvent. However, as reaction went on, the chemical properties of the solvent became increasingly more important. Among the three solvents employed, tetralin was the one continuing to provide higher conversions as residence time elapsed. The reactions with the other two solvents experienced significant drops in conversion after 10 minutes of residence time, indicating the occurrence of recombination of free radicals due to lack of hydrogen atoms in the reaction system.

There are two mechanisms existing in the literature concerning donor solvents in liquefaction. Traditionally, coal structure has been thought to come apart by the thermolysis of inherently weak bonds upon application of heat. Thermolysis would lead to a pair of radicals that can abstract hydrogen from the donor solvents, producing solvent radicals that can, in turn, abstract hydrogen from coal structure. Hence the hydrogen exchange is a natural result of the spontaneous bond scission reactions generally considered to be responsible for coal liquefaction. According to this mechanism, the efficiency of donor solvents should correlate with the weakness of their C-H bonds. However, it was noticed that literature data on liquefaction yields in different solvents did not correlate with their ability to scavenge radicals. For example, among the common donor solvents, dihydroanthracene is the most efficient radical scavenger, and yet it is recognized that it is a poorer liquefaction solvent then a number of other hydroaromatics [McMillen et al., 1983 and 1987]. Furthermore, in studies with model compounds, it was observed [McMillen et al., 1983 and 1987] that even strong linkages, like C_{aryl}-C_{aryl} bonds, undergo cleavage under liquefaction conditions (e. g. donor solvents, 400°C, 1 h). Simple thermolysis of this bond will proceed with a half-life time no less than 10^6 years, and thus it is impossible to be observed under the experimental conditions. However, these bonds would be expected to cleave if a hydrogen atom were to be first transferred to the *ipso* position. The lack of correlation between liquefaction effectiveness and scavenging ability of different donor solvents, together with the observed cleavage of relatively strong bonds under liquefaction conditions, prompted McMillen et al. to propose another mechanism. The key element of it is that the solvent-derived radicals mediate the cleavage of the bonds, and hence this mechanism is named solvent-mediated hydrogenolysis (SMH) [Malhotra and McMillen, 1993]. In reactions involving strong bonds, the hydrogen is first transferred to the *ipso* position from donor solvents, inducing bond cleavage and molecular weight reduction. Thus in the second mechanism, liquefaction is a result of hydrogen-exchange, which is the opposite of the first mechanism. The two mechanisms are schematically shown in Figure 2.4 .

A large number of people have investigated the hydrogen donating ability of many organic solvents. Excellent hydrogen donor solvents are found to be nitrogen- or oxygen-containing aromatics, such as tetrahydroquinoline (THQ) [Kamiya et al., 1986; Derbyshire et al., 1984; Bockrath, 1983; Hausigk et al., 1969; Brocker and Kolling, 1965; Schlosberg et al., 1981, and Burgess and Schobert, 1991], tetrahydronaphthol [Kamiya et al., 1986], and hydroaromatic hydrocarbons, such as 9,10-dihydroanthracene, 9,10-

Scheme I. Schematic Showing Conventional and Solvent-Mediated Hydrogenolysis Models of Coal Liquefaction



Solvent merely stabilizes thermally generated radicals, is not involved in inducing bond cleavage.

Solvent engenders bond scission.

Figure 2.4 Schematic showing conventional and solvent-mediated hydrogenolysis models of coal liquefaction [Malhotra and McMillen, 1990] dihydrophenathrene and tetralin [Kamiya et al., 1986; Artok et al., 1992]. The donating ability of the oxygen- or nitrogen-containing aromatics is ascribed to their similar character as hydroaromatic and phenol or secondary amine; and that of hydroaromatics is due to the lability of the benzylic C-H bond [Kamiya et al., 1986; Sato et al., 1986]. Usually the bigger the aromatic ring system is, the greater the donating ability is. Therefore, the order of donating ability of the solvents is dihydropyrene > dihydrophenathrene ~ dihydroanthracene > tetralin >> benzene [McMillen et al., 19485, 1987a and 1987b, 1991; Malhotra et al., 1993; Derbyshire et al., 1981].

2.2.1.3 Hydrogen-Shuttler

Hydrogen-shuttler is an organic compound which can transfer hydrogen to coal either from the gas phase or from other organic compounds which may undergo dehydrogenation. Usually, the hydrogen-shuttler is an aromatic compound, such as aromatic hydrocarbons or phenols [Larsen et al., 1981a and b]. Its ability of transferring hydrogen depends on the aromatic ring size. Davis et al. [1977] noticed that the extraction efficiency of non-donor aromatic hydrocarbons measured in tubing bombs generally increased with the size of the aromatic compounds. Therefore, the order of effectiveness in terms of transferring hydrogen is pyrene > phenanthrenes > naphthalene. It is interesting to notice that even though they both possess three rings, anthracene has a much poorer transferring ability than phenanthrene.

The mechanism of hydrogen-shuttling effect has puzzled many people for a long time. As early as 1950s, Golumbic et al. [1950] showed that phenanthrene could extract 95% of a bituminous coal. This work was later duplicated by Heredy and Fugassi and it was found that a total of 10-15% of the hydrogen in the coal was exchanged with that of phenanthrene. This extensive exchange of hydrogen between coal and phenanthrene strongly suggested that the occurrence of shuttling reactions. Analysis of the phenanthrene extracts indicated that the hydrogen exchanged between phenanthrene and coal involved phenolic and carbon-hydrogen sites [Heredy and Fugassi, 1966]. Other investigators studied the behavior of naphthalene and found that the hydrogen exchange took place on the α-position of naphthalene several times faster than that at the β-position [Rotto et al. 1980, and Rotto and Goldberg, 1981], and the exchange preferred to occur near sites with high electron density [Goldberg, 1980]. Recent study on the mechanism of hydrogen shuttling has focused on the use of pyrene as a solvent. Without the presence of gas-phase H_2, the effectiveness of pyrene is associated with its ability to dissolve fragments of coal and maintain a low viscosity in the reaction system (a physical solvator) [Davies, 1977; Mochida, 1979 and 1980]. In addition to this, the innate thermal stability of pyrene is also an important factor in preventing the formation of char [Mochida, 1979]. A study by Derbyshire et al. [1981], where pyrene was mixed with coal in the presence of hydrogen or argon atmosphere, demonstrated that the majority of hydrogen consumed to form dihydropyrene is derived from molecular hydrogen rather than the coal itself. Once the dihydropyrene is formed, it can act as an excellent hydrogen donor. On the other hand, in the mixture of coal-H_2-pyrene, alkylation of pyrene will take place to produce methylpyrene and dimethylpyrene which provide an additional source of hydrogen. The beneficial effects of solvents which are organic compounds with large aromatic ring systems on coal liquefaction rely on a combination of their solvation ability, hydrogen transferring ability and hydrogen donating ability.

2.2.2 Catalyst in Coal Liquefaction

In coal liquefaction, a catalyst is usually applied. The use of a catalyst has one or several of the following advantages:

1) to increase the total conversion from coal to liquid product;

2) to improve selectivity, that is to produce more oil (hexane-solubles) instead of asphaltene (toluene-solubles but hexane-insolubles), preasphaltene (tetrahydrofuran-solubles but toluene-insolubles) or gas (The details of definitions of the products are in Chapter 3);

3) to improve product quality, which means to increase hydrogen content, and decrease the viscosity and heteroatom content of the product;

4) to enhance efficiency of hydrogen consumption, and thus to reduce the overall cost of liquefaction.

Liquefaction catalysts, according to their functions, can be classified as cracking catalyst and hydrogenation catalyst. The cracking catalyst is used to cleave the linkages connecting coal structural units and to crack the aromatic structures at temperatures below those required to initiate free-radical reactions. Examples of this kind of catalyst can be found in acid catalysts, such as $ZnCl_2$, $SnCl_2$, and $FeCl_3$. Intensive research work can be found in the literature [Wiser et al., 1970; Sapre et al., 1981; Broderick et al, 1982; Haynes et al, 1983; Kikkawa et al, 1976; Nakatsuji, 1978; Miyake et al, 1982; Song et al., 1988; Salim and Bell, 1984; Ogata et al., 1984; Song et al., 1986a, 1986b, 1987, 1988a, 1988b and 1989]. The hydrogenation catalyst, as the name implies, is to enhance the hydrogenation of free radicals produced from the cracking of the coal, or to enhance the hydrogenation of aromatic structures and further to induce cracking of some linkages (in this case, it is usually called hydrocracking). In reactions when hydrogen-donor solvents are involved, the hydrogenation catalysts can also help to regenerate the donor by adding hydrogen to the dehydrogenated form. Among the hydrogenation catalysts, which usually contain a transition metal, the most extensively studied ones are Mo, Sn and Fe compounds. Researches have found that the active forms of the catalysts during liquefaction are metal sulfides. They are thermodynamically stable and can be formed by reacting with sulfur in the coal, or with added CS_2 or H_2S/H_2 [Derbyshire et al., 1986]. In most cases, Mo and Sn catalysts are more active than Fe catalyst. The reason that Fe catalysts are of interest is that they are abundant and of low cost.

The high activities of those acid cracking catalysts such as $ZnCl_2$, are realized only at high catalyst-to-coal ratio [Zieke et al., 1966a]. A typical weight ratio is one part catalyst to one part coal. Such a high catalyst amount necessitates its recovery. However, during reactions, some $ZnCl_2$ will react with compounds containing heteroatoms and one of the products is HCl. For example

$$ZnCl_2 + H_2S \rightarrow ZnS + 2\,HCl$$

$$ZnCl_2 + H_2O \rightarrow ZnO + 2HCl$$

$ZnCl_2$ and HCl will cause lots of corrosion problems as well as environmental problems. The hydrogenation catalysts, on the other hand, usually have much lower loading, e. g. 1% of dry and mineral-matter free basis of coal or even less. They can be considered as once-though or disposable catalysts, for example, Fe catalysts, which eliminates the recovery process.

In principle, catalyst activity depends on its active form and the degree of dispersion under a given reaction condition. In this section, studies on catalyst dispersion and catalyst active form during reaction will be summarized. The mechanism of catalysis will also be reviewed.

2.2.2.1 Catalyst Dispersion

As early as 1951, S. Weller and M. G. Pelipetz realized that the best possible catalyst distribution on coal should be sought for highest catalyst activity [Weller and Pelipetz, 1951]. They compared three catalyst loading methods: physical mixing, where the powered catalysts were added to the powered coal samples; ball-milling, where the catalyst and the coal were ball-milled for six hours; and impregnation, where the catalyst was first dissolved in water and then the solution was mixed with the coal sample. Their results clearly showed that the activity of a catalyst, determined by the overall conversion and yields of light product (e. g. oil), was much greater when it was impregnated on the coal from aqueous solution than that when it was added as powders to the coal. The ball-milling methods gave intermediate catalyst activity. Later Hawk and Hiteshue [1965] stressed the importance of catalyst dispersion as "catalyst must be present at the site of the smallest and most remote particle of coal at the instant when pyrolysis begins. Apparently, if catalyst is there, progressive and orderly molecular weight reduction predominates at temperatures where kinetics favor hydrogenation. If the catalyst is not there, formation of coke-like product and gases tends to be favored."

Comparing with the "dry method", that is, physical mixing or ball-milling, the "wet" impregnation method is more advantageous because it can spread the catalyst uniformly (on a molecular scale) in a solution before loading to the coal sample, while a dry method always loads clusters of a catalyst on to a coal. In the impregnation methods, there are different ways to dissolve the catalysts and impregnate them onto coal. The commonly used ones are solvent slurry [Weller et al., 1951; Hawk et al., 1965; Derbyshire et al., 1986; Cugini et al., 1988; Stansberry et al., 1987; Garcia and Schobert, 1989; and Artok et al., 1992a], incipient wetness [Cugini et al., 1991; Utz et al., 1992; Huang et al., 1992; and Eyring et al. 1992], preswelling [Joseph, 1991a and 1991b; Artok et al., 1991; Artok et al., 1992b, and Artok, et al., 1993], ultrasound [Eyring et al., 1992], microemulsion [Vaidyanathan, et al., 1992], and supercritical fluid (SCF) method [Warzinski, 1992].

In the solvent slurry method, a catalyst or a catalyst precursor is first dissolved in a certain amount of distilled water. Usually, the volume ratio of water to coal is one to one, or 1.5 to one. The solution is then added to the coal sample and stirred for at least 30 minutes followed by vacuum drying. In the incipient wetness method, the catalyst or catalyst precursor is also dissolved in a solvent similar to that in slurry method. However the amount of distilled water is predetermined so that it will be just enough to cover the coal surface. After mixing with the catalyst or catalyst precursor, the solution is added to the coal drop by drop while the coal is being stirred constantly in an effort to achieve a uniform coverage. In the ultrasound method, the mixing of the solution and the coal sample is done in an ultrasound bath in order to have the catalyst deposit inside pores of coal particles.

Because coal is a highly porous material with most of its surface area enclosed in micropores less than 20 Å in diameter [Mahajan, 1982], it is very important to open these pores and let the catalyst deposit on the internal surface of the coal. This is why the preswelling method is introduced as an impregnation technique. In this method, the catalyst or the precursor is dissolved in a swelling agent then added to the coal. The mixture is allowed to sit for at least 24 hours for coal swelling before drying.

A few groups have tried to study catalyst dispersion on coal. Davis' group has used scanning electron microscopy (SEM) associated with energy dispersive spectroscopy (EDS) to investigate iron and molybdenum catalysts dispersed on coal [Davis, 1989]. They studied ammonium tetrathiomolybdate (ATTM) dispersed on individual particles embedded in epoxy resin and dispersed on pulverized particulate coal sample by impregnation method. Their results showed that the catalyst precursor and the coal surface did not have strong bonds and, as time went on, the layer of ATTM might peel off from the coal surface. Even those catalyst particles which might initially penetrate into fractures during preswelling could be drawn out of the fractures and form clusters on the edges of fractures.

Eyring et al. [1992] used electron probe microanalysis (EPMA) to determine whether or not the method of catalyst impregnation seriously affects the yields of tetrahydrofuran (THF) solubles during hydropretreatment. The impregnation methods employed were incipient wetness and ultrasound. Their EPMA micrographs indicated that catalyst mobility occurred during hydropretreatment and therefore the impregnation techniques did not significantly affect the THF solubles yield after hydropretreatment.

Even though some people have attempted to compare some of the impregnation techniques, so far there is no comprehensive conclusion on whether or not the most commonly used technique will affect the catalyst efficiency. Neither is there an extensive study by physical methods to determine the dispersions of a catalyst using all the techniques. In an early stage of the research, three most commonly used impregnation methods, solvent slurry, incipient wetness and swelling were compared. The best one in terms of liquefaction conversion and product distribution was selected and used throughout the remainder of the research.

2.2.2.2 Active Form of Catalyst

Molybdenum compounds, such as ammonium tetrathiomolybdate (ATTM, $(NH_4)_2MoS_4$), molybdenum hexacarbonyl ($Mo(CO)_6$) or molybdate naphthanate, are widely used as catalysts or catalyst precursors, though other compounds, e. g. nickel acetylacetonate, are also used as catalyst precursors. This review will focus on the molybdenum compounds, especially ammonium tetrathiomolybdate.

Anderson and Bockrath [1984] tested several forms of molybdenum. Their liquefaction conversion, X-ray diffraction and Mossbauer spectrometry results indicated that the most active form is molybdenum disulfide. Since MoS_2 is usually generated in situ, it is necessary to understand the conversion from a precursor, i. e., ATTM, to the active form.

Early study by Prasad et al [1973] found that ammonium tetrathiomolybdate decomposed in two distinct steps under nitrogen atmosphere. The first step involved the decomposition to the trisulfide and the second step involved the decomposition of the trisulfide to the disulfide and elemental sulfur. The first decomposition started at 155°C with a maximum rate at 220°C, and completed at 280°C. The second decomposition started at 335°C. Their and Ya et al's [1961] differential thermal analysis (DTA) results showed that the first decomposition was endothermic. In the second decomposition, there was an exothermic peak between 350°C and 400°C, presumably representing the combined effects of the decomposition of the trisulfide, volatilization of sulfur and recrystallization of the amorphous disulfide. The two reactions can be expressed as the following:

$$(NH_4)_2MoS_4 \rightarrow 2\,NH_3 + H_2S + MoS_3$$

$$MoS_3 \rightarrow MoS_2 + S$$

Romanolvski et al. [1963] also studied the decomposition of thiomolybdate but under hydrogen atmosphere. They found that, fortunately to our benefit, the decomposition of trisulfide to disulfide in the second step is faster under hydrogen atmosphere. In this case, the second decomposition step may be expressed as

$$MoS_3 + H_2 \rightarrow MoS_2 + H_2S$$

The trisulfide and disulfide have been studied by many people [Wells et al., 1950; Wilson et al., 1969; Dickson et al., 1923; Hassel et al., 1925; Bell et al., 1957; Jellinek et al., 1960; and Wildervanck et al., 1964]. The former is amorphous regardless of the preparation method while the latter has a layered structure with weak forces between layers. Each layer consists of a sheet of Mo atoms sandwiched between two sheets of S atoms [Joensen et al., 1986]. Surface area of molybdenum disulfide depends on its preparation procedure. Eggertsen et al. [1959] demonstrated that temperature, rate and atmosphere under which MoS_3 was converted to MoS_2 determined the surface area. The optimum condition, producing MoS_2 with surface area as high as 158 m^2/g, was found at 450°C, under H_2 atmosphere and with fast heating rate. While at the same condition but with a slow heating rate, the surface area was only 2 m^2/g. At other temperatures lower or higher than 450°C, or under inert atmosphere, MoS_2 of lower surface area will be produced.

2.2.2.3 Mechanism of Catalysis

The sulfided transition metals such as Mo and Fe are believed to function as hydrogenation catalysts. The role of the catalysts is to provide hydrogen atoms by catalytic dissociation of molecular hydrogen. The hydrogen atoms can stabilize coal-derived free radicals, induce bond cleavage [McMillen et al., 1985a, 1985b, and 1987; Vernon, 1980], or regenerate hydrogen donor-solvent. Thus the catalysts can be considered as transformers which take in hydrogen molecules, break the H-H bond and inject H-atoms into coal or coal-solvent mixture and thereby increase the amount of available hydrogen. To use the H-atoms efficiently, the catalyst or the H-atom has to be present at the reaction sites. This again shows the importance of a high catalyst dispersion. However, even at high levels of dispersion, a large proportion of the catalyst centers are still in remote distances from the reaction sites where the H-atoms are needed mainly due to the fact that the catalyst loading is usually low and the number of reaction sites can be tremendously large. Derbyshire [1990 and 1991] proposed a spill-over mechanism. It is suggested that H_2 molecules are dissociated at an active site on the surface of a catalyst, the resulting H-atoms then diffuse from the site into the structure of a coal, Figure 2.5. Therefore, the effectiveness of a catalyst depends on its composition, which determines the catalytic ability to dissociate hydrogen molecules, and its dispersion on the coal, which determines the availability of the derived H-atoms to the reaction sites.

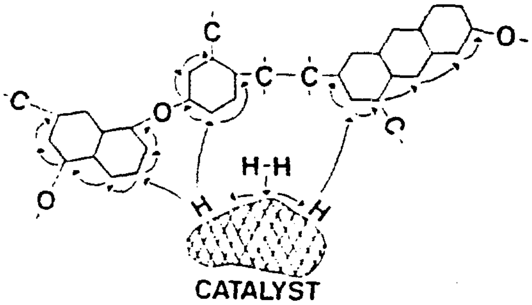


Figure 2.5 Distribution of H atoms by hydrogen spillover. The H atoms were produced by catalytic dissociation of H2. H atoms induce bond cleavage and stabilize radicals. [Derbyshire, 1990]

2.2.3 Temperature Condition in Coal Liquefaction

The "temperature-condition" refers to temperature level, reaction time and how temperature changes with time during reaction. Low-rank coals are characterized by small aromatic ring clusters, long-chain and crosslinked aliphatics, abundant heteroatom contents [Schobert, 1990]. This structural feature determines that the coal macromolecule may be broken down at low temperatures. As it is known that once the coal matrix is broken down and free radicals are produced, the next step is to stabilize the free radicals by hydrogenation. Very often, the rate of hydrogenation can not catch up with that of formation of free radicals, which will result in undesirable retrogressive reactions. In order to match the rate of hydrogenation and the rate of free-radical formation, two approaches can be taken. The first one is to accelerate the rate of hydrogenation by using a good reaction solvent or an active hydrogenation catalyst as mentioned in the previous two sections. The second is to slow down the rate of free-radical formation by controlling the reaction temperature properly, which is the main discussion of this section.

The most often used temperature conditions can be classified into three categories: single-staged liquefaction (SSL), temperature-staged liquefaction (TSL) and temperature-programmed liquefaction (TPL). In single-staged liquefaction, only one temperature level is applied. The reaction time is usually 30 minutes to one hour. According to the heat-up procedure, the single-staged liquefaction can further be classified as slow heat-up SSL, where the reactants are slowly heated up from room temperature to the desired temperature, and fast heat-up SSL, where the reactants are heated up to the reaction temperature in a very short time, usually less than 5 minutes. In temperature-staged and temperature-programmed liquefaction, two temperature levels are involved. The low temperature, usually between 200 to 350°C, is designed for pretreatment, and the high temperature is between 400 to 500°C for reaction. In temperature-staged liquefaction after pretreatment, the reactor is immediately heated to the high temperature either by fast heating or by moving the reactors from one surrounding (i. e. a sandbath) with the low temperature to another one with the high temperature. In temperature-programmed liquefaction, there is a slow heat-up period between two temperature stages. The heat-up time is usually 30 minutes or longer. The reactions at the lower temperature and those during the heat-up period in TPL are considered as pretreatment stages designed for 1) the transformation of the catalyst from its precursor form to the active catalyst form; 2) the penetration of reaction solvent into coal particles to achieve a good contact between the solvent and the coal; 3) slowing down some cracking of the coal structure, which may occur too fast at high temperature and cause retrogressive reactions.

The single-staged liquefaction is the most commonly used procedure. It is simple but the drawback is that it may cause problems, especially for low-rank coals. This is because different kinds of chemical bonds may be broken at the reaction temperature. Some of them will be broken so fast that hydrogenation can not catch up, which causes retrogressive reaction. Some of them will be broken so slowly that reactions may not be able to go to a significant extent during the reaction time. Both of these cases will result in low conversion and hence are undesirable. Therefore, it is worthwhile to carry out the liquefaction of low-rank coals under more complicated temperature conditions, that is the temperature-staged or temperature-programmed conditions. In fact, some people [Derbyshire et al., 1986; Epstein, 1987; Derbyshire, 1988; Derbyshire et al., 1986; Derbyshire et al., 1983; Bockrath et al., 1986; Narian, 1985; Potte, and Broche, 1934; Tsucarda et al., 1987] have compared results of SSL and TSL and found that liquefaction conversions as well as yields of light distillation fraction were improved by using TSL. Recently, some work done at Penn State [Song et al., 1992; Song and Schobert, 1992; Huang et al.,1992] comparing the three temperature conditions also suggests that it is beneficial to chose a TPL or TSL over a SSL condition.

In this work, the three conditions will be applied to low-rank coals and reactions will take place in the presence of different solvents or catalysts. Liquefaction conditions and product distributions will be studied to evaluate the benefit of different temperature conditions. The effect of temperature condition will also be compared with those of solvents or catalyst so to find the optimum condition for a given coal.

CHAPTER 3

CHARACTERIZATION OF THE COALS AND BACKGROUND SETUP

Liquefaction is a process to break macromolecules of coals into small ones. Different coals may behave differently according to their structural characteristics. For high-rank coals, carbon contents are high; hydrogen and oxygen contents are low; aromaticities (f_a) and ring condensations (R) are high. This implies that the coals contain high percentages of aromatic carbons and aromatic ring clusters are large; on the other hand, alkyl bridges between aromatic rings and oxygen functional groups are not as abundant as in low-rank coals. This structural feature determines the liquefaction behaviors of high-rank coals. For instance, it may require high temperatures for thermal cleavages of the bonds, and also retrogressive reactions caused by oxygen functional groups and condensation of aromatic rings may not be as severe as for low-rank coals. Therefore, in order to make liquefaction reaction efficient, it is very necessary to study the structures of coals first.

Liquefaction has been studied for a long time; many results and conclusions are based on different reaction conditions. For example, some investigators dry their coal samples before using them for liquefaction reactions, while others claim that the moisture inherently existing in the coals is beneficial for high conversions [Song et al., 1994]. Another example is that liquefaction reaction time ranges from a few minutes to a few hours depending on the researchers. Therefore it is necessary to establish a standard condition for this study before we start it.

In this chapter, results of a study of the coal samples, especially on their compositional and structural properties, are presented. Comparative studies regarding drying and reaction time were carried out and standard reaction conditions were set for later studies.

3.1 Characterization of the Selected Coals

Three low-rank coals have been chosen to be studied. They are a Texas subbituminous C (DECS-1), a North Dakota lignite (DECS-11) and a Montana subbituminous B coal (DECS-9). The coals were obtained from the Pennsylvania State University coal sample bank. The samples were stored in multi-layer laminated bags under argon atmosphere. Information about their origins, data of proximate analysis and ultimate analysis is summarized in Table 3.1.

Proximate analysis indicates that these low-rank coals contain 30% moisture on an as-received basis. If the moisture is kept as it is within coals, some energy will have to be used to transport moisture from one place to other. It is also true that a considerable amount of energy will be used to heat moisture to the desired temperature in liquefaction process. Therefore it is economically undesirable to keep the moisture. Therefore the inherent moisture in coals should be kept only if it is proved that it can be significantly beneficial to liquefaction.

Ultimate analysis shows that all of the three coals have carbon contents around 75% and hydrogen contents about 5% on a dry and mineral-matter free basis, which

Table 3.1 Analysis of the three coal samples

	DECS-1	DECS-11	DECS-9
Sources & Rank			
state	Texas	North Dakota	Montana
county	Freestone	Mercer	Bighorn
city	Fairfield		Decker
seam	Bottom	Beulah	Dietz
ASTM rank	subbit C	lignite	subbit B
sampling date	12/11/89	6/15/93	6/12/90
Proximate (wt%, ar)			
moisture	30.0	33.4	24.7
ash	11.1	6.4	4.8
volatile	33.2	37.4	33.5
fixed carbon	25.8	22.9	37.1
Elemental (wt%, dmmf)			
carbon	76.1	74.2	76.1
hydrogen	5.5	4.4	5.1
nitrogen	1.5	1.0	0.9
organic sulfur	1.1	0.4	0.3
oxygen (by difference)	15.8	20.0	17.5

suggests that atomic ratio of hydrogen to carbon (H/C) is about 0.9. Roughly speaking, the goal of liquefaction is to make solid coals to petroleum-like liquid fuels by breaking bonds and adding hydrogen. For petroleum the atomic H/C ratio is approximately 2. A straightforward arithmetic calculation indicates that in order to achieve the liquefaction goal, approximately 3.8 mole (or 7.5 gram) of H_2 should be added to every 100 grams of coal if there is no other consumption of H_2 in the process. However for low-rank coals, oxygen contents are high, e. g. about 15% for these three coals. For example, the oxygen in coals can react with H_2 and form H_2O. Thus hydrogen consumption should be higher than 7.5 grams of H_2 per 100 grams of coal in order to achieve a H/C ratio of 2.

Solid-state ^{13}C NMR and Fourier transform infrared spectroscopy can be combined to obtain insight into coal structural features. In principle, FTIR measurements can be used to quantitatively determine the aliphatic CH, aromatic CH and OH contents of coal, whereas solid-state ^{13}C NMR spectroscopy can be used to determine the proportions of aromatic carbon in a coal (f_a) [Miknis et al., 1979, 1981; Zilm et al., 1981; Painter et al., 1983]. With these measurements, a number of functional structural parameters (such as Har/Car, Hal/Cal, Har/Hal) can be calculated. Furthermore, with one additional parameter, the number of methyl groups (as measured by the fraction of aliphatic carbon or hydrogen involved in these groups), it should be possible to determine the distribution of aliphatic carbon (i. e. the relative proportions of CH, CH_2.and CH_3 groups) and then to describe "mean structural units" in terms of average aromatic ring size and the type and distribution of bridging units and substituents [Painter et al., 1985].

The solid-state ^{13}C NMR spectra were acquired on a Chemagnetic M-100 NMR spectrometer at a frequency of 25.1 MHz. High-power proton decoupling, cross-polarization and magic-angle-spinning (CPMAS) techniques were combined for high-quality spectra. The measurement conditions for all the samples were as follows: a cross-polarization contact time of 1 ms and a pulse delay time of 1 second. Instrumental calibration test was performed with hexamethylbenzene (HMB) for correct chemical shifts assignment. For each experiment, about 0.4-0.6 g of a sample was packed in a 0.4 mL bullet-type rotor made of polychlorotrifluoroethylene (Kel-F). The spinning speed of the rotor was about 3.5 kHz. In order to obtain spectra with high signal-to-noise ratios, the number of scans accumulated was between 10,000 to 40,000, depending on the amount of mineral matter contained in the sample. For quantitative evaluation, the NMR spectra were first digitized using a UN-PLOT-IT program (version 3) developed by Silk Scientific, Inc. in 1990. The digitized data were then input into computer and processed for peak separation and quantitative calculation of specific bands using Lab Calc software developed by Galactic Industries Co. in 1990. Aromaticity of a sample can thus be calculated using the peak area of aromatic carbons divided by the peak areas of both aromatic and aliphatic carbons.

Table 3.2 presents the NMR peak assignments. In general, there are two major spectral bands: an aromatic band centered at 130 ppm and an aliphatic band centered at 30 ppm. Among the aliphatic carbons, methyl groups are located at 0-25 ppm, methylene carbons at 25-50 ppm, methoxyl groups around 50-60 ppm, and ether groups between 65 to 80 ppm [Yoshida et al. 1987; Franco et al. 1991; Song et al., 1992 and Song et al., 1993]. The two shoulders on the left-hand side of the aromatic band are due to catechol-like carbons (around 142 ppm) and phenolic carbons (around 152 ppm). The two bands with lower intensities are carboxyl groups at 170-190 ppm and carbonyl groups at 190-230 ppm.

Table 3.2 Chemical shifts of carbon in ^{13}C NMR spectra of coal extracts [reproduced from Snape et al., 1979]

Chemical Shift, ppm	*Carbon type*
170-210	carbonyl
148-168	aromatic C-O
129.5-148	mainly aromatic C-C and aromatic C-NH
100-129.5	mainly aromatic C-H with aromatic C-H ortho to C-OH between 100 and 115 ppm
37-60	ring joining methylene (32-43 ppm), CH in alkyl groups (except iso-alkyls) and naphthenic ring; CH_2 in alkyl groups adjacent to CH
27.5-37	CH_2 in alkyl groups not adjacent to CH (except some α-CH_2 and CH_2 adjacent to terminal CH_3 in alkyl groups >C_4. CH_2 in ring joining ethylene groups. α-CH_2 and CH, β-CH in hydroaromatic rings; naphthenic CH_2
24-27.5	naphthenic CH_2; shielded α-CH_2 groups, β-CH_2 in indan and propyl groups; β-CH_3 in isopropyl
22.5-24	CH_2 adjacent to terminal CH3 in alkyl groups>C_4; β-CH_2 in unsubstituted tetralin structures; CH_3 on hydroaromatic and naphthenic rings (18-24 ppm)
20.5-22.5	α-CH_3 not shielded by any adjacent rings or groups
18-20.5	α-CH_3 shielded by 1 adjacent ring or groups
15-18	β-CH_3 in ethyl groups
11-15	CH_3 γ or further from an aromatic ring α-CH_3 shielded by two adjacent rings or groups

Figure 3.1 shows the NMR spectra of these three raw coals. Generally speaking, these three coals contain significant amounts of aliphatic carbons and considerable amounts of oxygen, as expected for low-rank coals. Comparing the three coals, DECS-1 has a sharp and intense peak at about 30 ppm, indicating that this coal contains more long-chain aliphatic carbons than the other two coals. The DECS-11 and DECS-9 coals seem to have higher percentages of methoxyl groups than the DECS-1 coal. All of the these coals contain catechol and phenolic groups, but the ratio of catechol-like carbons to phenolic carbons (C/P) are different. The DECS-1 coal has the highest C/P value while the DECS-11 coal has the lowest. In the 170-190 ppm region, considerably intense peaks are observed in all three spectra suggesting that the coals all possess carboxyl groups. After curve-fitting and integration using the Lab-Calc program, aromaticities of the three coals were calculated. They are 0.48, 0.53, and 0.62 for DECS-1, DECS-9 and DECS-11 respectively.

The structural features of the three coals were also qualitatively and semi-quantitatively compared by Fourier transfer infrared spectra. The spectra were recorded on a Digilab FTS 600 system. For each spectrum, at least 400 scans were accumulated at a resolution of 2 cm^{-1}. The samples were prepared in the form of KBr pellets. About 2 to 3 mg of coal sample was accurately weighed, mixed and ground with about 30 mg KBr for 30 s in a Perkin-Elmer Wig-L-Bug. An additional 270 mg KBr was added to the mixture and ground for 1 minute for a good dispersion. The mixture was transferred to a mold and pressed to make a pellet with diameter of 13 mm. The pellet was weighed and the actual weight of coal in the pellet was calculated. All FTIR spectra were normalized to 1 mg of organic matter of coal.

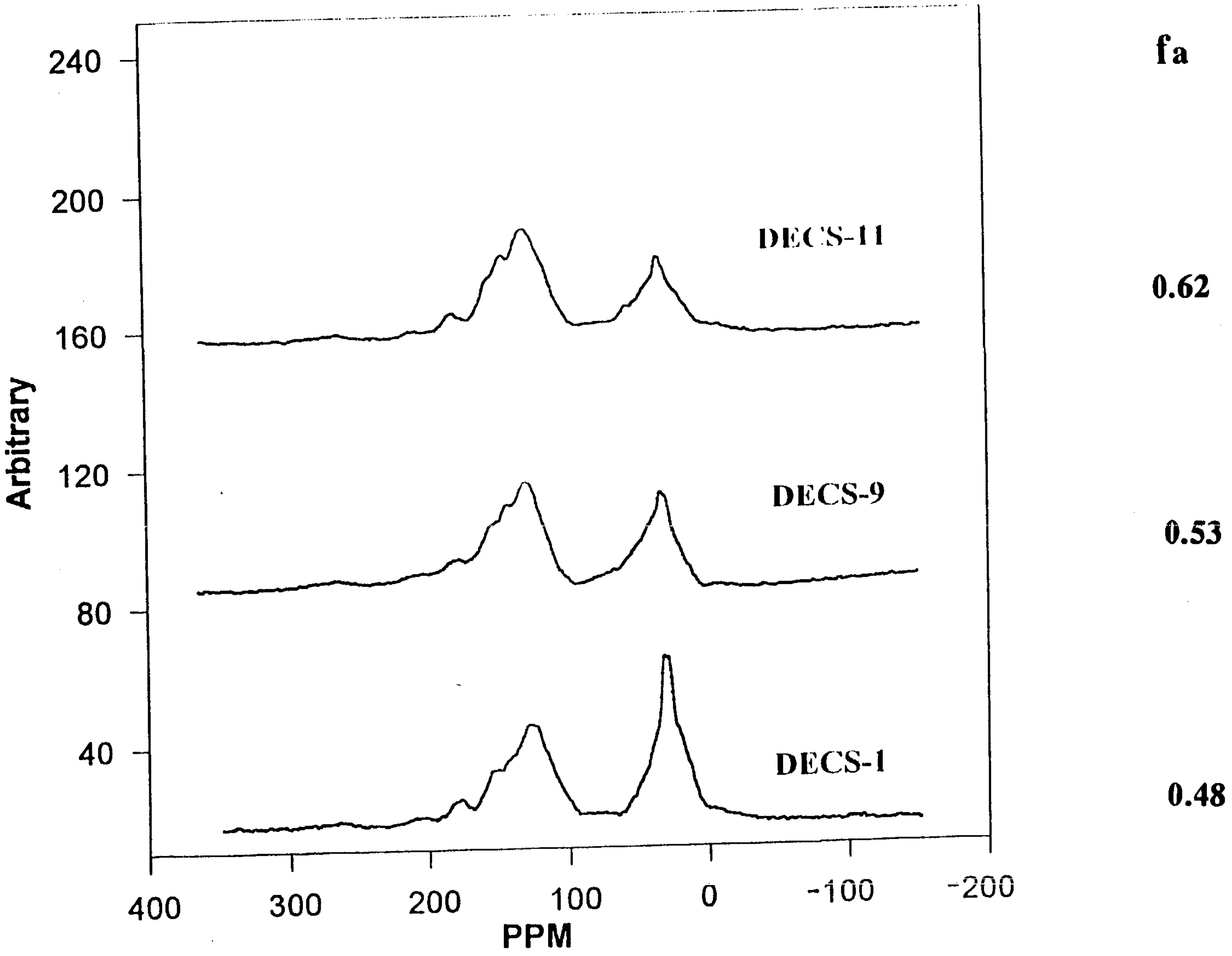


Figure 3.1 ^{13}C NMR spectra of the three dried coals

Figure 3.2 presents the FTIR spectra of the three coals, where the ordinate represents the absorbance in arbitrary units, and the abscissa represents the wavenumber in reciprocal wavelength (cm^{-1}). The broad band around 3550-3350 cm^{-1} is due to phenolic OH group and water. Several overlapped bands are observed between 2700 and 3000 cm^{-1}. The modes at 2950 and 2923 cm^{-1} can be considered as a composite of various overlapping contributions. Methyl groups directly attached to aromatic rings have a band near 2950 cm^{-1} (as well as a strong mode at 2925 cm^{-1}), methyl groups attached to other alkyl groups have bands between 2960 and 2970 cm^{-1}, and methylene groups in certain types of hydroaromatic structures absorb near 2950 cm^{-1}. Because of these complications it is of little use to distinguish the band between 2900 cm^{-1} and 3000 cm^{-1} for various types of aliphatic structures. The modes at 2850 and 2865 cm^{-1} are potentially of some value in providing at least an approximate measurement of methylene and methyl group contents. In order to obtain a measurement of total aliphatic CH content of a coal, the entire area between 2995 and 2750 cm^{-1} has to be integrated, assuming that the average value of the absorption coefficient (relating band intensities to the concentration of the appropriate functional groups) stays approximately constant from coal to coal [Painter et al, 1985]. Comparing these three coals, DECS-1 has the largest area in this range followed by DECS-9 and DECS-11, suggesting that the DECS-1 coal has the highest content of total aliphatic CH groups while the DECS-11 coal has the lowest. This is in a good agreement with the NMR data.

The shoulders observed in the three spectra at about 1700 cm^{-1} are assigned to carbonyl groups, which are also seen in NMR spectra. The relative intensities of the peak at 1600 cm^{-1} and that at 1450 cm^{-1} are found to be different for these three coals. The first peak can be attributed to an aromatic ring stretching mode and the latter is assigned to an aliphatic bending mode. For the DECS-1 and DECS-9 coals, the relative intensities

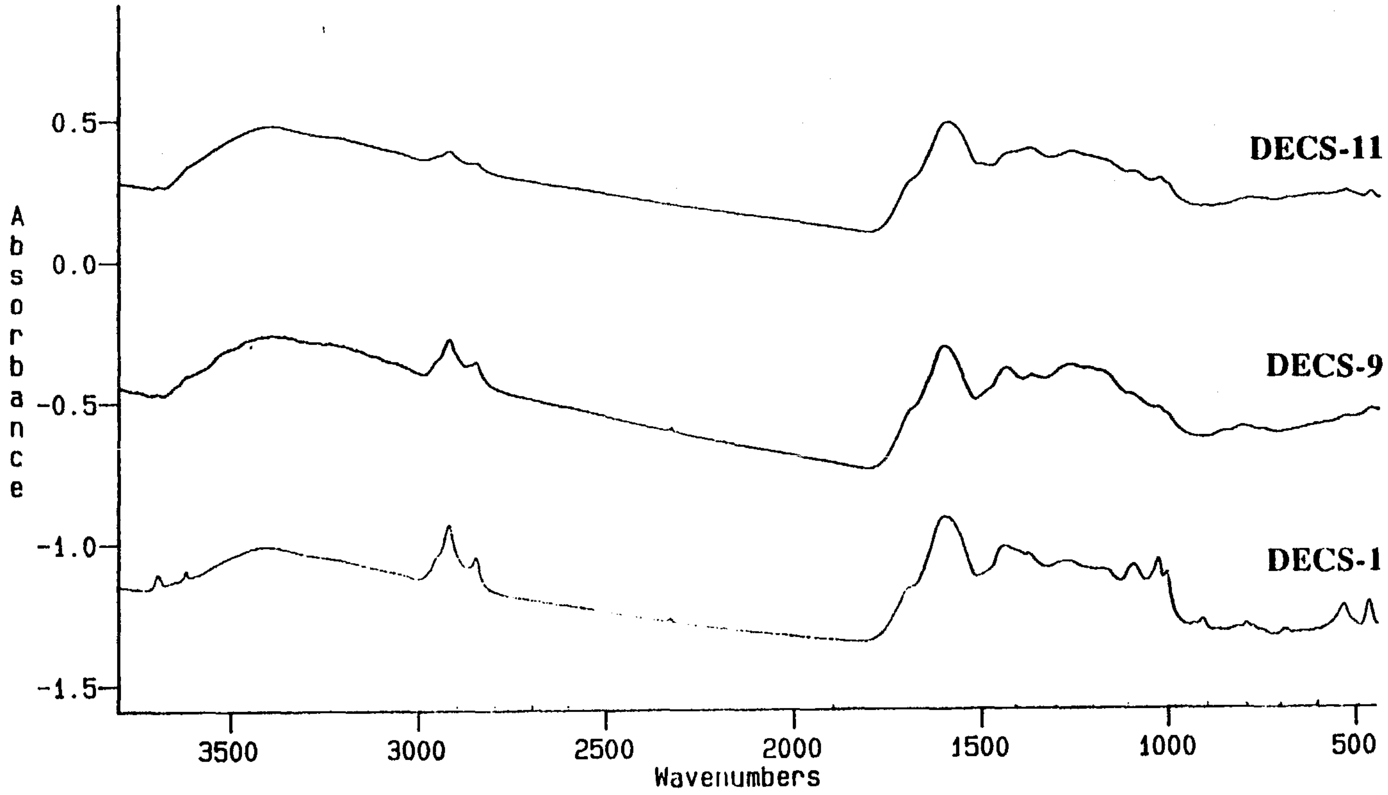


Figure 3.2 FTIR spectra of the three dried coals

of the peak at 1450 cm^{-1} are higher than that of the DECS-11 coal, which again suggests that the DECS-11 coal has lower aliphatic content than the other two coals.

3.2 Background Setup for further Study

3.2.1 Reaction Procedure and Product Work-up

Liquefaction experiments were carried out in horizontal microautoclave reactors (tubing bombs). The reactors were made of type 316 stainless steel tubing (3/4" o.d.) with threaded Swagelok weld-on fittings at both ends. In the middle of the reactor tube, a piece of 1/4" stainless steel tubing was welded vertically. On top of the 1/4" tubing, a gauge, a needle valve and a quick-connect stem were attached for purging and pressurizing the reactor. Prior to each reaction, the tubing bombs were tested for possible leakage by pressurizing the reactors to 7 MPa with N_2 and immersing into water.

For each experiment, 4 grams of a coal sample and 4 grams of solvent (if a solvent is used) were loaded to a reactor. The reactor was sealed and tested for leakage. Then it was purged with hydrogen three times to remove any captured air. Subsequently, the reactor was pressurized to 7 MPa with hydrogen at room temperature. Once a reactor was loaded, sealed and pressurized, it was ready for experiment. It was attached to an oscillator and plunged into a pre-heated fluidized sandbath with a desired temperature. The reactor usually can reach the desired temperature in about 3 to 5 minutes. Once it reached the reaction temperature, the reactor was kept at that temperature in the sandbath for 30 minutes unless otherwise indicated. The reaction time will be further discussed in section 3.2.3. The reactor was oscillated at 200 revolutions per minute at an amplitude of

2.5 cm during the course of the reaction. After reaction, the oscillation was stopped and the reactor was rapidly removed from the sandbath and immediately quenched in a water bath to ensure an instantaneous cooling. After staying in the water bath for a few seconds, the reactor was removed and dried by blowing pressurized air towards it to make sure that there were no water drops remaining inside the threads of the tubing bomb. The reactor was allowed to sit for a few hours to equilibrate with room temperature before product separation.

The gas sample was carefully collected into a gas sample vial and the volume was measured using water displacement method. The reactor was uncapped and the contents were scraped out and transferred with a spatula to a weighed ceramic thimble. The reactor, including the stem, was thoroughly washed using hexane. The liquid coming out of the reactor was filtered through the thimble. The product mixture was then separated by Soxhlet extraction using hexane, toluene and tetrahydrofuran in sequence, Figure 3.3. Usually the amount of solvent used for extraction was about 250 mL (contained in a weighed flask) and the time for each extraction was approximately 24 hours (until the liquid coming out of the thimble was colorless). The hexane solution was concentrated using a rotary evaporator and then collected and stored in a small sample vial under nitrogen atmosphere. The toluene and THF were evaporated by the rotary evaporator and the remaining product was dried in a vacuum oven at 105°C for 6 hours. The solid left behind in the thimble was washed several times with acetone first and then with pentane followed by drying in a vacuum oven at 105°C for at least 6 hours. After drying, the products were weighed, and stored under nitrogen atmosphere. The products were classified as oil, asphaltene and preasphaltene for the hexane solubles, toluene solubles and THF solubles respectively, Figure 3.3. The THF insolubles are called residues. The conversion and yields of gas, asphaltene, preasphaltene and residue were calculated based

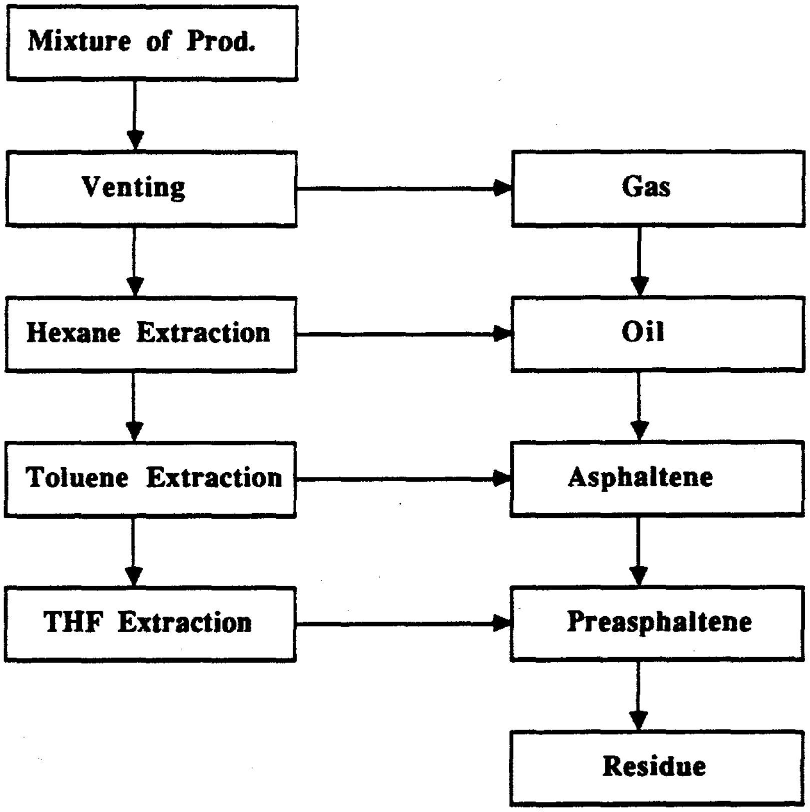


Figure 3.3 Procedure of products separation in liquefaction

on the dry and mineral-matter free coal. The oil yield, however, was obtained from the difference between the dry and mineral-matter free coal and the the total amount of gas, asphaltene, preasphaltene and residue.

3.2.2 Effect of Moisture in Liquefaction

Since the three coals under study contain moisture as high as 30%, it is necessary to determine whether or not we should dry the coal samples before any use. Liquefaction experiments were carried out using raw coals and dried coals. The so-called raw coals are the samples sealed in multi-layer laminated bags under argon atmosphere, as provided by the Penn State Coal Sample Bank. The dried samples are obtained by keeping the raw coals in a vacuum oven at 95°C for about 3 hours so to remove 98% of moisture. After drying, the samples were kept in glass sample vials under N_2 atmosphere. Table 3.3 shows the results of liquefaction reactions at 400°C with no added solvent or catalyst. This mild reaction condition (with no organic solvent, no catalyst) was chosen to minimize the (organic) solvent and catalyst effect and maximize the effect of moisture, if there is any. Comparing results of the liquefaction experiments, the dried coals and the raw coals give very close conversion values, but remarkably different product distributions. For a better comparison, the conversion and product distribution of the DECS-11 coal are selected to be an example and plotted in Figure 3.4. It is apparent that the drying process yields more desirable products, such as oils and asphaltenes. The moisture, in the experiments with raw coals, seems to have an effect on breaking down molecules (i.e. preasphaltenes) and formation of small ones, such as gases, and thus shifts the average molecular weight of product to the lower end. Therefore even though the raw coals and the dried coals do not show any significant difference in terms of

Table 3.3 Moisture effects on the three coals at 400°c without a solvent or a catalyst

Coal Number	Sample Condition	Conv. (%dmmf)	Gas	Oil	Asph.	Preasph.
DECS-1	**raw**	40.1	16.3	16.0	4.0	3.7
	dried	45.0	11.6	19.8	3.4	10.2
DECS-9	**raw**	21.0	12.1	4.2	1.7	3.0
	dried	24.2	7.1	11.0	1.5	4.6
DECS-11	**raw**	29.7	19.3	6.2	1.9	2.2
	dried	30.6	11.7	14.3	0.4	4.2

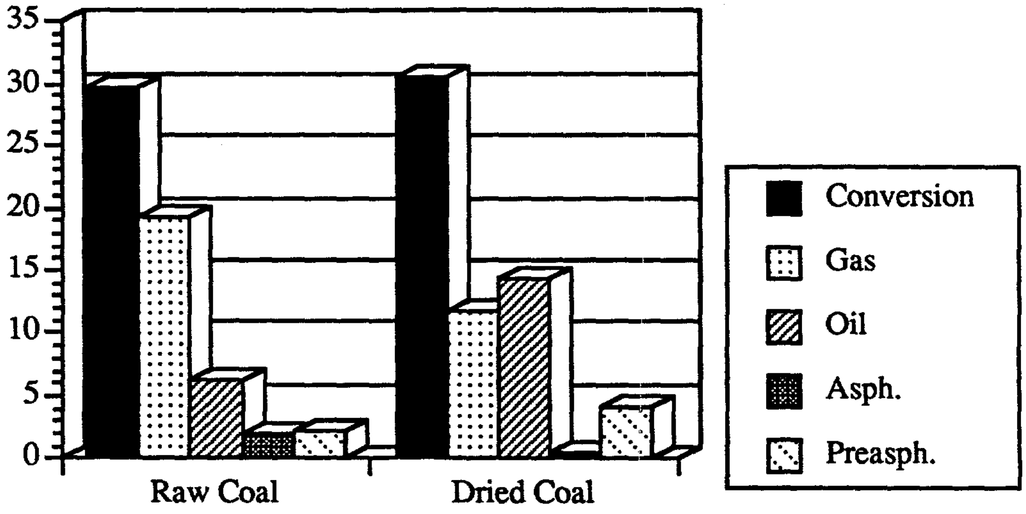


Figure 3.4 Effects of moisture on liquefaction of the DECS-11 coal at 400°C with no solvent or catalyst

conversion, the drying is beneficial for a desirable product slate under this reaction condition. The behavior of the moisture is certainly of great interest and is worthy of future research. Nevertheless, for the purpose of this work, the coal samples were all dried before liquefaction reaction.

3.2.3 Reaction Time

To determine the effect of reaction time on the liquefaction conversion and thus to set a standard for later study, the DECS-1 coal was used. Reactions were carried out at 400°C, and the reaction times were 10 minutes, 30 minutes and 60 minutes. Ammonium tetrathiomolybdate was applied as a catalyst precursor, and it was dispersed on the coal samples before reactions. The experiments can be studied in three categories: the first group involves reactions with no reaction solvent; the second one with a hydrogen-donor solvent, tetralin; and the third one with a non-donor solvent, 1-methylnaphthalene.

The conversion and product distribution of reactions with no solvent are presented in Figure 3.5. At 10 minutes, about 84% of the dried and mineral-matter free coal has converted to THF solubles with 45% (of the coal) contributed by oil, 23% by asphaltene, 9% by preasphaltene and 7% by gas. As reaction time increases to 30 minutes, an additional 8% of conversion is achieved, and more oil while less asphaltene are obtained. In other words, increasing the reaction time from 10 minutes to 30 minutes favors the conversion from heavy products to light products. However, further increase of the reaction time to 60 minutes does not seem to be beneficial. The total conversion drops as well as the oil yield, while the yield of gas, the undesirable product, increases. Therefore in liquefaction with no solvent, the proper reaction time is 30 minutes at this temperature.

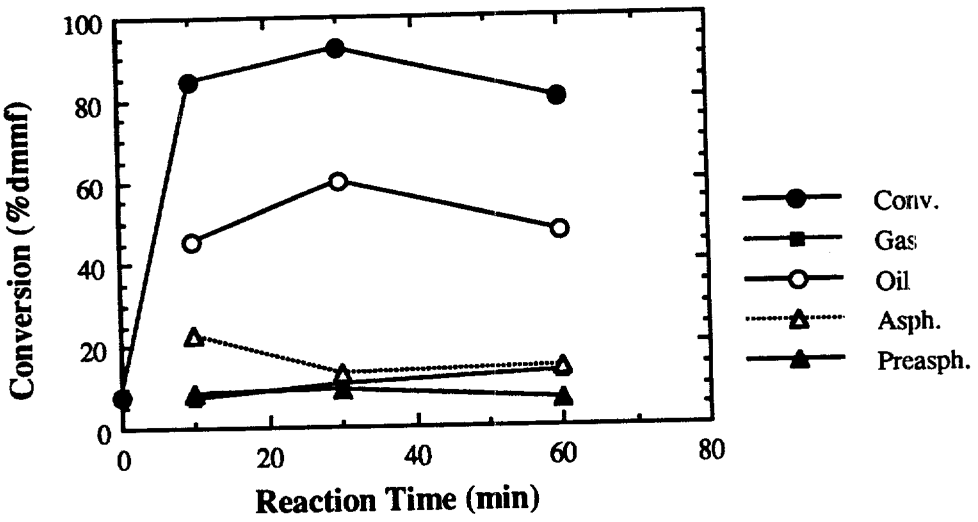


Figure 3.5 Effects of reaction time on the catalytic liquefaction of the DECS-1 coal with no solvent

Reactions with the presence of tetralin are shown in Figure 3.6. The 10 minutes reaction with the hydrogen donor solvent does not yield conversion (67%) as high as that with no solvent (84%). This indicates that the donor solvent has not yet fully penetrated into the pores and to the reaction sites, which is in a good agreement with an earlier finding by Tye et al. [1985] that tetralin, because of its large size, is unable to penetrate some of the pores of coal at room temperature. The existence of the solvent builds a barrier between H_2 gas and the coal, so hydrogenation by H_2 is inhibited. On the other hand, because of the existence of the solvent, more time might be needed in order to heat the reactants to the desired temperature. Therefore the use of the donor solvent under this condition is actually not beneficial. When reaction time increases to 30 minutes, there are drastic jumps in conversion as well as in oil and asphaltene yields. The yield of preasphaltene, however, drops slightly. Different from the reactions with no solvent, when reaction time further increases to 60 minutes, the conversion reaches (practically) the maximum, about 95%. The oil yield continues to increase in this case at the expense of asphaltene. The gas yield as well as the preasphaltene yields remain almost unchanged compared with those with 30 minutes reaction time. The continuing increases in conversion and oil yield represent an advantage of using the donor solvent.

Reactions with the non-donor solvent (1-methylnaphthalene) show a similar trend to that with the donor solvent regarding changes in reaction time, Figure 3.7. In a 10 minute reaction, only 60% of the coal is converted to THF solubles with 22% oil. As time increased to 30 minutes, 85% conversion and 40% oil yield are achieved. When the time is increased to 60 minutes, the conversion remains the same while the oil yield continues to increase at the expense of preasphaltene, which is different from the reactions with tetralin.

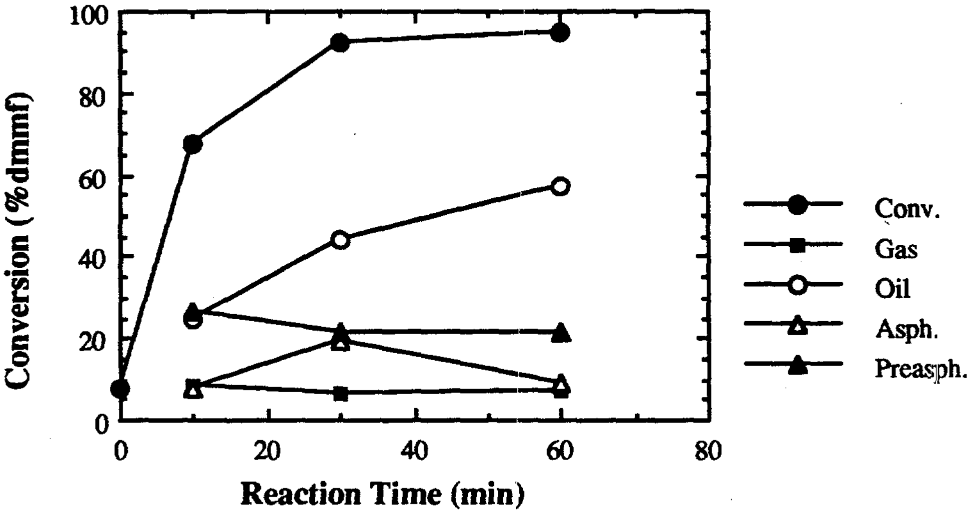


Figure 3.6 Effects of reaction time on the catalytic liquefaction of the DECS-1 coal with tetralin

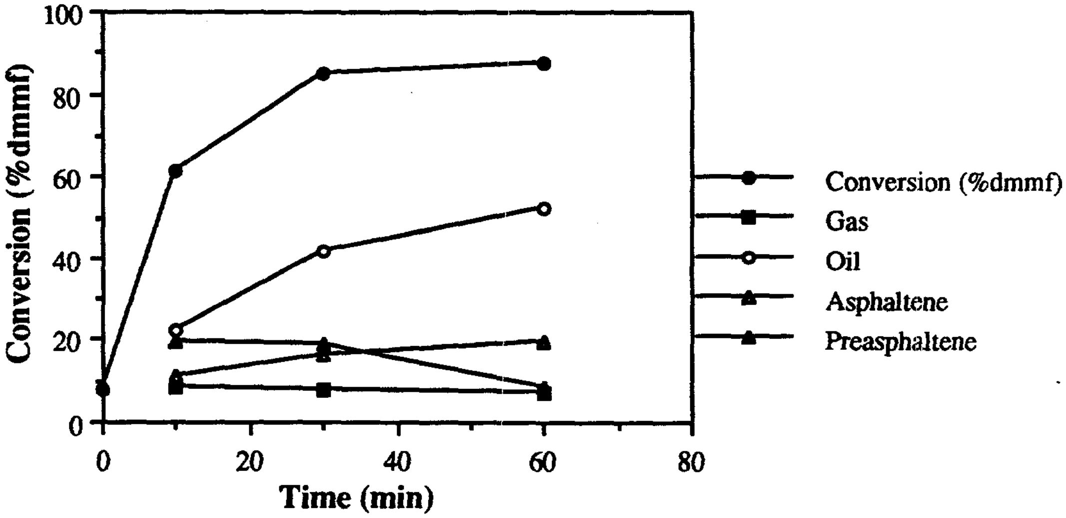


Figure 3.7 Effects of reaction time on the catalytic liquefaction of the DECS-1 coal with 1-MN

Based on the above study, it is apparent that the conversion from the coal to THF solubles is a fast process. Within 10 minutes, considerably high conversion can be achieved. The conversions from asphaltene to oil and from preasphaltene to oil are slow, and they require longer reaction time. However, if the reaction time is too long (e. g. 60 minutes), the conversion as well as oil yield may drop, especially in reactions with no solvent. Therefore to achieve a useful compromise, it seems that 30 minutes is the proper reaction time.

CHAPTER 4

EFFECT OF TEMPERATURE CONDITIONS

It was recently recognized that low-rank coals are more reactive than had been thought previously, and their conversions in high-severity process are accompanied by significant retrogressive reactions [DOE COLIRN Panel, 1989]. Low-rank coals are characterized by small aromatic ring clusters, abundant aliphatic and hydroaromatic carbon and hydrogen, high oxygen contents and various functional groups [Schobert, 1990]. Because of the presence of various C-O and C-C bonds in low-rank coals, bond dissociation energy (BDE) may be distributed in a broad range. At relatively low temperature, some bonds, for instance some C-O bonds, may be readily broken. In fact, Song et al. [1991 and 1986] demonstrated that more bonds in low-rank coals were thermally broken at low temperature than high-rank coals. Once a bond is cleaved, a pair of free radicals is generated. If these radicals are stabilized by hydrogenation, molecular weight reduction is achieved and the goal of liquefaction is accomplished. Therefore for low-rank coals, the question is how to effectively stabilize free radicals which may be generated in a wide temperature range. Since different bonds may be cleaved at different temperatures, it may not be the optimum condition if only one temperature is applied. The temperature-staged liquefaction (TSL) and temperature-programmed liquefaction (TPL) conditions are thus designed in an effort to cleave some weak bonds at low temperatures with reasonable rates so to match the rate of hydrogenation. In this chapter, experimental procedures of TPL, TSL, and SSL (single-staged liquefaction) will be described in detail. Comparative studies among the three conditions using low-rank coals will be demonstrated.

4.1. Experimental Procedure

In general, the single-staged reaction involves one temperature. The temperature-staged has a low-temperature stage for pretreatment. The temperature-programmed condition, in addition to the the two temperature stages in TSL, has a slow heat-up period between the two temperature stages. Under all three conditions, reactants were kept at the high temperature (the reaction temperature) for 30 minutes, based on the study in Chapter 3. Details of the reaction procedure will be stated in the following.

Figure 4.1 shows the temperature profile in a single-staged reaction. In practice, the sandbath is preheated to the desired reaction temperature before the reactor (tubing bomb) is plunged into it. Usually the reactor can be heated to the sandbath temperature in about 5 minutes. Starting at the moment that the reaction temperature is reached, the reactor will be kept in the sandbath for 30 minutes for reaction to take place. Then the tubing bomb will be quickly removed from the sandbath and quenched in water for rapid cooling, as described in Chapter 3.

The change of temperature with time in a temperature-staged reaction is presented in Figure 4.2. Practically, this type of experiment requires two sandbaths. The first one is pre-heated to a temperature desired for the pretreatment stage, usually 200°C unless otherwise stated. The other sandbath is heated to the higher temperature, the reaction temperature. Once the reactor reaches the temperature of the first sandbath, 15 minutes will be counted. The reactor is then rapidly removed from the first sandbath and plunged into the second one. As in SSL, the reaction time in the sandbath with the higher temperature is also 30 minutes. The total time required in TSL is thus 45 minutes.

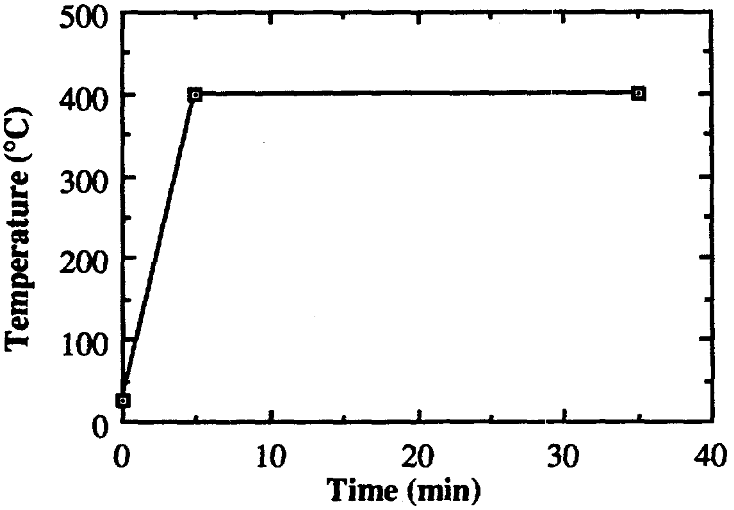


Figure 4.1 Changes of temperature under the single-staged condition

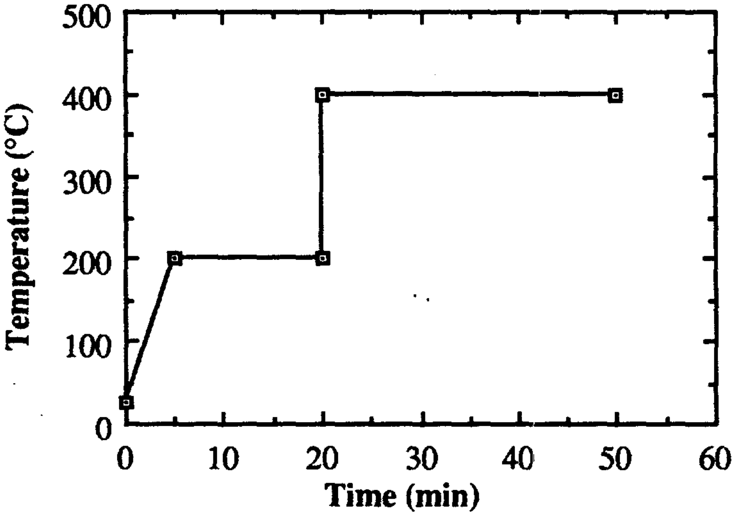


Figure 4.2 Changes of temperature under temperature-staged condition

The difference between the TSL and TPL is that the latter has a heating period between the two temperature stages, as indicated in Figure 4.3. In this type of experiment, one sandbath is adequate. The sandbath is first heated to the lower temperature (e.g. 200°C). After the pretreatment at the low temperature for 15 minutes, the temperature is immediately set to a higher level. In experiments with temperature levels of 200°C/400°C, the temperature is set to 425°C (instead of 400°C). When it reaches 330°C, temperature is reset to 400°C. This procedure ensures that the heating period between the two levels is about 30 minutes. The total time in a TPL reaction is therefore about 75 minutes, and the reactor is kept inside the sandbath in the entire period.

4.2. Study of Temperature Condition on the DECS-9 Coal

The DECS-9 coal was selected to be studied first because it has been found earlier that the TPL was superior to the SSL with this coal [Song et al., 1991; Huang et al., 1992; Song and Schobert, 1992; and Song et al., 1992]. The coal sample was dried, and in a catalytic run it was impregnated with ATTM before reaction. Wilsonville middle distillate (WIMD), a coal-derived process solvent, was used as reaction solvent rather than a model compound in this reaction.

Compositional study on WIMD has been carried out at Penn State by Lai et al. [1992] as shown in Figure 4.4. It is observed that WIMD has high contents of aromatics with two or more rings. Integration of peak areas in the gas chromatogram indicates that pyrene and multi-hydropyrenes are the most abundant compounds in WIMD. Since pyrene and hydropyrenes have been identified as hydrogen shuttler and hydrogen-donor

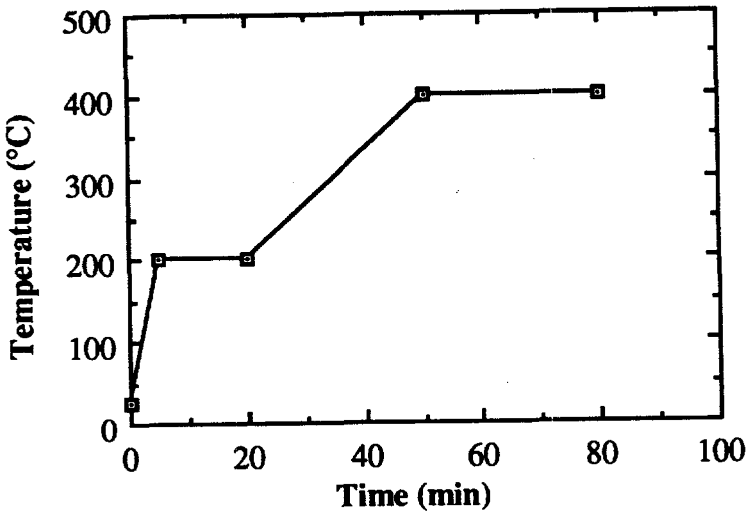


Figure 4.3 Changes of temperature under the temperature-programmed condition

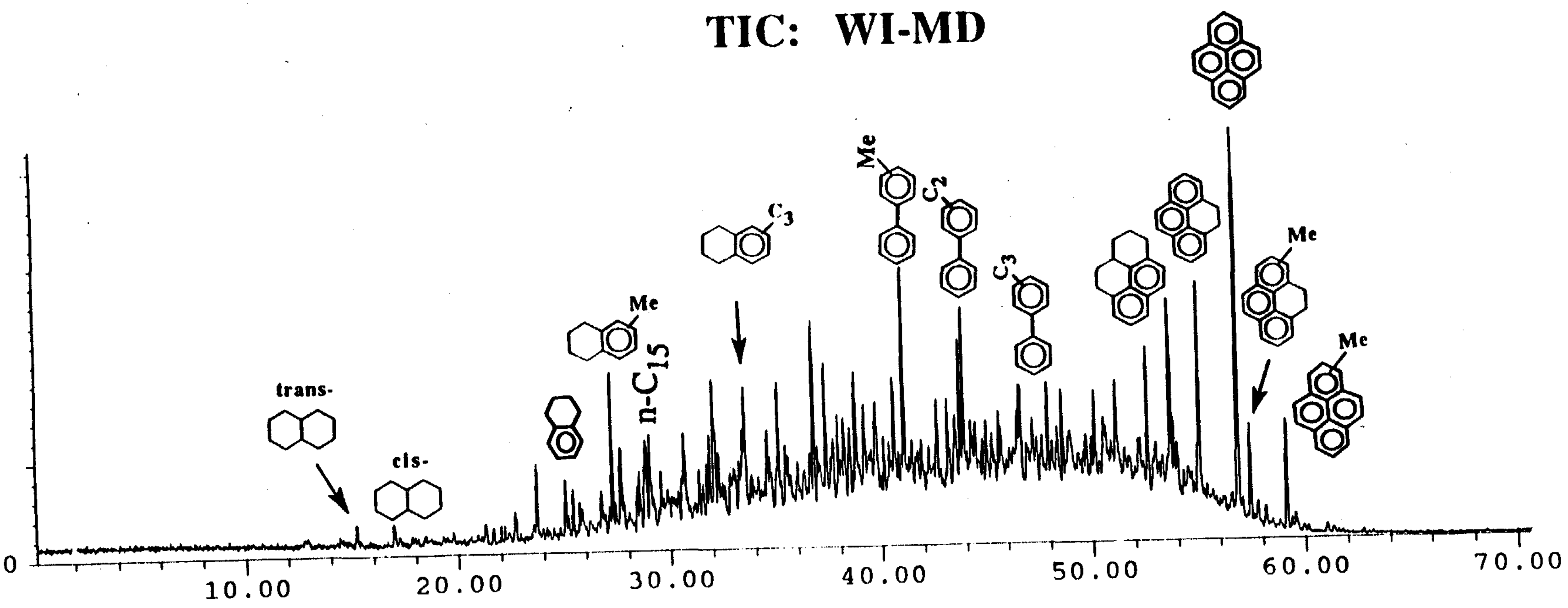


Figure 4.4 Total ion chromatogram of the sample of WIMD
[Lai et al., 1992]

solvents [Davies et al., 1977; Mochida et al., 1979, 1980; Derbyshire et al., 1981], WIMD is therefore considered as a hydrogen shuttler and hydrogen donor.

Figure 4.5 presents the results of liquefaction under the single-staged, temperature-staged and temperature-programmed conditions. All experiments were repeated at least once and the results shown in Figure 4.5 are the averages, with experimental errors less than 3 percentage units. The lower temperatures in TPL and TSL are 200°C, and the reaction temperature in all three cases is 400°C. The total conversions are 84.4%, 89.5% and 90.9% for the SSL, TSL and TPL respectively. The "extra" conversion in TSL is due to the increase in preasphaltene compared with the single-staged reaction, while that in TPL is mainly contributed by the increase in oil and gas yield. From Figures 4.1, 4.2 and 4.3, it can be seen that the difference between the SSL and TSL is that the latter has a low-temperature pretreatment, while the TPL, in addition to that, has a heating-up period between the two temperature stages. Comparing these three types of reaction conditions and the experimental results, the advantage of the low-temperature pretreatment is to "knock off" more preasphaltene from coal, while the heat-up period is to further convert heavy products to light ones, such as from preasphaltene or asphaltene to oil and gas.

To test whether the beneficial effect of pretreatment can be further improved, experiments with the pretreatment temperature (the one at the lower temperature stage) of 300°C were carried out, while the temperature at the higher stage remained 400°C. The results are shown in Figure 4.6. The total conversions are 84.4%, 87.9% and 89.7% for SSL, TSL and TPL respectively. The small differences, comparing with the 200°C/400°C reactions, are within experimental error. It is found that the additional conversion in TSL comparing with SSL is due to the increase in preasphaltene, and that

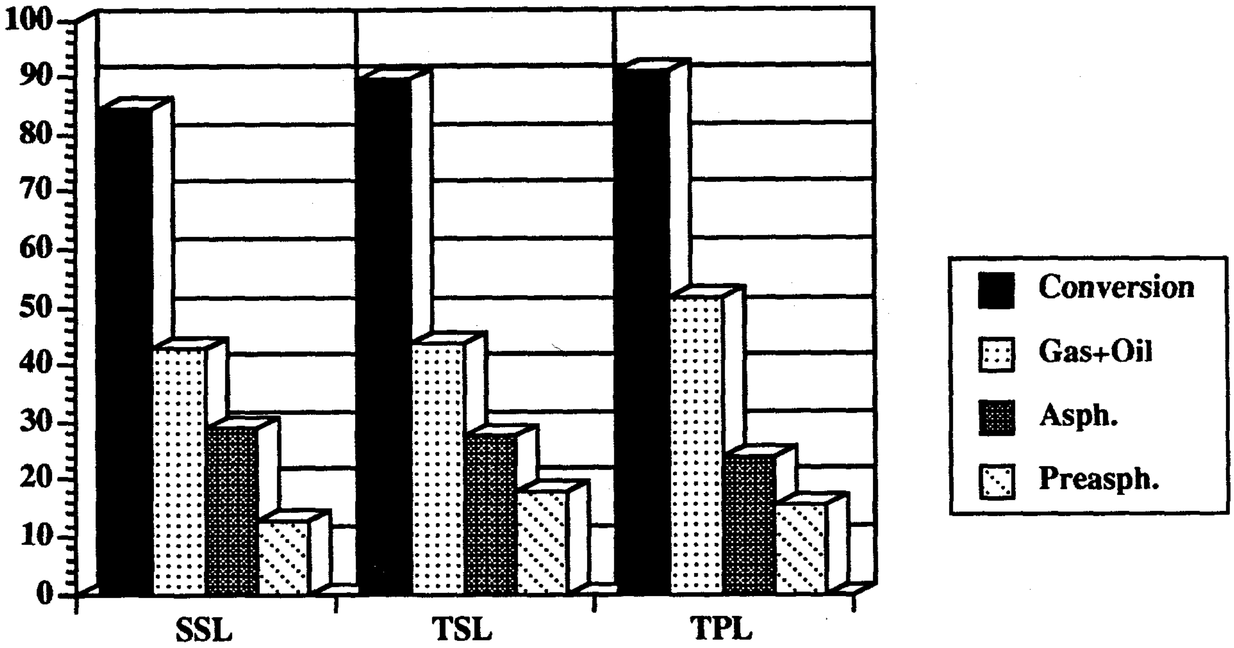


Figure 4.5 Comparison of the three reaction conditions with the DECS-9 coal in the presence of ATTM and WIMD. The reaction temperature was 400°C; in the TSL and TPL reactions, the lower temperature was 200°C

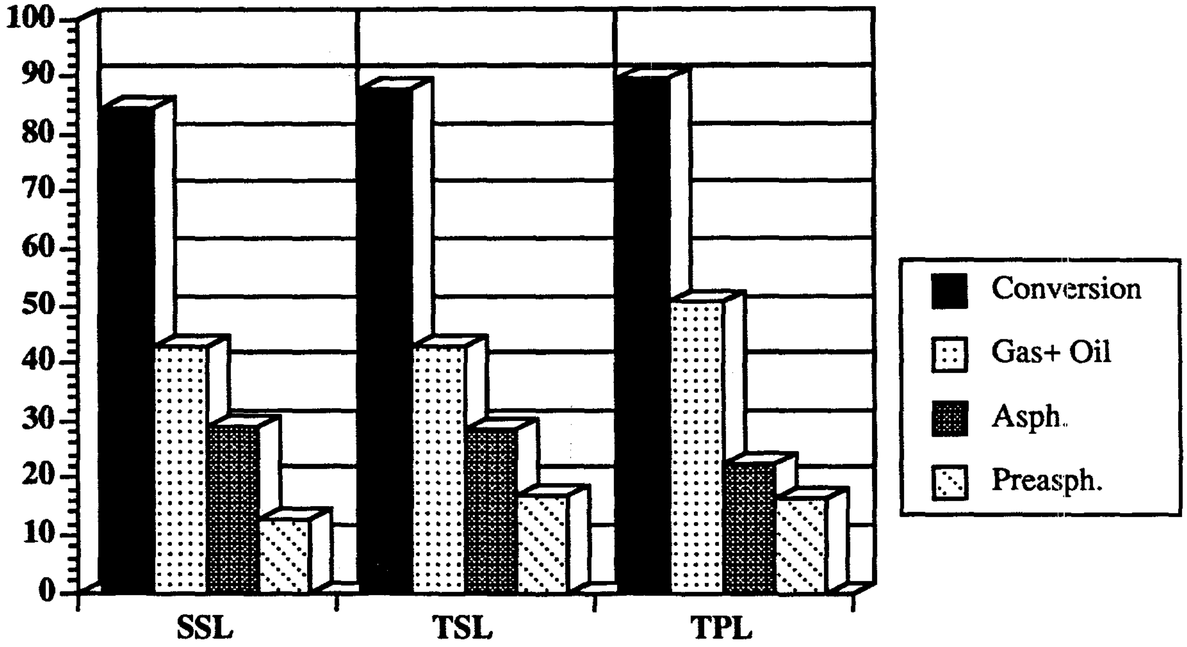


Figure 4.6 Comparison of the three reaction conditions with the DECS-9 coal in the presence of ATTM and WIMD. The reaction temperature was 400°C; in the TSL and TPL reactions, the lower temperature was 300°C

in TPL is a result of higher yield in oil and gas. It is also observed that the asphaltene yield in the TPL reaction is lower than those in SSL and TSL. This again suggests that the low-temperature pretreatment is beneficial to the conversion from coal to heavy product while the slow heat-up period between the two temperature stages is to further convert preasphaltene or asphaltene to gas or oil.

Comparing the conversion and product yields data in Figure 4.5 and Figure 4.6, the increase in the temperature of the first stage from 200°C to 300°C does not seem to have a significant effect on either conversion from coal to heavy products or the conversion from heavy products to light ones. To further verify this, three reactions (actually four if we consider the single-staged reaction as a temperature-programmed one with room temperature as the pretreatment temperature) with different first-stage temperature are examined in Figure 4.7. The three TPL reactions all have higher conversions, higher gas and oil yields, while the yields of asphaltene and preasphaltene are almost the same comparing with the SSL reaction. The additional amount of coal conversion, which we might have expected to see as an increased yield of heavy product, is actually observed as increased yields of oils and gases, because some of the heavy material was converted to light products (oil and gas) under these experimental conditions. Comparing the three TPL reactions, the first-stage temperature, ranging from 200°C to 300°C, does not show a noticeable influence on the reactions. In other words, the beneficial effect of the pretreatment may not be affected by temperature, at least not significantly affected. Recall that in these reactions, one of the hydrogen sources is the solvent, WIMD; the other one is hydrogen gas. For hydrogenation taking place at all reaction sites, the two hydrogen providers should first be mixed well with the coal sample in a reactor and then diffuse into the porous structure of the coal so that the hydrogen atoms can be available when needed. The pretreatment at a low temperature for 15

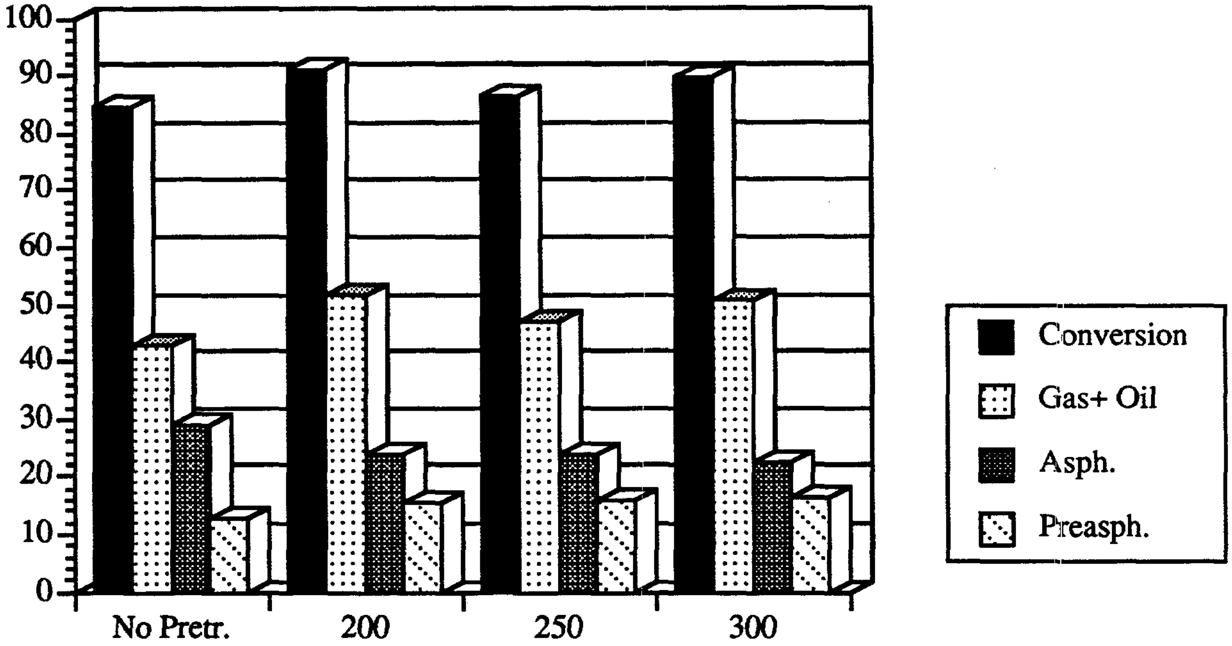


Figure 4.7 Effects of the first-stage temperature on the TPL of the DECS-9 coal with ATTM and WIMD. The second-stage temperature (the reaction temperature) was 400°C.

minutes may provide the opportunity for the mixing and diffusing to take place. The other possibility is that the low-temperature pretreatment also provides an opportunity for the loaded catalyst to be activated and redistributed for a better dispersion.

Effect of the second-stage temperature on TPL reactions was also studied and results are presented in Figure 4.8. As temperature is increased from 400°C to 425°C, conversion and preasphaltene yield remain the same within experimental error. The gas and oil yield increases from 51.5% to 60.3%, while the asphaltene yield decreases from 24.0% to 17.7%. Therefore the increase of temperature from 400°C to 425°C redistributes the liquefaction products by converting asphaltene to oil and gas. With further increase in the temperature from 425°C to 450°C, the conversion drops about 7% units (from 91% to 84%), the oil and gas yield, as well as the asphaltene yield, remain unchanged, while the preasphaltene drops about 7% (from 13% to 6%). Hence the net effect of increasing the second-stage temperature (from 425°C to 450°C), considering that there may be some "inter-conversions" among the products, is to lose some preasphaltene, which may be caused by retrogressive reactions at 450°C (Details will be discussed in Chapter 5). Comparing the single-staged reaction at 400°C and the temperature-programmed reaction at 200°C/450°C, the only benefit of pretreatments at low temperature and at the heat-up period is to convert asphaltene and preasphaltene to gas and oil. The total conversion is not affected in this case.

In catalytic reactions, the effect of catalyst might be so significant that the effect of temperature condition becomes secondary. To magnify the latter, reactions without the presence of ATTM were carried out at 400°C for SSL and 200°C/400°C for TPL. Figure 4.9 shows the comparison. Without the catalyst, the differences in conversion and product yields actually become smaller than those with the catalyst. The yields of gas

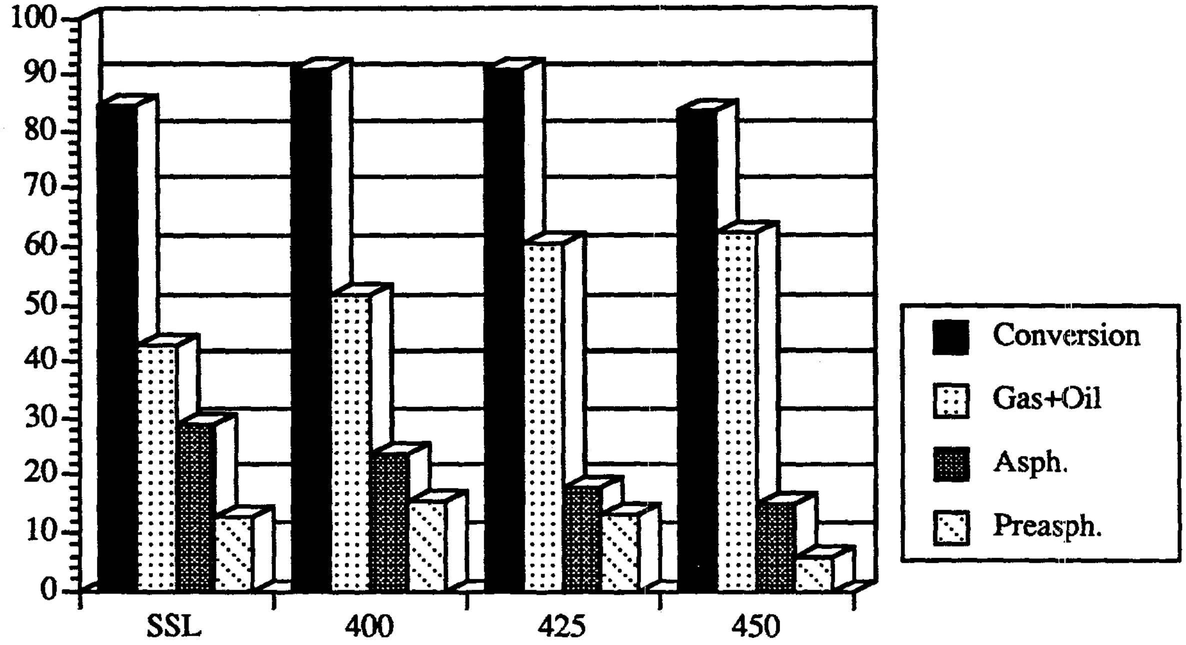


Figure 4.8 Effects of the second-stage temperature on the TPL of the DECS-9 coal with ATTM and WIMD. The first-stage temperature (the reaction temperature) was 200°C.

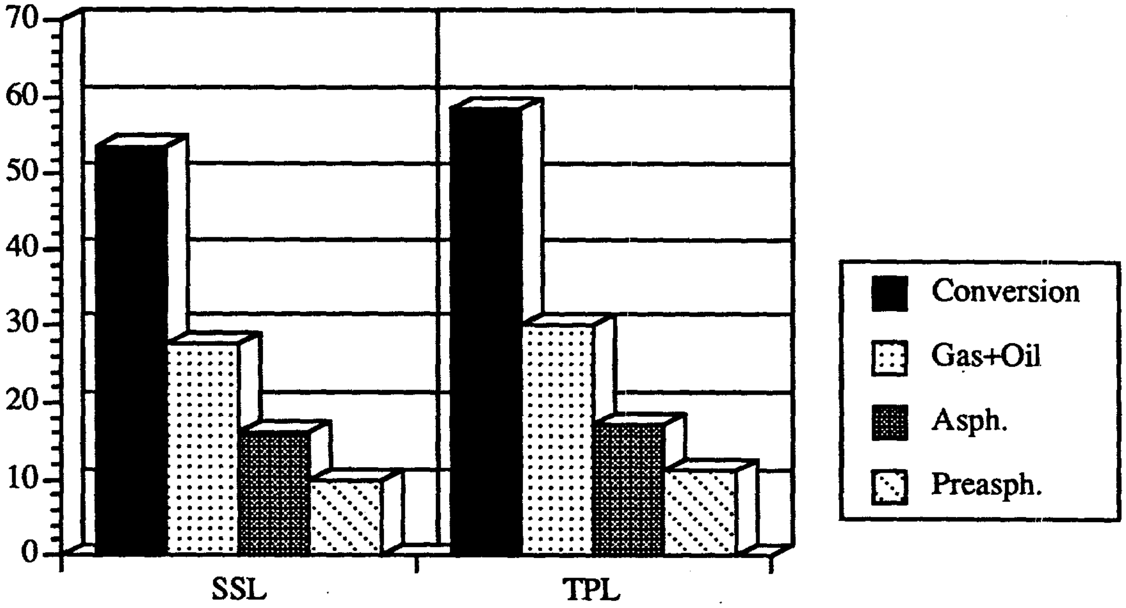


Figure 4.9 Comparison of the single-staged and temperature-programmed conditions on non-catalytic liquefaction of the DECS-9 coal

and oil, asphaltene and preasphaltene in TPL are all slightly higher than those in SSL, though the differences are within experimental error. That the beneficial effect of temperature-programmed condition becomes less significant when the catalyst is absent suggests that the TPL condition has a positive influence on the performance of the catalyst, such as that it may help to achieve a better catalyst dispersion and/or it may help to achieve an effective catalytic hydrogenation during the pretreatment stages.

4.3. Study of Temperature Condition on the DECS-1 Coal

Liquefaction experiments of the DECS-1 coal were carried out with the presence of ATTM but without any solvent. Figure 4.10 shows the results of reactions under single-staged (400°C), temperature-staged (200°C/400°C) and temperature-programmed (200°C/400°C) conditions. The conversions are 95.5%, 84.4% and 95.6% for the SSL, TSL and TPL respectively. The oil yield, the asphaltene yield, as well as the preasphaltene yield in the single-staged reaction, are very close to those in the temperature-programmed reaction. The temperature-staged reaction shows no advantage at all over the single-staged reaction. It in fact has slightly lower conversion and oil yield than the single-staged reaction. The comparison of the three conditions suggests that the single-staged condition is quite competitive to the other two conditions for this coal even though they show considerable advantages for the DECS-9 coal. Recalling that one of the benefits of the low-temperature pretreatment and the treatment during the heat-up period is to let the reaction solvent mix with the coal and/or diffuse into the coal structure, the reason that the TSL and TPL show advantages over the SSL condition with the DECS-9 coal is because a solvent is present in those reactions. In the reactions with the DECS-1 coal, there was no solvent. Therefore the TSL and TPL show no significant

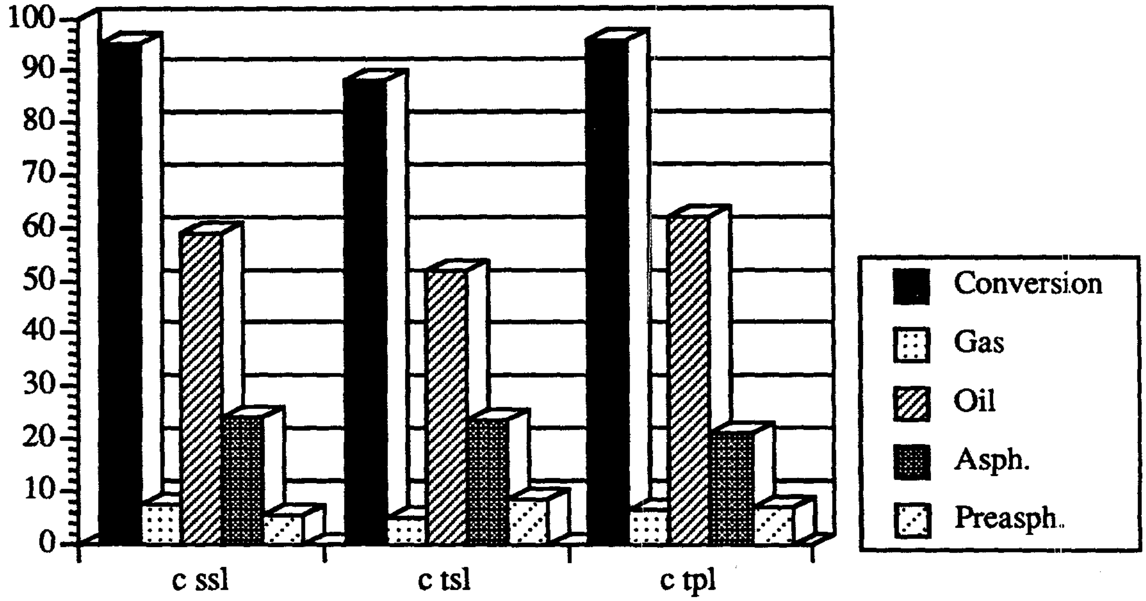


Figure 4.10 Comparison of the three reaction conditions in catalytic liquefaction of the DECS-1 coal with no solvent. The reaction temperature was 400°C; in the TSL and TPL reactions, the lower temperature was 200°C.

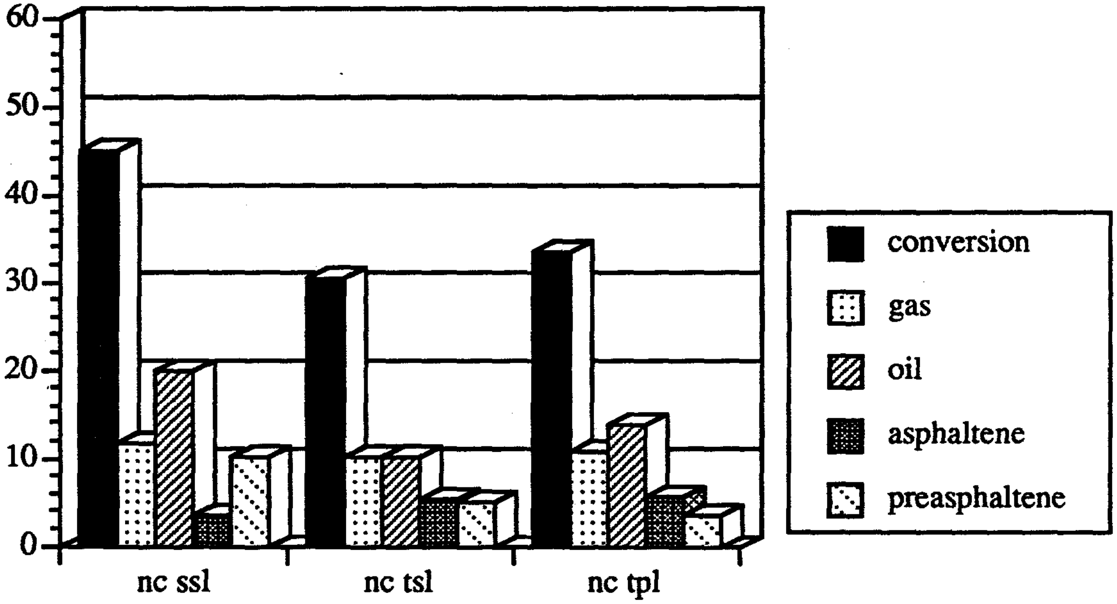


Figure 4.11 Comparison of the three reaction conditions in non-catalytic liquefaction of the DECS-1 coal without a solvent. The reaction temperature was 400°C; in the TSL and TPL reactions, the lower temperature was 200°C.

difference from the SSL condition when no solvent was involved. On the other hand, conversion of the SSL already reaches about 96%, thus it is unnecessary for further improvement by using different reaction conditions, even though the temperature-staged and temperature-programmed processes may be advantageous over the single-staged under certain circumstances, such as with a presence of a solvent.

Experiments without the catalyst were also carried out and the results are shown in Figure 4.11. With the absence of the catalyst, the conversions drop remarkably in all three cases: from 95.5% to 45.0% for the SSL, from 88.4% to 30.6% for the TSL and from 95.6% to 33.5% for the TPL. The three conditions follow the same trend in terms of oil produced as that in conversion, which is SSL>TPL>TSL. The pretreatment again shows no benefit at all in these experiments. This is in agreement with the previous postulation that the pretreatment in TPL and TSL improves liquefaction reaction via providing an opportunity for a good contact between the coal and the solvent and for a better dispersion of the catalyst. Since there is no catalyst nor solvent in these cases, the pretreatment thus has no advantage.

It is interesting to notice that without the presence of a catalyst or a solvent, the SSL condition results in more desirable conversion and oil yield than the TSL and TPL conditions. The pretreatment steps in TSL and TPL are designed to achieve a better contact between the coal and the solvent and also to achieve a better catalyst dispersion. However in the reactions without a catalyst or a solvent, those steps may actually slow down or even deteriorate the reaction. During the pretreatment, for instance when temperature reaches 350°C in TPL, the coal matrix may already be broken down and free radicals are formed, while the hydrogenation by H_2 is not ready to take place, or the rate of hydrogenation is too low at this temperature. The free radicals will have to undergo recombination reactions and form more crosslinked and more stable structure. The SSL reactions, on the other hand, reach the high reaction temperature in a very short time, which favors the hydrogenation by H_2. An other explanation is based on the heating rates of the three conditions. In the single-staged reactions, the coals were heated to the reaction temperature at a much higher rate than those in the temperature-staged and temperature-programmed reactions. Earlier studies by Eser et al.[1991] and Scaroni et al. [1986] found that at a high heating rate, reactive components of the volatile matter can participate in secondary reactions which may promote the conversion of the coal. .Therefore the SSL condition actually prevents retrogressive reactions and thus higher conversion and oil yield are achieved.

4.4. Study of Temperature Condition on the DECS-11 Coal

Liquefaction of the DECS-11 was first carried out under the single-staged condition at 400°C. The conversion (63.5%) is much lower than that of the DECS-1 coal (95.5%) achieved under the same condition, suggesting that the DECS-11 coal is less convertible. It is thus necessary to pursue a better reaction condition. Experiments under temperature-staged and temperature-programmed conditions were then performed. Figure 4.12 graphically compares the three types of reactions. Using the TSL condition increases the conversion as well as the oil yield by about 10 percentage units. The TPL condition increases the conversion by 5%, not as efficient as the TSL. It however increases the oil to a greater extent (about 15 percentage units) than the TSL. Therefore for a coal which is less easily converted to THF solubles, the temperature-staged and temperature-programmed conditions are advantageous over the simple single-staged condition.

4.5. Summary

The temperature-staged and temperature-programmed conditions are designed to maximize the reaction conversion and quality of products and to minimize retrogressive reactions by matching the rate of hydrogenation with the rate of free-radical formation. The investigation carried out in this section with the three low-rank coals has demonstrated that the goal of using TSL and TPL can be achieved, especially with the coals which are less easily converted to THF solubles (e.g. DECS-11 and DECS-9 coals).

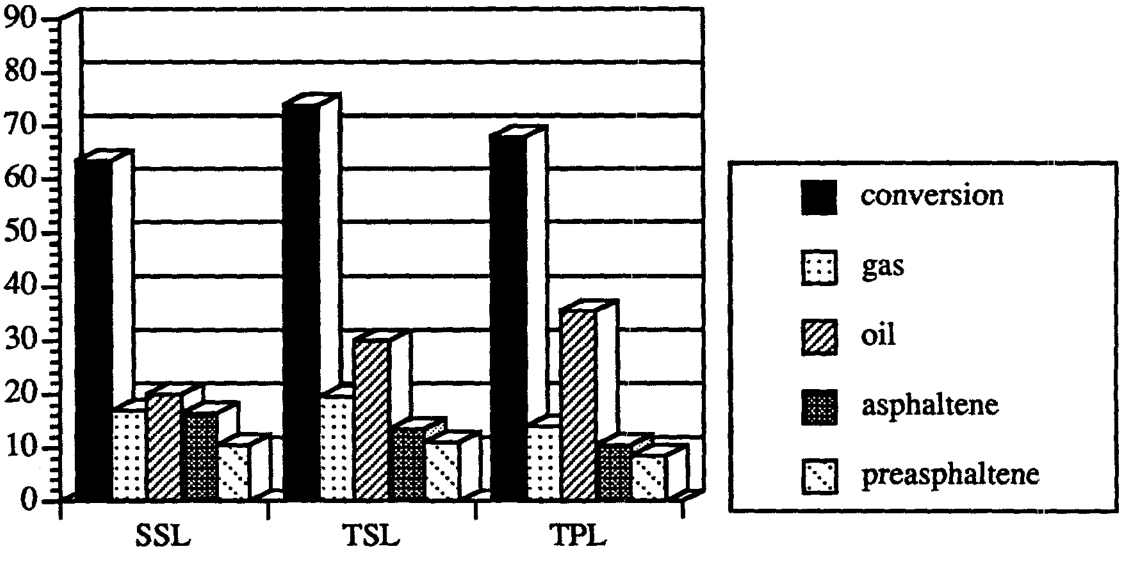


Figure 4.12 Comparison of the three reaction conditions in catalytic liquefaction of the DECS-11 coal without a solvent. The reaction temperature was 400°C; in the TSL and TPL reactions, the lower temperature was 200°C.

It has been observed that the pretreatment steps in TSL and TPL are most effective with the presence of both a catalyst and a solvent, and least effective when neither a catalyst nor a solvent is present, suggesting that the pretreatment has positive influence on the performance of the catalyst and the solvent.

It is postulated that both chemical processes and physical processes are involved in the pretreatment steps. At temperatures as low as 200°C, reactions are unlikely to take place to a great extent; it is thus believed that some physical processes play important roles here. Usually a coal and a solvent are loaded into reactor without further mixing before reaction. During the low-temperature pretreatment, the reactor is extensively oscillated (as described in Chapter 3), providing an excellent opportunity for a thorough mixing. On the other hand, to accomplish the beneficial effect of reaction solvent, the solvent, especially the solvent with hydrogen donating ability, must be present at the coal surface. Since a large proportion of surface area of low-rank coals is enclosed in micropores with diameter less than 20 Å, the performance of the solvent and the rates of chemical reactions are limited by the rates of diffusion of solvent into the micropores [Mahajan, 1978, Spear et al, 1991]. The low-temperature pretreatment facilitates the diffusion of solvent into coal structure, thus the rate of reaction is increased and higher conversion is achieved. The third possible physical process of the pretreatment is that the solvent, once diffused into the coal micropores, may induce swelling and open up more pores that are solvent-inaccessible at room temperature.

The beneficial chemical process in the pretreatment lies in the heat-up period in temperature-programmed reactions. Because of the abundance and variety of functional groups in low-rank coals, the bond dissociation energies (BDEs) are distributed in a broad range. In order to control the rate of bond dissociation (or the rate of free-radical formation) and prevent retrogressive reactions, it is important to have the bonds with low BDE cleaved at low temperature so that the rate of hydrogenation can catch up. The heat-up period is designed to ensure that certain chemical bonds will be selectively broken at certain temperature range with controlled rates.

The pretreatments in TSL and TPL also have beneficial effect on the performance of a catalyst. In this study, the catalyst precursor was impregnated onto the coal sample before reaction. It has been shown that the catalyst precursor is activated at about 350°C [Garcia and Schobert, 1989] which is in the pretreatment period in TPL. The slow heat-up process may have some positive impact on activation of the precursor. Also, possibility exists that the catalyst and/or catalyst precursor may be redistributed during heat-up and hence a better catalyst dispersion is achieved.

The temperature-staged and temperature-programmed reactions are advantageous over the single-staged reaction due to the pretreatments. However, the extent of the beneficial effect of the pretreatment does not appear to be as significant as that of the catalyst, as comparing Figure 4.5 with 4.9, and Figure 4.10 with 4.11. Extensive studies on the effects of catalyst and solvent will be reported in the next chapter, and comprehensive comparisons of the effects of temperature condition, catalyst and solvent will be presented in the last chapter.

CHAPTER 5

EFFECTS OF SOLVENTS AND CATALYST

Coal liquefaction is a process to break the coal macromolecule into fragmental radicals and to stabilize these radicals by hydrogenation. Usually thermal energy is enough to break the coal macromolecule, otherwise a cracking catalyst can be applied to achieve this goal. The more difficult task in liquefaction is to hydrogenate the free radicals. Hydrogenation can be done by a hydrogen donor solvent or by H_2. To maximize hydrogenation to achieve the highest conversion, both the donor solvent and H_2 are usually present in the reaction. A catalyst is often used to enhance the hydrogenation by H_2. Therefore in many cases both a solvent and a catalyst are involved in a reaction. It is thus impossible and unpractical to discuss the solvent effect and catalyst effect separately. Based on this thought, the two effects were studied together and the results are reported in this chapter.

When a catalyst is present in a reaction, a rising question is how to load the catalyst onto the coal surface. As reviewed in Chapter 2, several impregnation methods can be applied to achieve the catalyst loading. The most often used ones are incipient wetness, swelling and slurrying. It is necessary to compare these methods and to identify the best one before carrying out the major study on the catalyst behavior in liquefaction. Therefore the impregnation methods were investigated first.

After the best impregnation method was identified, studies on the effects of solvent and catalyst were conducted. The study includes how the solvents and the catalyst affect reaction conversion and product distribution, and how they influence the product characteristics, such as compositions of the products. Several techniques were used in this study. They were gas chromatography, gas chromatography/mass spectrometry, solid-state ^{13}C NMR and FTIR.

5.1 Study on Catalyst Impregnation Methods

5.1.1 Impregnation Solvent

In studies where a catalyst is involved, one has to pay close attention to impregnation method to ensure that a high catalyst dispersion is achieved. In wet methods, a solvent is used to dissolve the catalyst and deposit it onto the surface of a material, in this case, to deposit the catalyst onto the surface of a coal. For that purpose, the solvent has to possess certain properties. Firstly, it has to be able to dissolve the catalyst, or the catalyst precursor. Secondly, it has to have a high affinity toward the surface of the coal in order to spread the catalyst uniformly on the surface and to achieve a high catalyst dispersion. Thirdly, it is desired that the solvent can swell the coal structure to open up some of the pores which are too small for the solvent and catalyst to penetrate. In this study, an inorganic solvent and an organic solvent were applied as the impregnation solvents. The inorganic solvent may have low affinity and the organic solvent, such as THF, may have a high affinity toward the surface of a coal, because THF has both hydrophilic and hydrophobic sites. On the other hand, some organic solvents have the ability to swell a coal structure, which will allow catalyst molecules to be deposited inside the pores. The most commonly used inorganic solvent is water and therefore it was chosen for this study. For an organic solvent, experiments were carried out using methanol, acetone and THF in the thought that the first two are widely used organic solvents and the last one is well-known in the study of coal and it has been observed that it has the ability to swell a coal structure [Artok et al., 1993].

In incipient wetness method, the volume of a solvent required to fully cover the surface of a coal first has to be tested. Table 5.1 presents the results of this testing on the DECS-9 coal. It is expected that water has the lowest incipient volume because it is an inorganic solvent and has the lowest affinity toward the coal surface. The order of the three organic solvents in terms of incipient volume is THF > methanol/acetone > methanol, indicating that THF has the highest affinity. Therefore, THF was selected as the representative for organic solvents. However THF does not dissolve the catalyst precursor, ammonium tetrathiomolybdate. Therefore water is added just for the purpose of dissolving ATTM. In practice, water is added to ATTM drop by drop until it completely dissolves, then THF, in equal volume to that of water, is added to the solution. By this way, a solution of ATTM/H_2O/THF can be achieved.

Comparative experiments were carried out with the ATTM-impregnated DECS-9 coal using H_2O or the mixture of H_2O and THF as solvents. Table 5.2 shows the results of liquefaction reactions under temperature-programmed and single-staged conditions. Since all samples were dried after impregnation to remove the impregnation solvent , i. e. water or THF, any difference in liquefaction is caused by the catalyst-impregnated coal samples. The experiments under the temperature-programmed condition are presented in Figure 5.1. The sample using H_2O/THF as impregnation solvent yields 9 percentage units higher than that using H_2O. The extra conversion is contributed mainly by the oil and gas yield. Therefore the use of H_2O/THF as impregnation solvent has two apparent

Table 5.1 Volume of solvents required for incipient wetness of the DECS-9 coal

Solvent	water	methanol	methanol/acetic acid (6:1)	THF	water/THF (1:1)
Volume (ml/g)	0.4	0.79	1	2.9	2.9

Table 5.2 Effects of impregnation solvent on liquefaction conversion and product yields of the DECS-9 coal

Reaction Conditions	Impregnation Conditions	Conversion (%dmmf)	Oil + Gas	Asphaltene	Preasphaltene
TPL, 200/400°C	H2O	81.9	40.1	21.5	20.0
	H2O/THF	90.9	51.5	24.0	15.5
SSL, at 400°C	H2O	65.8	37.6	21.5	6.6
	H2O/THF	81.9	40.1	21.5	20.1

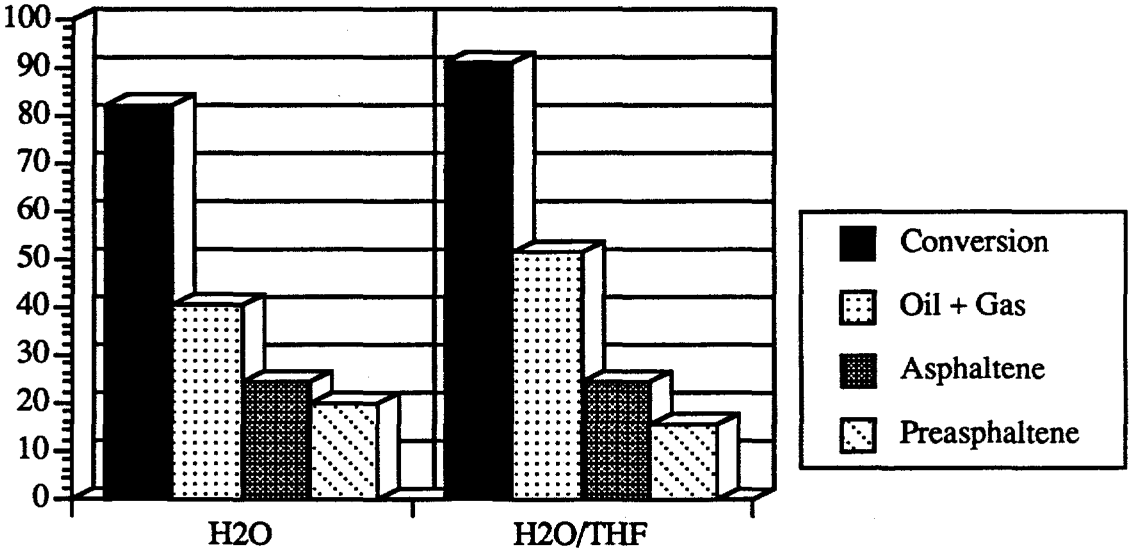


Figure 5.1 Effects of the impregnation solvents on the temperature-programmed (200°C/400°C) liquefaction of the DECS-9 coal

advantages on liquefaction over that using water. One is that it yields higher conversion; the other is that it can shift the product slate to the low molecular weight end.

Because the temperature-programmed condition has positive impacts on the liquefaction, as demonstrated in Chapter 4, it may minimize the effect of catalyst impregnation solvent. Therefore reactions under single-staged condition were carried out in an effort to maximize any difference caused by the solvents. Figure 5.2 compares the two reactions at 400°C. Both reactions yield conversions lower than those under temperature-programmed condition, which again shows that the latter is a better reaction condition. However the single-staged reaction condition has its advantage for the purpose of defining the role of impregnation solvent. As shown in Figure 5.2, the differences in conversion and product distribution caused by using the two solvents are more apparent than that in TPL. The conversion of the sample with the catalyst precursor impregnated by H_2O/THF is 16 percentage units higher than that by H_2O. However, different from that in TPL, the extra conversion is mainly due to the high yield of preasphaltene. This is in a good agreement with early conclusion made in Chapter 4 that the temperature-programmed condition is especially beneficial to the conversion from heavy product to light ones. Nevertheless, the comparative study carried out under single-staged condition has again demonstrated that using an organic solvent, i. e. H_2O/THF, is beneficial in promoting the performance of a catalyst, where the catalyst may be dispersed to a higher extent because of the higher affinity of the organic solvent toward the surface of the coal.

Based on the above study, it is concluded that organic binary solvent (H_2O/THF) has an advantage over inorganic solvent in dispersing the catalyst onto a coal sample. Therefore the mixture of H_2O and THF (with ratio of 1:1) was used as the impregnation solvent throughout the study.

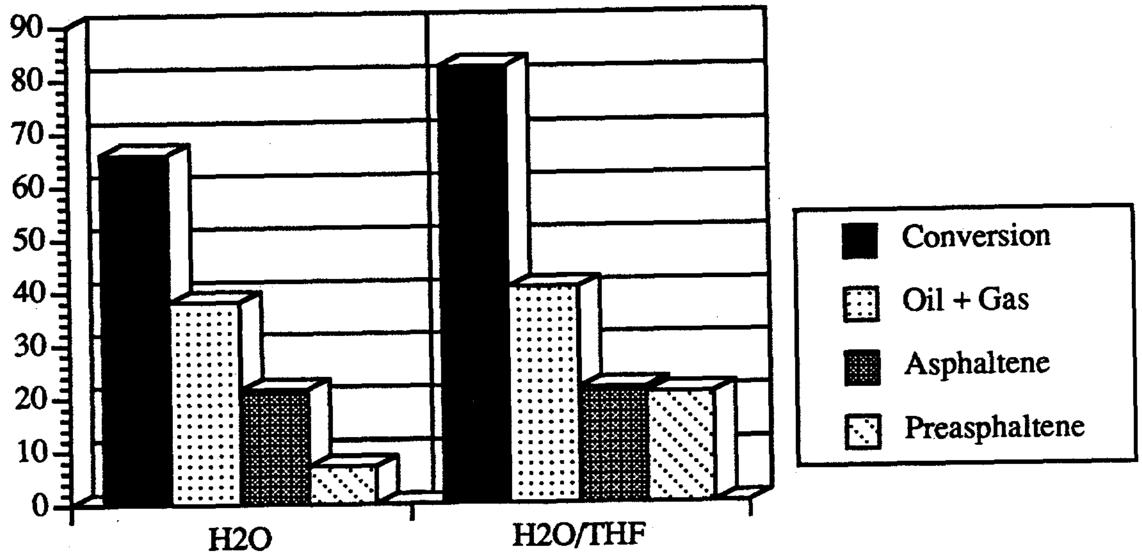


Figure 5.2 Effects of the impregnation solvents on the single-staged (400°C) liquefaction of the DECS-9 coal

5.1.2 Impregnation Methods

As mentioned in Chapter 2, three impregnation methods are often used in loading a catalyst onto a surface of a material, such as a coal. They are incipient wetness, slurry and preswelling. In this study, liquefaction experiments using samples prepared by these three methods were carried out under various conditions, such as temperature-programmed condition, and single-staged condition, using WIMD or 1-MN as reaction solvent, to compare these three impregnation methods.

In all three methods, the catalyst precursor was first dissolved in a desired amount of H_2O/THF mixture (1:1). The amount of the mixture was determined according to the specific method. In the swelling method, the volume of the H_2O/THF mixture was four times of the coal volume, because it was found that this was sufficient for complete swelling [Larsen and Shawver, 1990; Green et al., 1984].

Before the catalyst precursor was loaded to the coal, the swelling ratio was measured using the following procedure. Approximately 1 g of coal (-60 mesh) was placed in an 6-mm-o.d. Pyrex conical graduated screw-top centrifuge tube. The tube was placed in a centrifuge and repeatedly centrifuged at a rate of 2000 rpm and tapped by hand on a hard surface until the coal bed reached a minimum height, H_1. The tightly packed coal bed was broken up by tapping it against a hard surface so that the coal was distributed along the tube to prevent clumping caused by rapid swelling when solvent was added. A sample of H_2O/THF mixture with volume of four times of that of the coal was slowly added to the tube and mixed thoroughly with the coal. The tube was allowed to sit vertically for a certain amount of time. It was then again centrifuged and tapped until the measured height of coal bed reached a minimum value, H_2. The volumetric swelling ratio on a dry basis is defined as

$$Q_{v,dry} = H_2/H_1$$

The swelling ratios for the three coals are listed in Table 5.3 when they are soaked in the solvent for three hours and in Table 5.4 when they are soaked for 24 hours. It is observed that a three-hour period of soaking is sufficient for equilibrium. However for the sake of convenience, a twenty-four-hour period was always allowed.

To load the catalyst precursor onto the coal, a calculated amount of ATTM (1% of dry and mineral-matter free coal) was first dissolved in water with volume twice as much as that of the coal. THF, with same volume, was then added to the solution. The swelling procedure was carried out in a round-bottom flask under N_2 atmosphere. The swollen coal with the catalyst precursor was then dried in a vacuum oven at room temperature for 48 hours to remove THF, followed by drying at 40°C for 24 hours and 95°C for 48 hours to remove the remaining THF and H_2O.

In the incipient wetness method, the precursor was dissolved in the desired volume of the H_2O/THF for a certain amount of the coal sample (2.9 ml of H_2O/THF mixture per gram of coal). This solution was added drop by drop to the coal while the coal was constantly stirred manually. After all the solution was added, the coal was dried in the vacuum oven at 95°C for 4 h to remove THF and H_2O.

In the slurrying method, the same amount of THF/H_2O mixture as that in the incipient wetness method was used to dissolve the ATTM. The solution was then added

Table 5.3 Swelling ratio of the three coals after three hours of soaking. The swelling agent was THF/H2O (1:1)

Coal Sample	Weight (g)	H1(ml)	H2 (ml)	Qv, dry
DECS-1	1.0053	1.6	3.0	1.9
	1.0264	1.8	3.2	1.8
DECS-9	1.0254	1.8	3.5	1.9
	1.0053	1.8	3.4	1.9
DECS-11	1.0125	1.7	3.3	1.9
	1.0310	1.6	3.2	2.0

Table 5.4 Swelling ratio of the three coals after twenty-four hours of soaking. The swelling agent was THF/H2O (1:1)

Coal Sample	Weight (g)	H1 (ml)	H2 (ml)	Qv, dry
DECS-1	1.0162	1.6	3.0	1.9
	1.0680	1.8	3.3	1.8
DECS-9	1.0292	1.7	3.5	2.0
	1.0885	1.7	3.6	2.1
DECS-11	1.0130	1.6	3.2	2.0
	1.0368	1.7	3.2	1.9

to the coal sample to make a slurry. The slurry was stirred by a magnetic stirrer for 15 minutes at room temperature under N_2 atmosphere, followed by drying in the vacuum oven at room temperature for 48 hours, at 40°C for 48 hours and at 95°C for 6 hours to remove THF and H_2O.

5.1.2.1 Comparison of the Three Impregnation Methods under Temperature-Programmed Condition

Table 5.5 shows the results of temperature-programmed liquefaction of DECS-1 using the three impregnation methods with Wilsonville middle distillate (WIMD) as the reaction solvent. Comparing with the non-catalytic TPL experiments, all the runs with ATTM, regardless of the impregnation methods, produced much higher total conversion as well as higher gas and oil yields. The data also show that without the catalyst, the preasphaltene yield was higher than those reactions with catalyst. This suggests that the catalyst speeds up the rate of hydrogenation and thus prevents the retrogressive reactions which produce heavy materials such as preasphaltene and residue. If the catalyst is dispersed all over the reaction sites where the free radicals are produced, the oil yield will be increased as well as the total conversion. A comparison of the three impregnation techniques shows that the order of them in terms of the total conversion is swelling > incipient wetness > slurrying. This can be explained by that in the swelling method, the coal matrix is swollen and some of the pores are opened up by the swelling agent, such as THF/H_2O mixture. This provides the possibility that the catalyst precursor penetrates into the pores and deposits on the internal surface of the coal [Davis et al., 1993]. For the incipient wetness method, the coal matrix is not swollen, so the catalyst may not be able to deposit inside the pores. However, compared with the slurrying method in which the

Table 5.5 Effects of the impregnation methods on conversion and product distribution of the temperature-programmed liquefaction of the DECS-1 coal with WIMD

Impregnation Methods	Conv.	Gas +Oil	Asphal.	Preasphal.
Swelling	95.7	53.2	20.2	22.3
Incipient Wetness	92.7	62.4	14.4	15.9
Slurry	88.2	55.4	18.2	14.7
Dried Coal	70.5	28.5	14.8	27.2

solution of the catalyst precursor and the coal are mixed at once, the incipient wetness may have a better chance to disperse the catalyst uniformly on the coal surface. Therefore, the incipient wetness gave a higher total conversion than the slurrying method due to a better dispersion.

Table 5.6 shows the results of the temperature-programmed liquefaction of DECS-11 using the three impregnation methods. Similar to DECS-1, the DECS-11 coal had much higher conversions while ATTM was applied regardless of the impregnation methods. The difference is that, without the catalyst, the coal produced almost as much preasphaltene as the catalyst-loaded coal. The factor causing the total conversion to be lower is the lower yields of oil and asphaltene. This observation suggests two possibilities. The first possibility is that the formation of the free radicals is slower than that from the DECS-1 coal, and these free radicals are relatively stable, in other words, the rates of retrogressive reactions are low. In the case without the catalyst, an equilibrium is built up between the formation and the consumption of the free radicals. In the case of catalytic liquefaction, the equilibrium is broken by enhancing the consumption of the free radicals by hydrogenation. If this possibility is true, the conclusion derived is that for this coal, retrogressive reaction is not a severe problem, at least under this reaction condition. Therefore to achieve a high oil yield as well as high total conversion is a problem of how to enhance the formation and hydrogenation of the free radicals, without worrying about the retrogressive reactions. The second possibility is that the free radicals produced are large in size. When retrogressive reactions dominate, heavy materials, such as residues but not preasphaltenes, are produced; when hydrogenation dominates, the oil yield will be increased, but the preasphaltene yield does not decrease to a great extent.

Table 5.6 Effects of the impregnation methods on conversion and product distribution of the temperature-programmed liquefaction of the DECS-11 coal with WIMD

Impregnation Methods	Conv.	Gas +Oil	Asphal.	Preasphal.
Swelling	83.6	50.1	17.7	15.9
Incipient Wetness	85.0	49.4	19.9	15.7
Slurry	81.2	51.0	19.1	11.1
Dried Coal	67.1	38.6	15.4	13.1

For the DECS-11 coal, the comparison of the three impregnation methods does not give a clear trend, or in other words, these three methods do not make any difference in terms of total conversions and oil yields. They all have total conversion in the low 80 percent range and oil yield around 50%. Comparing with the DECS-1 coal, this coal had lower oil yield as well as lower conversion. This indicates that the DECS-11 coal is not as easy to convert as the DECS-1 coal under this reaction condition.

Table 5.7 shows the results of temperature-programmed liquefaction of DECS-9 using WIMD as reaction solvent. The same phenomenon was observed: that as the catalyst was used, no matter how it was impregnated to the coal, the liquefaction had much higher total conversion as well as oil and gas yield. The difference is that when the catalyst was applied, all three yields (oil + gas, asphaltene, and preasphaltene) were increased, though the oil and gas yield increased to a large extent and the preasphaltene yield increased to a small one. The increase in preasphaltene may be due to some catalytic hydrogenation of the large free radicals which end up as the preasphaltene.

Similar to the DECS-11 coal, the DECS-9 coal shows roughly the same total conversion for all the three impregnation methods. The incipient wetness and slurrying method provides slightly higher oil and gas yield and slightly lower preasphaltene yield than the swelling method.

5.1.2.2 Comparison of the Three Impregnation Methods under Single-Staged Condition

For the DECS-11 and DECS-9 coals, it is not clear whether the catalyst impregnation methods have any influence on the activity of the catalyst and the coal

Table 5.7 Effects of the impregnation methods on conversion and product distribution of the temperature-programmed liquefaction of the DECS-9 coal with WIMD

Impregnation Methods	Conv.(%dmmf)	Gas +Oil	Asphaltene	Preasphaltene
Swelling	90.9	43.6	24.5	22.8
Incipient Wetness	90.9	51.5	23.9	15.5
Slurry	91.9	50.7	25.2	16.0
Dried Coal	58.6	30.3	17.2	11.1

liquefaction. This may be due to the fact that the temperature-programmed condition is a very optimum reaction condition which is designed to balance the formation of the free radicals and the hydrogenation of the radicals in order to achieve the highest possible total conversion and oil yield. The effect of the temperature program could be so strong that any difference of the catalyst dispersion caused by different impregnation methods may be diminished. To reduce the effect of reaction conditions, the liquefaction of catalyst-loaded coals using the three impregnation methods was conducted under single-staged conditions, such as 350°C for 30 minutes.

Table 5.8 includes the results of single-staged liquefaction of DECS-1 coal at 350°C using WIMD as the reaction solvent. Most experiments were repeated once or even twice. Comparing with the result of the dried coal without any catalyst, all three types of experiments (using different impregnation methods) show that the catalyst is active under this reaction condition, though it did not cause a drastic increase in both the total yield and the oil and gas yield. The impregnation methods, however, do not seem to have any significant impact on liquefaction conversion under this reaction condition.

The results of single-staged liquefaction of DECS-11 using WIMD as reaction solvent are presented in Table 5.9. The effect of the catalyst on the liquefaction is stronger for this coal than for the DECS-1 coal. The total conversion increased from about 25%, in the case of non-catalytic liquefaction, to 36 % in catalytic liquefaction using the incipient wetness method, to 37% in that using the swelling method, and to about 45% in that using the slurrying method. Although the oil and gas yield did not increase a lot when the catalyst was used, both the preasphaltene and asphaltene increased to greater extents. This can be explained by the fact that at 350°C, only the relatively weak bonds can be broken to form free radicals. Since the majority of the bonds can not

Table 5.8 Effects of the impregnation methods on conversion and product distribution of the single-staged liquefaction (350°C) of the DECS-1 coal with WIMD

Impregnation Methods	Conv.(%dmmf)	Gas +Oil	Asphaltene	Preasphaltene
Swelling	39.5	22.6	11.5	5.4
Incipient Wetness	33.6	16.5	11.0	6.1
Slurry	36.4	20.3	11.0	5.1
Dried Coal	28.6	15.7	6.2	6.7

Table 5.9 Effects of the impregnation methods on conversion and product distribution of the single-staged liquefaction (350°C) of the DECS-11 coal with WIMD

Impregnation Methods	Conv.(%dmmf)	Gas +Oil	Asphaltene	Preasphaltene
Swelling	37.5	22.0	11.2	4.4
Incipient Wetness	36.0	20.1	6.8	8.4
Slurry	45.1	27.7	9.1	8.3
Dried Coal	25.5	18.4	3.6	3.6

be cleaved at this temperature, the size of the free radicals is large. In this case, even though the hydrogenation is greatly enhanced, the final products are still heavy in terms of molecular weight and thus appear as preasphaltenes and asphaltenes [Song et al., 1991c and 1992c].

Table 5.10 presents the results of the single-staged liquefaction of DECS-9 coal at 350°C using WIMD as reaction solvent. Once again, the catalytic runs show great increases in total conversion, indicating that the catalyst is active under this reaction conditions. Similar to the DECS-11 coal, the increases of total conversion of the catalytic runs using swelling and incipient wetness methods are mainly contributed by the increases in preasphaltene and asphaltene, suggesting that under this reaction condition, only some of the bonds are broken to form relatively large free radicals. For the catalytic runs using slurrying for impregnation, all three portions (oil + gas, asphaltene, and preasphaltene) are increased markedly with the portion of oil and gas increased the most.

Table 5.10 Effects of the impregnation methods on conversion and product distribution of the single-staged liquefaction (350°C) of the DECS-9 coal with WIMD

Impregnation Methods	Conv.(%dmmf)	Gas +Oil	Asphaltene	Preasphaltene
Swelling	44.0	5.3	17.2	21.5
Incipient Wetness	44.0	5.3	17.2	21.5
Slurry	54.9	24.5	15.2	15.2
Dried Coal	26.8	8.6	8.8	9.3

5.1.2.3 Comparison of the Three Impregnation Methods under Single-Staged Condition using 1-MN

In the study of liquefaction, once the coal sample is chosen, there are three factors which affect the course of reaction. They are reaction condition (including temperature, H_2 pressure, time), catalyst, and reaction solvent. In the previous two sections, the catalytic (ATTM) liquefaction under different reaction conditions was discussed. In this section, the effect of the reaction solvent will be presented. As stated in the last section, the effect of reaction condition can be so strong that it will cover the small difference caused by the impregnation methods. The effect of the reaction solvent, on the other hand, can also be very strong and thus shade the effect of the impregnation methods. To reduce the effect of solvent, 1-methylnaphthalene (1-MN), a well-known hydrogen non-donor solvent, was used to replace WIMD.

Table 5.11 shows the results of single-staged liquefaction of DECS-1 using 1-MN as reaction solvent. Unexpectedly, the non-donor solvent actually helped to produce higher total conversions as well as the oil and gas yield than the recycle solvent WIMD in all three cases (using three different impregnation methods), indicating that the WIMD does not have hydrogen shuttling and hydrogen donating abilities (Section 4.2) at 350°C, as it can also be seen in later results (Figure 5.3) when no catalyst is used. The swelling method had the highest total conversion (54%). The total conversion of incipient wetness and slurrying are the same within experimental error. This again shows that for the DECS-1 coal, the swelling method is superior to the incipient wetness and the slurrying methods.

Table 5.11 Effects of the impregnation methods on conversion and product distribution of the single-staged liquefaction (350°C) of the DECS-1 coal with 1-MN

Impregnation Methods	Conv.(%dmmf)	Gas +Oil	Asphaltene	Preasphaltene
Swelling	54.5	27.2	14.5	12.7
Incipient Wetness	47.4	24.3	13.1	10.0
Slurry	49.7	25.3	13.9	10.5
Dried Coal	29.0	12.5	9.1	7.6

5.1.2.4 Summary for the Impregnation Methods

For the DECS-1 coal, the order of the impregnation methods in terms of the total conversion is swelling > incipient wetness > slurrying under both temperature-programmed and single-staged condition. For the DECS-11 coal and the DECS-9 coal, no clear trend is observed.

The three applied impregnation methods, though they are quite different in the preparation procedure, do not appear to be different in terms of the liquefaction conversion and oil and gas yield. This may be explained by the process itself. In the swelling methods, the catalyst precursor is uniformly distributed in the swelling agent. Some of precursor molecules, together with the agent, penetrate into the pores of the coal, others remain outside of the pores. It was observed by Davis et al. [1993] that there were intergrown crystals of ATTM that appeared be associated with coal fractures. This suggests that the ATTM/swelling agent may once have been concentrated at the coal fracture, but during evaporation of the solvent and inherent coal moisture under vacuum, ATTM may have been draw out of the fracture system. Therefore, the benefit of the swelling method, which can load the precursor inside the pores [Davis et al, 1993], is diminished during the drying process; and this method is no longer superior to the others.

The observation on the catalytic reactions suggests that the total conversion and the product distribution are strongly related to the structural characteristics of the coal. For the DECS-1 coal, the catalyst can effectively enhance the formation of oil and reduce the formation of preasphaltene. For the DECS-11 coal, two assumptions are proposed. The first one is that the retrogressive reactions are not severe for this coal. The second is that the free radicals derived from the coal are large in size. When the retrogressive reactions take place, they will combine with each other and form residue (not asphaltene or preasphaltene); while when hydrogenation takes place, they will be stabilized to form oil. Either assumption can satisfy the fact that the preasphaltene yield is not strongly affected by the presence of the catalyst. For the DECS-9 coal, all the yields of oil, asphaltene, and preasphaltene increased when the catalyst was applied, indicating that free radicals of various size were produced and hydrogenated during liquefaction.

To reduce the effect of reaction conditions, single-staged liquefaction was conducted. However, a clear relationship of these three impregnation methods, especially for the DECS-11 and the DECS-9 coals, was still not observed. A study was also carried out using a non-donor solvent, 1-MN, in an effort to reduce the solvent effect on DECS-1 coal. It was shown that the swelling method gave a higher total conversion than the other two methods, which had very similar behaviors in liquefaction. However, comparing the reactions with WIMD and those with 1-MN, the former did not seem to have any advantage over the latter, possibly because that the reaction temperature was low (350°C) and diminished the hydrogen shuttling and donating effect of the WIMD. The solvent effects at 350°C will be discussed in detail in the following section (5.2.1). Therefore it is concluded that the differences in the catalyst performance caused by dispersion methods are insignificant. The slurrying method, which is relatively simple and less time consuming, is thus selected as the standard catalyst dispersion method throughout the study.

5.2 Effects of Reaction Solvents and Catalysts on Liquefaction Conversion and Product Distribution

5.2.1 Behavior of Solvents in the Absence of a Catalyst

Four solvents were compared in this study. They are tetralin (a donor solvent), WIMD (a liquefaction recycle solvent), 1-methylnaphthalene (non-donor solvents) and decalin (a less reactive donor solvent). Reactions using these four solvents were compared with those using no solvent. The study was first carried out under single-staged condition and then under the temperature-programmed condition without the presence of the catalyst. Table 5.12 to Table 5.14 present the experimental results. Most of the experiments were repeated at least once, and the data in the tables are the average. The raw data (before averaging) can be found in Appendix A, and the experimental errors are shown in Figure 5.3-5.8.

The solvent effects on the DECS-1 coal under single-staged condition without the present of a catalyst are shown in Figure 5.3. All of the four solvents, regardless of the fact that they are donor solvents or not, have positive impacts on liquefaction in terms of

Table 5.12 Solvent effects on the DECS-1 coal at 350°C without the presence of a catalyst

Solvent	Conversion	Gas	Oil	Asphaltene	Preasphaltene
None	19.1	6.5	7.4	1.1	4.1
Decalin	27.1	5.9	12.8	4.8	3.7
1-MN	31.4	5.0	11.2	8.3	7.2
WIMD	29.7	5.3	11.4	7.3	5.8
Tetralin	35.8	4.3	15.2	8.7	7.7

Table 5.13 Solvent effects on the DECS-9 coal at 350°C without the presence of a catalyst

Solvent	Conversion	Gas	Oil	Asphaltene	Preasphaltene
None	19.4	2.5	8.8	2.5	5.7
1-MN	29.6	4.7	7.0	10.3	7.7
WIMD	29.0	5.0	6.3	11.3	6.5
Tetralin	42.8	3.6	15.7	12.1	11.4

Table 5.14 Solvent effects on the DECS-11 coal at 350°C without the presence of a catalyst

Solvent	Conversion	Gas	Oil	Asphaltene	Preasphaltene
None	15.4	6.5	8.4	0.3	0.2
1-MN	23.3	6.8	11.3	3.9	1.3
WIMD	25.6	9.4	8.6	5.1	2.5
Tetralin	28.1	6.6	13.3	5.0	3.2

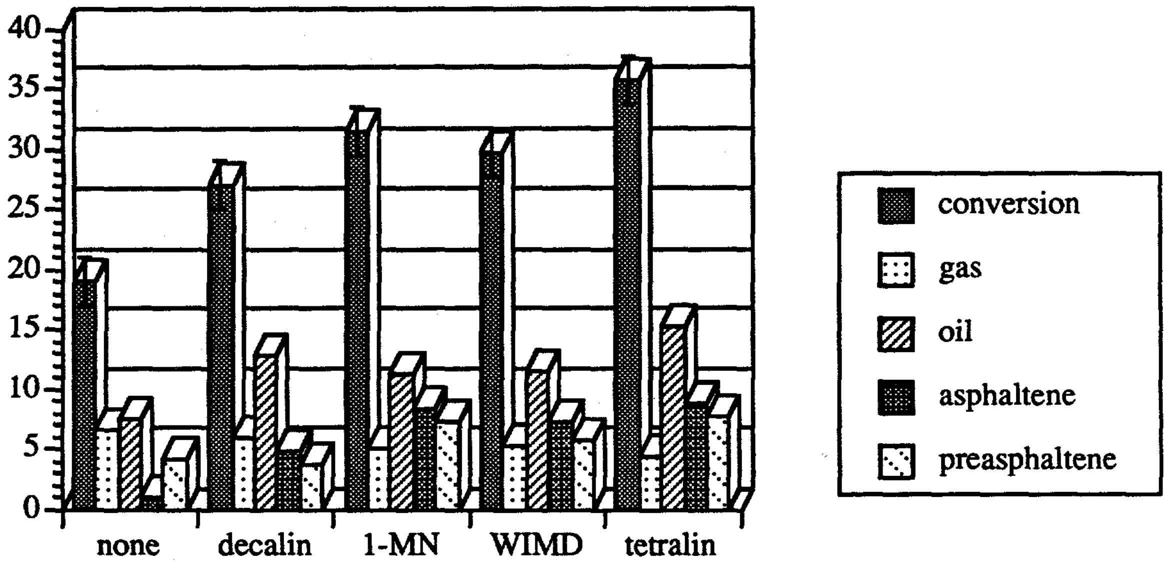


Figure 5.3 Solvent effects on liquefaction of the DECS-1 coal at 350°C with no catalyst

conversion and product yields. With the use of a solvent, liquefaction conversion was at least 50% greater than the conversion in a solvent-free reaction. If the solvent is a donor solvent, i. e. tetralin, the conversion was almost doubled. The gas yields in these three types of reactions, however, are all around 6%, which seems to be insensitive towards the use of a solvent. The yields of oil, asphaltene and preasphaltene are increased to similar extents no matter what type of solvent is used. The donor solvent gives a slightly higher oil yield, but the difference is insignificant.

The solvent effect on the DECS-9 coal is indicated in Figure 5.4. Three solvents were applied, and they are a non-donor solvent, liquefaction recycle solvent and a donor solvent. Since from the study on the DECS-1 coal, the two non-donor solvents do not show a remarkable difference from each other, only one was used here. Again, the use of a solvent, regardless of its type, has increased the liquefaction conversion. The increases in conversion are contributed by gains mainly in asphaltene yield. Only when tetralin was involved in the reaction were noticeable increases in oil and preasphaltene yields observed. The differences in the gas yields are within experimental error. In general, tetralin, compared with other solvents, has a stronger positive impact on this coal than on the DECS-1 coal.

The solvent effects on the DECS-11 coal are presented in Figure 5.5. Conversion of this coal appears to be lower than the DECS-1 and DECS-9 coal, indicating that this coal is less easily to liquefy and may need extra effort. Without the involvement of a solvent, the conversion is 15.4%, contributed by the gas and oil yield. The asphaltene and preasphaltene yields are close to zero. This observation suggests that at 350°C with no solvent or catalyst, all we have done is to release the trapped small molecules and, possibly, to liberate some fragments which are loosely attached to the coal

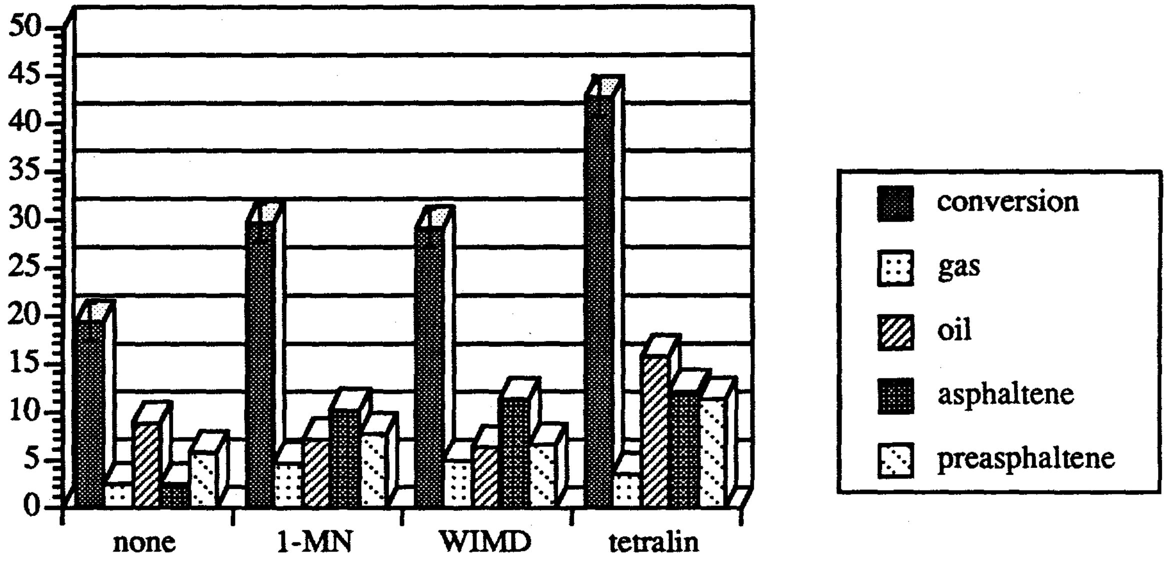


Figure 5.4 Solvent effects on liquefaction of the DECS-9 coal at 350°C with no catalyst

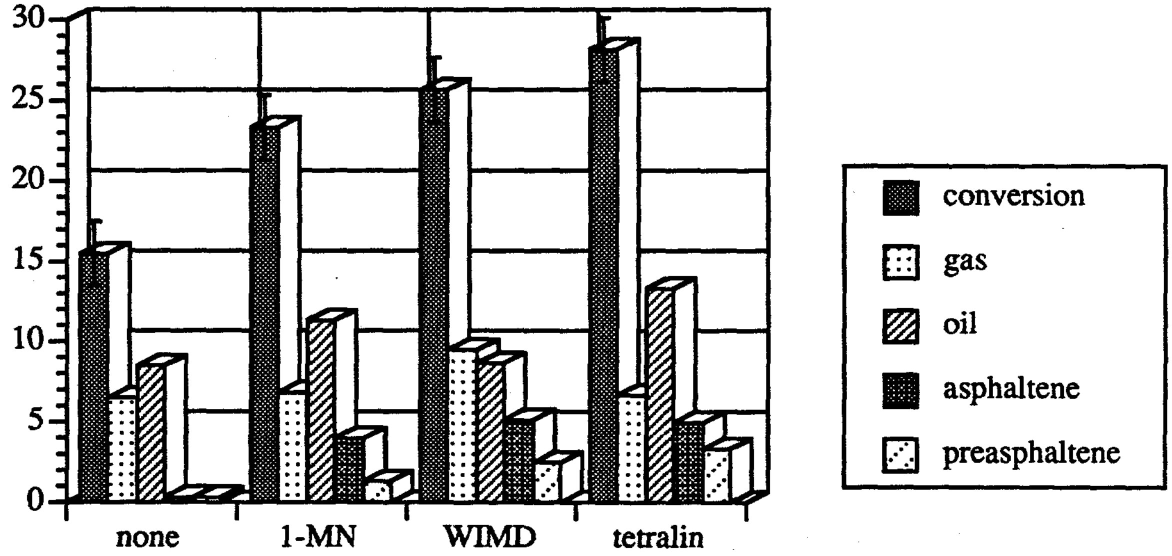


Figure 5.5 Solvent effects on the Liquefaction of the DECS-11 coal at 350°C with no catalyst

macromolecule. The use of a solvent helped to break more bonds, indicated by the fact that more asphaltene and preasphaltene, accompanied by oil, were produced.

In single-staged reactions at 350°C without a catalyst, solvents already show very positive impacts on liquefaction. They have increased reaction conversion by breaking more bonds and generating more soluble products. The differences among the solvents, however, were not clearly shown under this condition. The donor solvent has slight advantages over other solvents in terms of having higher conversion and oil yield, but they are not significant. In the course of reaction, solvent is mixed with the coal particles so it may have three functions related to dissolution. One is to dissolve the hydrogen molecules or the hydrogen radicals and transport them to the reaction sites. The second possible function of the reaction solvent is to dissolve the free radicals generated during the reaction and thus to reduce local concentration of free radicals to prevent retrogressive reactions. The third is that the solvent can also dissolve products of the reaction. At this reaction temperature, physical effects may be more significant than chemical effects, because the study by Hooper et al [1979] showed that at 350°C the donor solvent (tetralin) was quite stable. Therefore reactions with a donor solvent do not show a significant difference from those with a non-donor solvent. However, comparing with a reaction with no solvent, the ones with a solvent, no matter what type of solvent, have apparent advantages in terms of conversion and product distribution.

The solvent effects at various temperatures are also studied. The results of liquefaction of the DECS-1 coal at temperatures between 250°C to 450°C without catalyst are listed in Table 5.15. Conversions, shown in Figure 5.6, are in a large range, from 11.7% to 92.2%. At 250°C, the solvents do not show any significant effect on conversion or product distribution. As temperature increases to 300°C, the solvents start

Table 5.15 Solvent effects on the DECS-1 coal at various temperatures in non-catalytic reactions

Temperature (°C)	Solvent	Conversion	Gas	Oil	Asphaltene	Preasphaltene
250	none	11.7	1.9	8.2	0.8	0.8
	tetralin	13.3	0.6	6.0	3.7	3.1
	1-MN	11.9	2.8	5.6	2.4	1.2
300	none	16.2	3.5	7.9	0.9	3.9
	tetralin	20.8	3.5	9.8	3.5	4.0
	1-MN	22.2	3.5	10.2	2.0	6.5
350	none	19.1	6.5	7.4	1.2	4.1
	tetralin	38.2	4.4	18.2	8.3	7.4
	1-MN	33.8	5.0	14.8	7.4	6.7
400	none	45.0	11.6	19.8	3.4	10.2
	tetralin	82.0	9.5	36.7	16.6	19.2
	1-MN	55.5	9.7	24.4	10.4	11.0
450	none	51.5	17.6	28.8	0.9	4.2
	tetralin	92.2	19.2	49.0	8.4	15.6
	1-MN	57.0	16.3	31.8	4.3	4.6

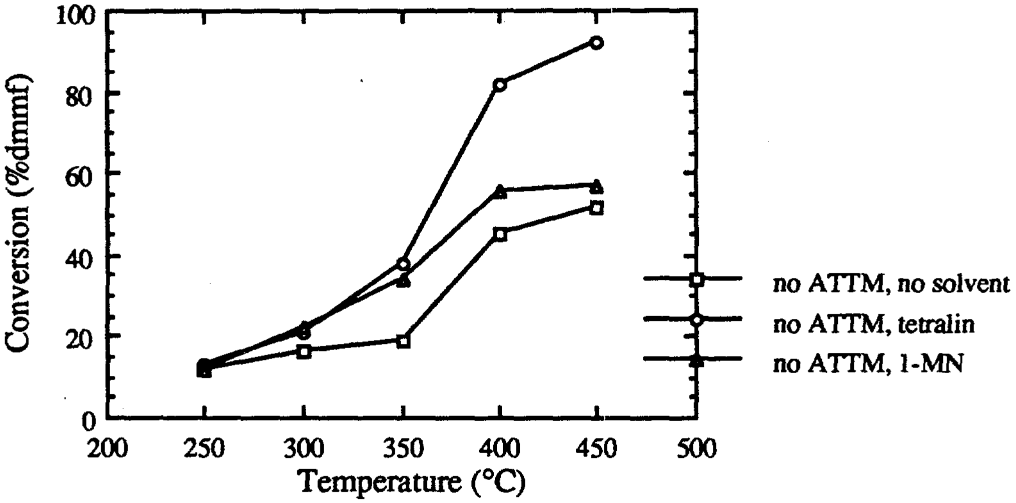


Figure 5.6 Solvent effects on the liquefaction of the DECS-1 coal at various temperatures without a catalyst

showing their advantage by providing slightly higher conversions than the reaction without solvent. At 350°C, there is a remarkable increase in oil, asphaltene and preasphaltene yields when a solvent is used. This indicates that in this temperature range, the solvents play a role which enhances the conversion, but since there is no difference between the reaction with tetralin and the reaction with 1-MN, this role may not relate to hydrogen donation. At temperatures ranging from 350°C to 400°C, there is a drastic increase in conversion no matter whether a solvent is applied or not, suggesting that in this temperature range, thermal energy is enough to break down the coal macromolecular matrix. At 400°C, tetralin made a tremendous difference from 1-MN and no solvent. The conversion reaches 82.0%, composed of gas, 9.5%; oil, 36.7%; asphaltene, 16.6%; and preasphaltene, 19.2%. With 1-MN or without solvent, the conversions are much less, 55.5% and 45.0% respectively. The differences of conversion and product distribution imply that tetralin is active in donating hydrogen at temperatures higher than 350°C. 1-MN, on the other hand, shows a very slight advantage over no solvent in gaining higher conversion and oil yield, but as temperature increases to 450°C, this advantage almost disappears.

Liquefaction of the DECS-9 coal with different solvents under single-staged condition is shown in Table 5.16. Since the study with the DECS-1 coal indicates that at a temperature of 300°C or lower, reactions do not proceed to significant extents, the reactions of the DECS-9 coal were carried out at temperatures of 350°C and higher. Figure 5.7 presents the conversions of the DECS-9 coal. At 350°C, the donor solvent already shows its advantage. As temperature increases, the advantage continues to be more apparent, because higher temperature is favorable for a higher rate of hydrogen radical generation which will be beneficial for high conversions. The non-donor solvent (1-MN), on the other hand, increases the conversion to the same extent at 350°C and

Table 5.16 Solvent effects on the DECS-9 coal at various temperatures in non-catalytic reactions

Temperature (°C)	Solvent	Conv. (%dmmf)	Gas	Oil	Asphaltene	Preasphaltene
350	None	19.4	2.5	8.8	2.5	5.7
	Tetralin	42.8	3.6	15.7	12.1	11.4
	1-MN	29.6	4.7	7.0	10.3	7.7
400	None	24.2	7.1	10.0	2.5	4.6
	Tetralin	74.2	6.9	18.9	21.8	26.6
	1-MN	37.6	7.1	13.8	8.8	8.0
450	None	38.5	12.5	21.9	0.3	3.8
	Tetralin	81.6	12.5	6.0	8.5	54.7
	1-MN	38.9	11.7	21.9	3.9	1.4

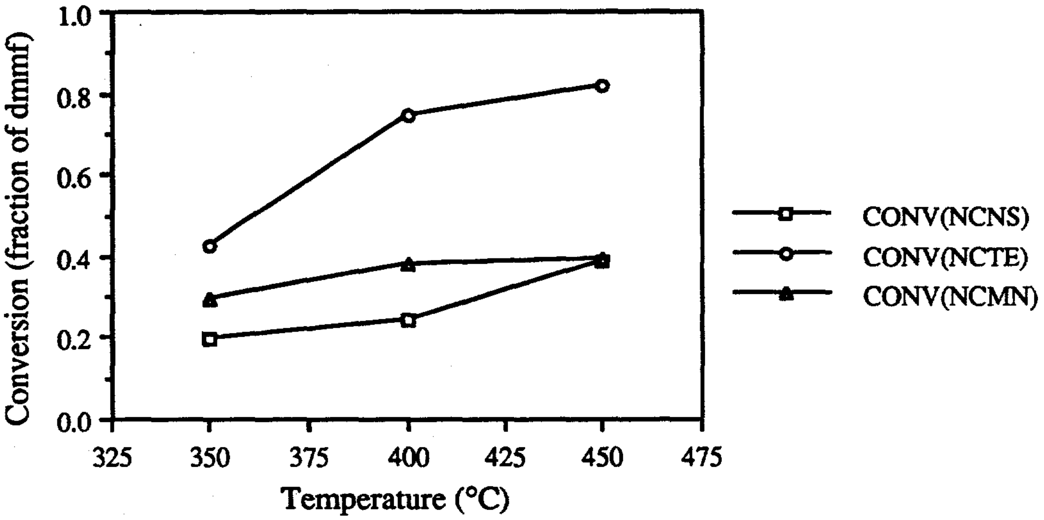


Figure 5.7 Solvent effects on non-catalytic liquefaction of the DECS-9 coal at various temperatures

400°C. When temperature is further increased to 450°C, 1-MN has no advantage. This again shows that the advantage of the non-donor solvent is due to physical processes, such as dissolving hydrogen radicals or the coal-derived radicals to prevent recombination of these radicals. The physical processes are not favored by the increase of temperature, because at a high temperature, a large portion of the solvent is vaporized and a small one is left in the liquid state acting as a solvator. On the other hand, the solubility of H_2 is lower at a high temperature.

Results of the DECS-11 coal are summarized in Table 5.17. Again these reactions were carried out at temperatures between 250°C to 450°C with different solvents but no catalyst. Figure 5.8 graphically shows the conversion data. Very similar to those of the

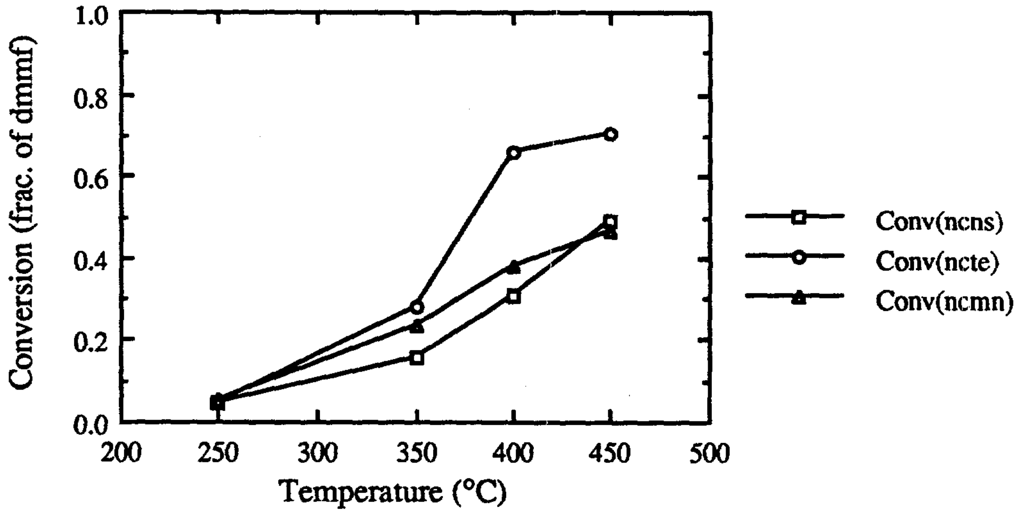


Figure 5.8 Solvent effects on non-catalytic liquefaction of the DECS-11 coal at various temperatures

Table 5.17 Solvent effects on the DECS-11 coal at various temperatures in non-catalytic reactions

Temperature (°C)	Solvent	Conv. (%dmmf)	Gas	Oil	Asphaltene	Preasphaltene
250	None	4.7	2.0	1.3	0.2	1.2
	Tetralin	4.6	1.7	0.0	1.2	1.7
	1-MN	5.3	2.0	1.5	1.2	0.6
350	None	15.4	6.5	8.4	0.3	0.2
	Tetralin	28.1	6.6	19.9	5.0	3.2
	1-MN	23.3	6.8	11.3	3.9	1.3
400	None	30.6	11.7	14.3	0.4	4.2
	Tetralin	65.9	12.5	25.3	12.3	15.7
	1-MN	37.7	10.6	16.2	4.0	6.9
450	None	49.1	16.8	25.3	0.6	6.4
	Tetralin	70.9	18.4	36.4	8.5	7.6
	1-MN	46.7	16.8	23.5	3.4	3.1

DECS-1 and the DECS-9 coals, the solvents, no matter what type they are, start to show their beneficial effects at 350°C. High temperature favors the donor solvent. Medium temperature, around 350°C to 400°C, favors the non-donor solvent, as shown in the experimental data.

In order to maximize solvent effect, reactions were carried out under more severe conditions, such as temperature-programmed condition. The lower temperature stage was 200°C and the higher one was 400°C. Again, no catalyst was applied. In Figure 5.9, reactions of the DECS-1 coal under temperature-programmed condition with different solvents are compared. Generally speaking, the use of a solvent increases liquefaction conversion to greater extents than the reactions under single-staged conditions, suggesting that the TPL condition enhances the beneficial effect of the solvent. This is expected because the low-temperature pretreatment in the TPL is designed for the solvents to penetrate into coal particles and to achieve a better mixing of the coal and the solvent. It is also possible that once the solvent molecules penetrate into the coal particles, they can further induce swelling, for example, Eser et al. [1991] observed that tetralin has the ability to swell a coal. Therefore the effectiveness of solvents is related to their swelling ability in addition to their hydrogen donating ability. Comparing the four different solvents, decalin and 1-MN yield very similar conversions, and WIMD and tetralin are quite close in terms of conversion. It is again observed that the donor solvents (tetralin and WIMD) perform much better at a high temperature. The reaction with tetralin has much higher gas plus oil yield, which may be either because hydrogenation is effective with the presence of tetralin or because tetralin has induced more hydrocracking to form small molecules such as those in oil and gas.

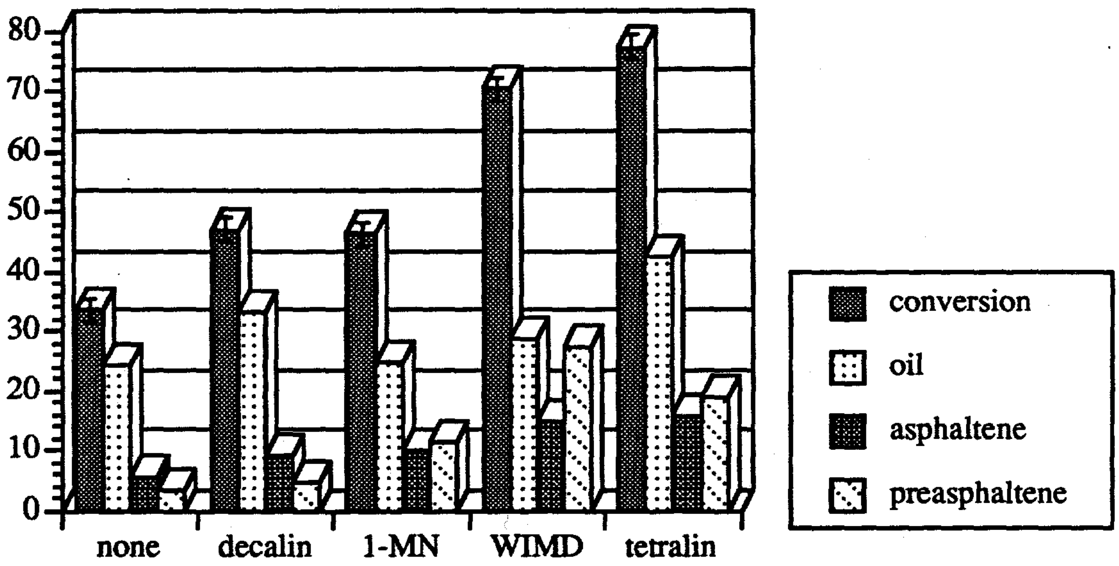


Figure 5.9 Solvent effects on non-catalytic liquefaction of the DECS-1 coal under temperature-programmed (200°C/400°C) condition

Reactions involving the DECS-9 and DECS-11 coals using decalin, WIMD and tetralin as solvents are presented in Figure 5.10 and Figure 5.11. The three solvents follow the same trend, that is, decalin < WIMD < tetralin in terms of conversion. Comparing the product yields in these three reactions, the donor solvents increase asphaltene and preasphaltene yields significantly; but they increase the oil plus gas yield only slightly.

In summary, the solvents have two major effects on non-catalytic coal liquefaction: one involves physical processes, the other one involves chemical processes. The physical processes include dissolving hydrogen radicals and coal-derived radicals and diluting the local concentration of these radicals thus to prevent recombination, and loosening the coal structure so that hydrogen radicals (or atoms) carried by a solvent can reach the reaction sites. The chemical process includes the dehydrogenation of the donor solvent and hydrogenation of the free radicals. The comparative study under the temperature-programmed condition yields the same conclusions as those under the single-staged condition. At a low temperature (350°C and below), using a solvent will enhance liquefaction to a noticeable extent. However, different types of solvent do not show significant differences, indicating that the advantages of the solvents at these temperatures are due to the physical processes, and thus the chemical characteristics of the solvents do not play an important role. At a medium temperature, between 350°C and 450°C, both the physical and the chemical processes are involved. The physical ones can be seen based on the fact that reactions with the non-donor solvent have higher conversions than those without any solvent. The reactions with a donor solvent, on the

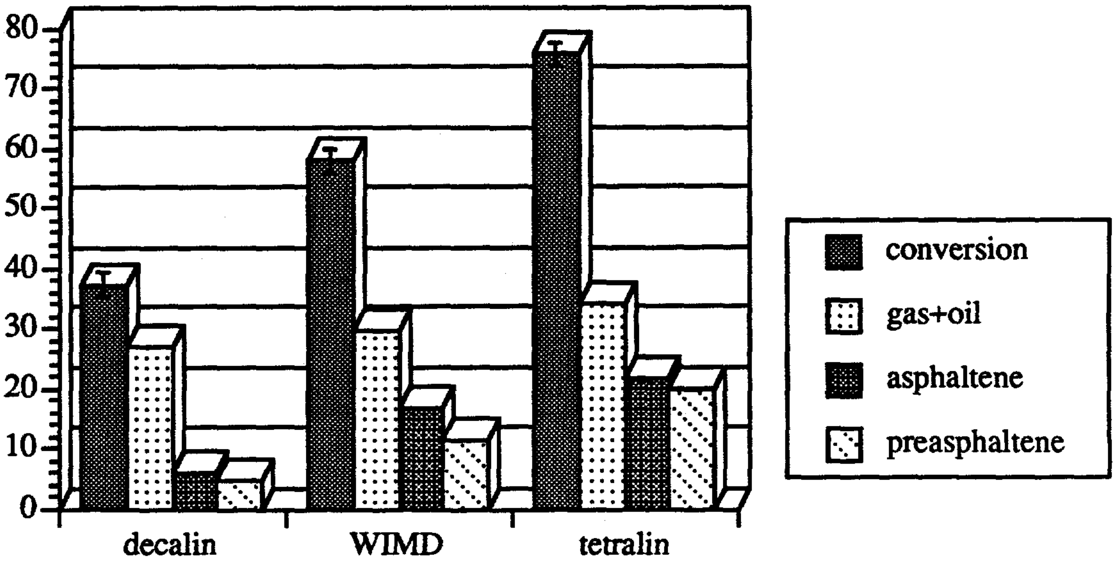


Figure 5.10 Solvent effects on the non-catalytic liquefaction of the DECS-9 coal under temperature-programmed condition

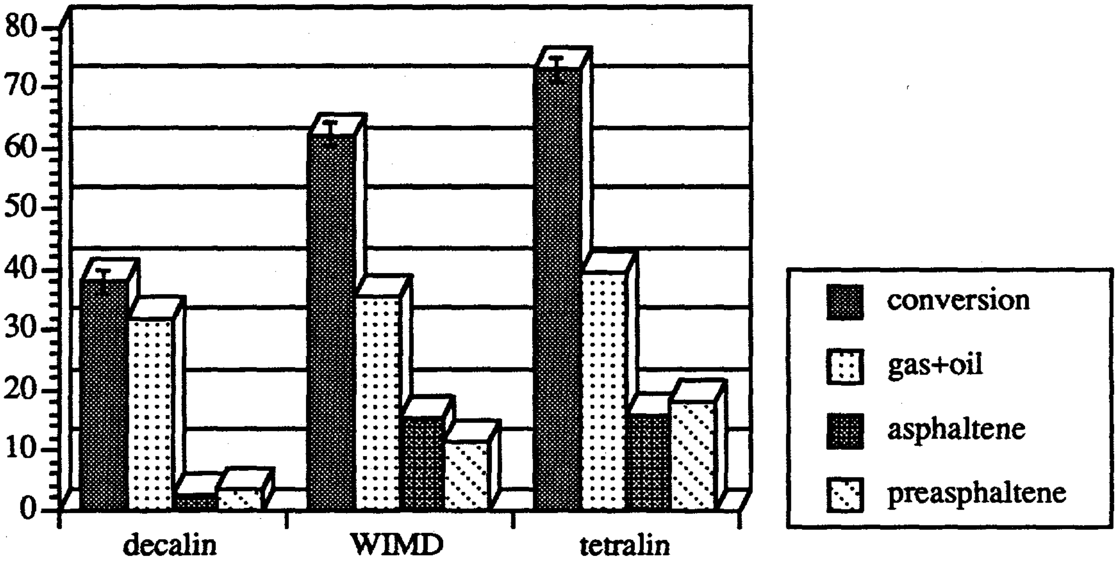


Figure 5.11 Solvent effects on the non-catalytic liquefaction of the DECS-1 coal under temperature-programmed condition

other hand, have even higher conversion than those with the non-donor solvent, indicating that hydrogen donation plays a role. When temperature further increases to 450°C, the physical processes are no longer important, according to the observation that the non-donor solvent, 1-MN, has no advantage in terms of providing a high conversion. At this temperature, significant amounts of the solvents are in the gas phase, which is unfavorable to some processes such as dissolving the hydrogen radicals or the coal-derived free radicals. The donor solvent, however, still shows its beneficial effects on all the three coals.

5.2.2 Behavior of Solvents in the Presence of a Catalyst

The results of catalytic liquefaction of the DECS-1 coal are shown in Table 5.18. In the presence of ATTM, the conversions in all experiments increase drastically as temperature increases from 250°C to 400°C, Figure 5.12. Comparing the reactions which has no solvent, tetralin, or 1-MN with the corresponding non-catalytic reactions, the catalyst increased the conversion, especially at temperatures higher than 300°C, suggesting that ATTM was converted to an active form at temperatures between 300°C and 350°C [Garcia and Schobert, 1989]. Furthermore, the product distribution shows that the increasing conversion is accompanied by an increasing yield of light materials, such as oil, when the catalyst is added. The other comparison is among the catalytic reactions using different solvents. At temperatures between 250°C and 400°C, there is no significant difference in conversion and product distribution (though at 400°C the reaction without solvent seems to have higher oil yield). It is postulated that, in this temperature range, the catalyst has a stronger effect than the solvents; thus any difference caused by the solvents is diminished. However, at 450°C, tetralin gave a slightly higher

Table 5.18 Solvent effects on the DECS-1 coal at various temperatures in catalytic reactions

Temperature (°C)	Solvent	Conversion	Gas	Oil	Asphaltene	Preasphaltene
250	none	5.0	0.9	0.0	3.1	3.8
	tetralin	3.8	0.9	0.0	2.3	1.7
	1-MN	3.6	0.6	0.0	2.3	2.5
300	none	17.2	2.5	9.3	1.8	3.6
	tetralin	22.0	0.9	12.4	5.5	3.2
	1-MN	22.9	2.4	10.2	6.0	4.3
350	none	39.4	4.0	23.2	6.2	6.0
	tetralin	46.6	3.7	23.9	11.4	7.6
	1-MN	44.0	3.4	18.5	9.9	12.2
400	none	95.5	7.4	58.9	24.0	5.2
	tetralin	92.0	6.8	44.3	19.3	21.6
	1-MN	84.8	8.1	41.6	16.4	18.7
450	none	69.4	18.0	44.6	5.2	1.6
	tetralin	95.8	14.2	66.1	10.4	5.1
	1-MN	67.2	16.1	37.4	8.4	5.3

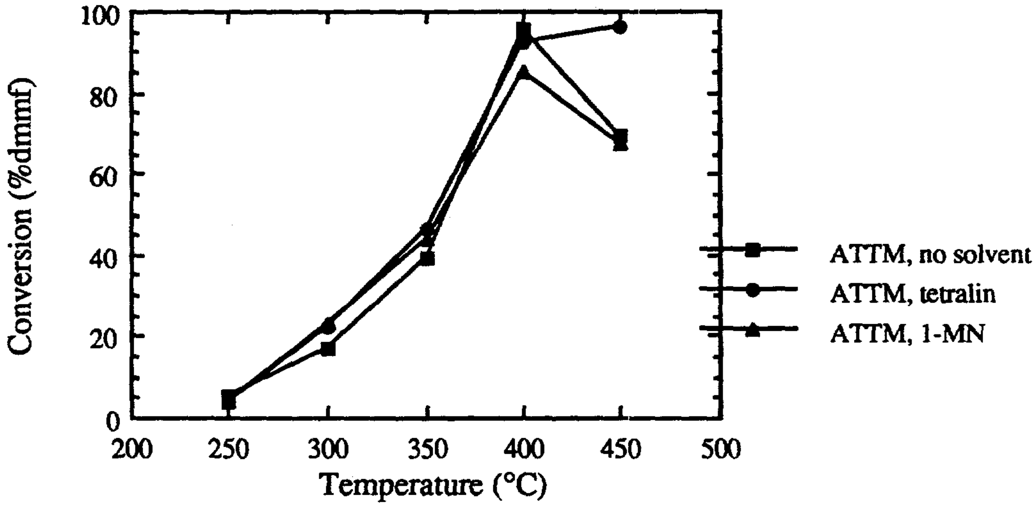


Figure 5.12 Solvent effects on catalytic liquefaction of the DECS-1 coal at various temperatures

conversion; both 1-MN and no solvent actually gave a much lower conversion (almost 20 percentage units lower) relative to those at 400°C. In the case of 1-MN at 450°C, the yields of gas, asphaltene and preasphaltene are still very similar to those in tetralin, but the conversion is much lower. The sole cause of this conversion difference is the decrease of the oil yield. With tetralin at 450°C, yields of asphaltene and preasphaltene dropped by 9 percentage units and 17 percentage units respectively, and the yield of oil increased by 22 percentage units compared with that at 400°C. This suggests that at this temperature (450°C), in the presence of both catalyst and a H-donor solvent, the conversion from preasphaltene and asphaltene to oil, or from heavy products to light products, is favorable. With the presence of the catalyst but absence of a donor solvent (meaning with no solvent or with a non-donor solvent), the conversion drops as well as all of the product yields, except gas, suggesting that retrogressive reactions take place and form heavier and more stable materials. The gas yield, however, does not seem to be affected by the catalyst or the donor solvent, which will be further discussed in Section 5.3.1.

To compare the solvent effects with or without the presence of the catalyst, results of the experiments at 400°C with different solvents are plotted in Figure 5.13 for the DECS-1 coal. In the non-catalytic reactions, the non-donor solvent and the donor solvent have apparent advantages in terms of providing high conversions and oil yields. However, the differences caused by the different solvents disappear upon the use of the catalyst, indicating that the catalyst has a much stronger influence on the reaction than the solvents. In hydro-liquefaction, there are two hydrogen sources. One is the gaseous hydrogen. The other one is hydrogen donor solvent. With the presence of the catalyst, the hydrogenation by the gas-phase hydrogen is significantly enhanced, which is shown in the reaction with ATTM but no solvent (92% of conversion and about 60% of oil).

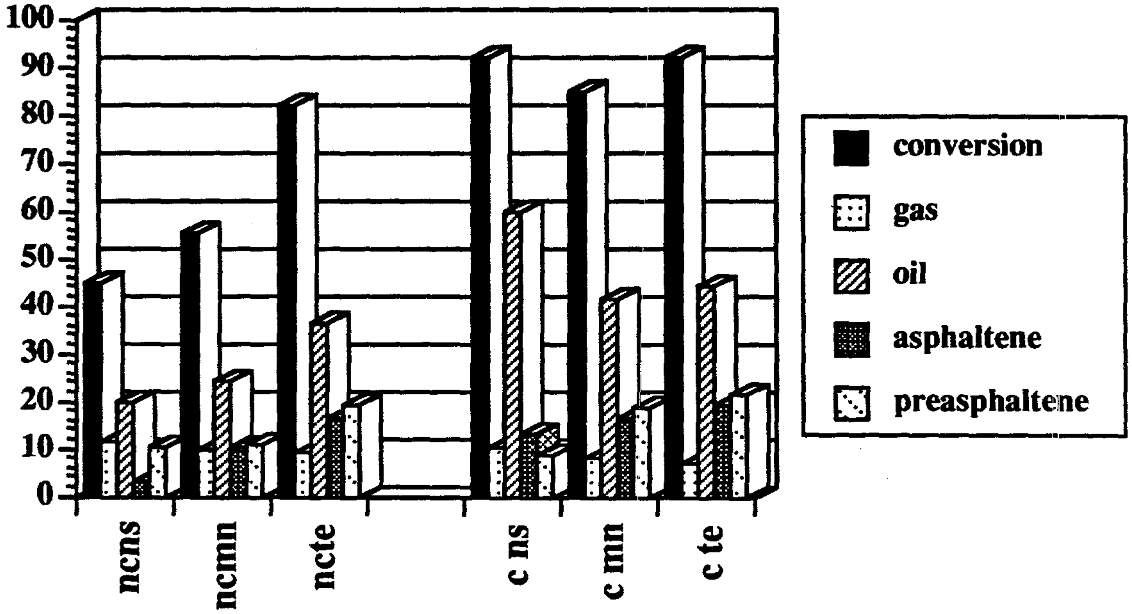


Figure 5.13 Comparison of the solvent effects on the DECS-1 coal at 400°C with and without the catalyst

The catalytic effect on the gas-phase hydrogenation will be further discussed in Section 5.3.4. The increases in conversion and oil yield due to the use of the catalyst are so significant that it is no longer necessary to use any donor solvent to obtain the maximum conversion and oil yield for this coal at 400°C.

The results of the liquefaction experiments of the DECS-11 coal with the presence of ATTM and different solvents are indicated in Table 5.19. Comparing with the DECS-1 coal, the DECS-11 coal has lower conversions at all temperatures, Figure 5.14, suggesting that this coal is less easily converted to THF solubles. On the other hand, with respect to the solvent effect on liquefaction, this coal also acts quite differently. At 350°C, reaction with either tetralin or 1-MN has markedly higher conversions than the one with no solvent. When temperature increases to 400°C and 450°C, the beneficial effects of the non-donor solvent disappear; while the donor solvent still leads to conversion over 10 percentage units higher than no solvent. Earlier studies in Chapter 3 have shown that this coal contains less aliphatic carbon and less hydrogen than the DECS-1 coal. The higher content of aromatic structure may make it more difficult to crack down the coal macromolecular structure; and during liquefaction, more hydrogens are needed to insert into the coal in order to obtain desirable products. Therefore in this case, hydrogenation only by the gas-phase hydrogen is no longer sufficient; a donor solvent has to be used.

Reactions of the DECS-9 coal with solvents and the catalyst are summarized in Table 5.20. The conversion data show quite different trends from the other two coals, Figure 5.15. At temperatures between 350°C to 450°C, the non-donor solvent has no advantage in terms of providing a high conversion. The donor solvent, however, has remarkable influences on the reaction throughout the temperature range. At 350°C, the

Table 5.19 Solvent effects on the DECS-11 coal at various temperatures in catalytic reactions

Temperature (°C)	Solvent	Conv. (%dmmf)	Gas	Oil	Asphaltene	Preasphaltene
350	None	17.1	6.2	5.7	2.2	3.0
	Tetralin	29.8	5.7	12.0	5.5	6.7
	1-MN	28.6	6.0	8.3	8.0	6.3
400	None	63.5	16.6	20.0	16.4	10.5
	Tetralin	76.8	12.3	23.2	21.8	19.5
	1-MN	65.5	11.7	18.6	14.7	20.5
450	None	53.6	20.3	26.0	4.0	3.4
	Tetralin	71.1	24.2	31.7	7.9	7.3
	1-MN	54.6	18.4	26.9	5.2	4.1

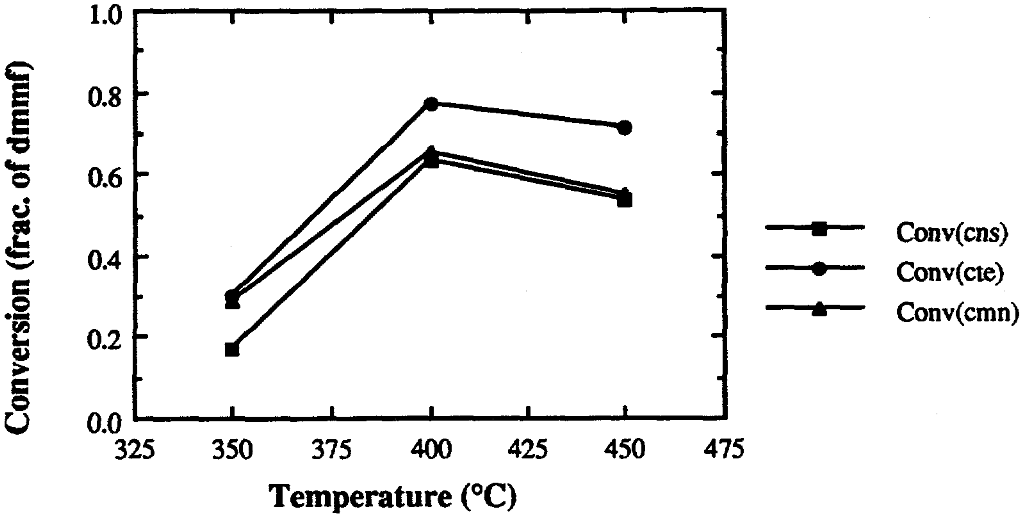


Figure 5.14 Solvent effects on catalytic liquefaction of the DECS-11 coal at various temperatures

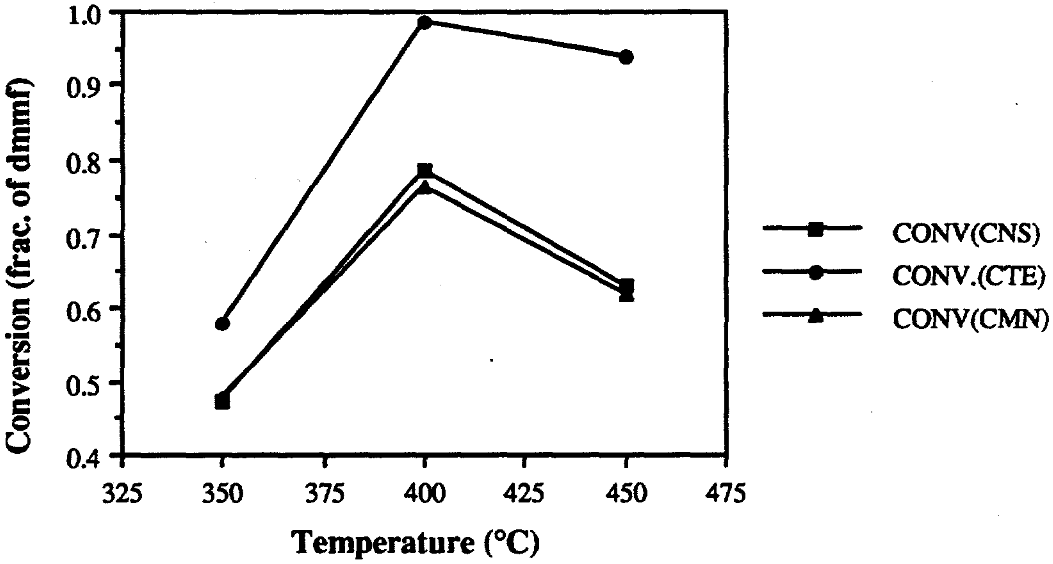


Figure 5.15 Solvent effects on catalytic liquefaction of the DECS-9 coal at various temperatures

Table 5.20 Solvent effects on the DECS-9 coal at various temperatures in catalytic reactions

Temperature (°C)	Solvent	Conv. (%dmmf)	Gas	Oil	Asphaltene	Preasphaltene
350	None	47.1	2.9	8.7	12.5	23.1
	Tetralin	57.9	2.9	14.6	20.2	20.3
	1-MN	47.7	2.9	10.8	13.9	20.0
400	None	78.5	6.3	34.1	23.5	14.6
	Tetralin	98.5	3.7	40.5	27.6	26.6
	1-MN	76.5	7.2	30.2	14.3	24.9
450	None	62.9	12.0	39.8	6.2	4.9
	Tetralin	93.8	13.2	41.0	9.2	30.5
	1-MN	61.7	11.5	35.9	11.2	3.0

donor solvent raises conversion by 10 percentage units, and at 400°C, by 20 percentage units. When temperature is further increased to 450°C, the reaction with the donor solvent decreases compared with the one at 400°C. However, the decrease in conversion of the reaction with the donor solvent is much smaller than the decreases in conversion of the reactions with the non-donor solvent and with no solvent. Therefore, at 450°C, the conversion of the reaction with the donor solvent is still about 30 percentage units higher than those with the non-donor solvent and no solvent.

The conversion decrease when temperature is increased to 450°C has been observed for all the three coals. This must be due to retrogressive reactions. In these experiments, the coal samples were heated to a high temperature (450°C) in a very short time. The coal macromolecules were cleaved and free radicals were produced very quickly. If these radicals are not stabilized immediately, they will recombine with each other and form very stable and crosslinked molecules which are difficult to break down. In the reactions with the non-donor solvent or no solvent, the only hydrogen source is the gas-phase hydrogen. The hydrogen molecules are catalytically dissociated to form hydrogen radicals. The radicals then have to migrate to the reaction sites to stabilize the coal-derived radicals. Apparently, the hydrogenation process by H_2 is insufficient in reactions at 450°C even with the presence of the catalyst, and therefore retrogressive reactions take place and cause lower conversion. In the reactions with the donor solvent, there are two hydrogen sources: one is the gas-phase hydrogen; the other is the donor solvent. Since the donor solvent is well mixed with the coal sample, owing to the constant shaking during reaction, the hydrogen radicals produced by the solvent are very close to the reaction sites. As soon as the coal-derived radicals are generated, hydrogenation takes place to produce soluble materials. Therefore reactions with the donor solvent have a much higher conversion than those without the donor solvent. Even though the donor solvent can significantly enhance hydrogenation, retrogressive reactions still occur at a high temperature due to the unbalance of radical formation and hydrogenation. This is why a decrease in conversion is observed when temperature increases to 450°C. Nevertheless, the only way to reduce retrogressive reactions and to achieve a high conversion is to use a good donor solvent. The hydrogenation by H_2 is certainly not sufficient, even when this catalyst is applied.

The behavior of the solvents in the presence of ATTM was also studied under temperature-programmed condition (at 200°C/400°C). Figure 5.16 graphically presents the comparison of reactions of the DECS-1 coal with no solvent, decalin, and WIMD. The experiment with no solvent yields conversion about 95% and oil plus gas close to 70%. Decalin, a non-donor solvent, gives conversion about 85% and oil plus gas about 60%; and even the WIMD, a donor solvent, results in 92% conversion and 62% of oil and gas, less than that with no solvent. However, the solvents behave quite differently with the DECS-9 coal, as shown in Figure 5.17, and with the DECS-11 coal (Figure 5.18). In the study of these two coals, tetralin was also used in addition to decalin and WIMD. The reactions with no solvent have much lower conversions than that of the DECS-1 coal; they are 72% for the DECS-9 coal and 68% for the DECS-11 coal. Comparing with the reactions with no solvent, adding the non-donor solvent does not seem to have any beneficial effect on the liquefaction results. The donor solvents, WIMD and tetralin, have remarkable impacts on the reaction. They increase conversion by about 20 percentage units for the DECS-9 coal and about 15 percentage units for the DECS-11 coal compared with the corresponding reactions with no solvent. The observation on the reactions under the temperature-programmed condition agrees with that under single-staged condition. For the DECS-1 coal, which is rich in hydrogen and aliphatic carbon, and thus easy to be converted to THF solubles, the catalyst is sufficient for a high conversion, hence adding a

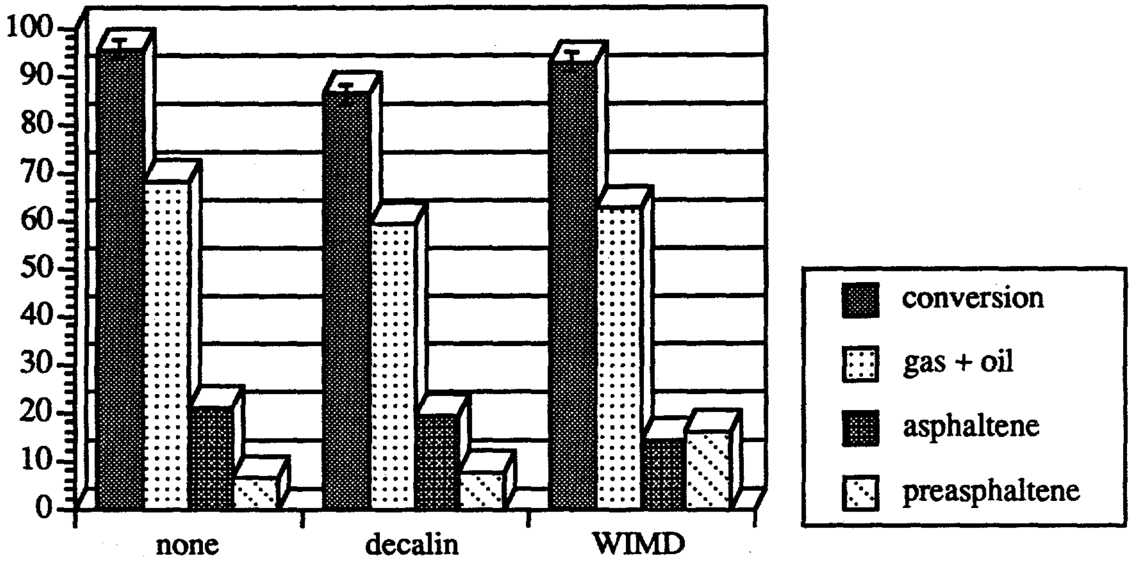


Figure 5.16 Solvent effects on liquefaction of the DECS-1 coal in the presence of ATTM under temperature-programmed condition

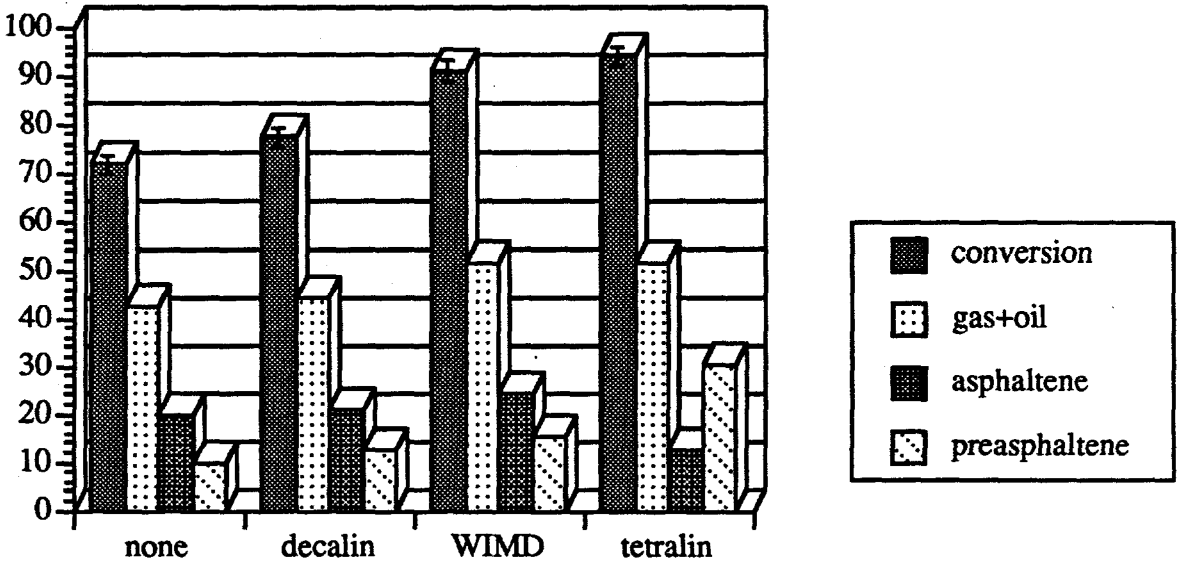


Figure 5.17 Solvent effects on liquefaction of the DECS-9 coal in the presence of ATTM under temperature-programmed condition

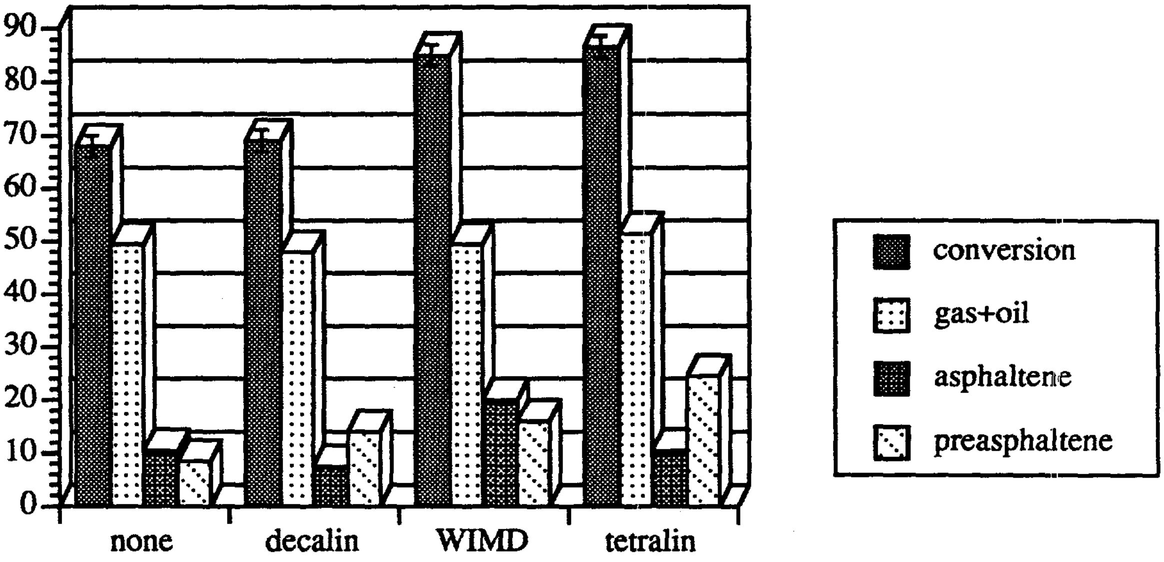


Figure 5.18 Solvent effects on liquefaction of the DECS-11 coal in the presence of ATTM under temperature-programmed condition

donor solvent is not necessary for this coal at 400°C and below. For the DECS-9 and the DECS-11 coals, which are less easily to be converted to THF solubles, reactions only with the catalyst do not result in the maximum conversion and oil yield. Therefore a donor solvent must be applied to these two coals in order to achieve a high conversion.

In order to compare the effects of the donor solvent and the catalyst, reactions at 400°C with no solvent or catalyst, with tetralin but no catalyst, with ATTM but no solvent, and with both tetralin and the catalyst are graphically plotted in Figure 5.19 for the DECS-1 coal, Figure 5.20 for the DECS-9 coal and Figure 5.21 for the DECS-11 coal. For the DECS-1 coal, the catalyst has a stronger impact on the coal to have higher conversion and oil yield. Because the effect of the catalyst is so strong that the conversion reaches its maximum value, using the donor solvent in addition to the use of the catalyst becomes unnecessary. For the DECS-9 and the DECS-11 coals, which are more difficult to be converted to THF solubles, the catalyst and the donor solvent have very compatible roles upon reaction. Since the reactions with either the donor solvent or the catalyst only have conversions about 65% for the DECS-11 coal and 75% for the DECS-9 coal, the co-existence of the catalyst and the solvent has synergistic effects on both conversion and the oil yield. According to the elemental analyses of the three coals (in Chapter 3), the DECS-1 coal contains the highest percentage of hydrogen. The NMR and FTIR data indicate that this coal possesses a significant amount of long-chain aliphatics. Therefore the structural features of this coal suggest that the hydrogenation of this coal may be easier than the other two coals.

The reactions at 450°C for the three coals are plotted in Figure 5.22, 5.23 and 5.24 for the DECS-1, DECS-9 and the DECS-11 coal respectively. At 450°C, retrogressive reactions may occur due to the unbalance of free-radical formation and hydrogenation.

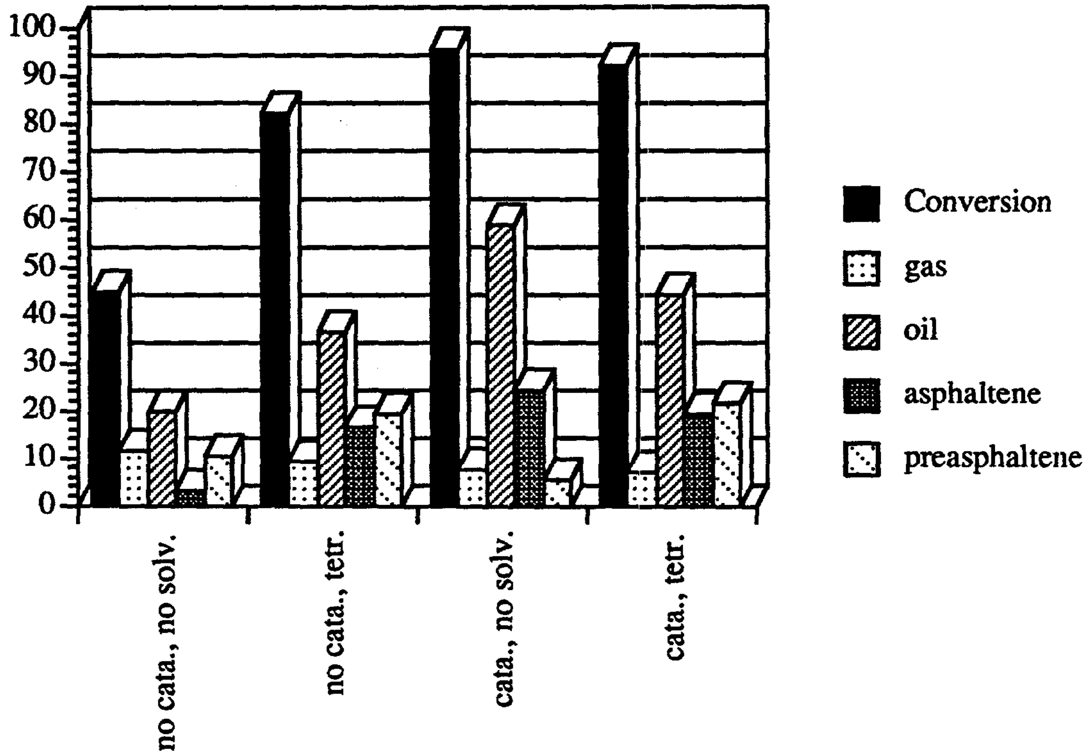


Figure 5.19 Comparison of the effects of the catalyst and the donor solvent on liquefaction of the DECS-1 coal at 400°C

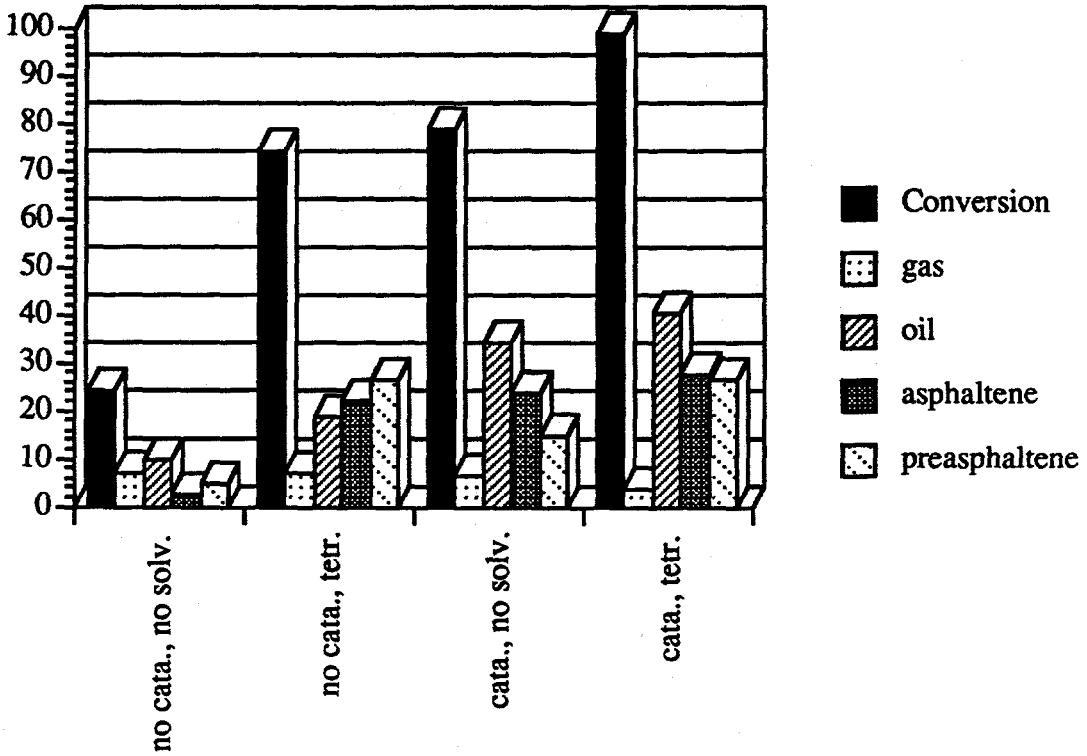


Figure 5.20 Comparison of the effects of the catalyst and donor solvent on liquefaction of the DECS-9 coal at 400°C

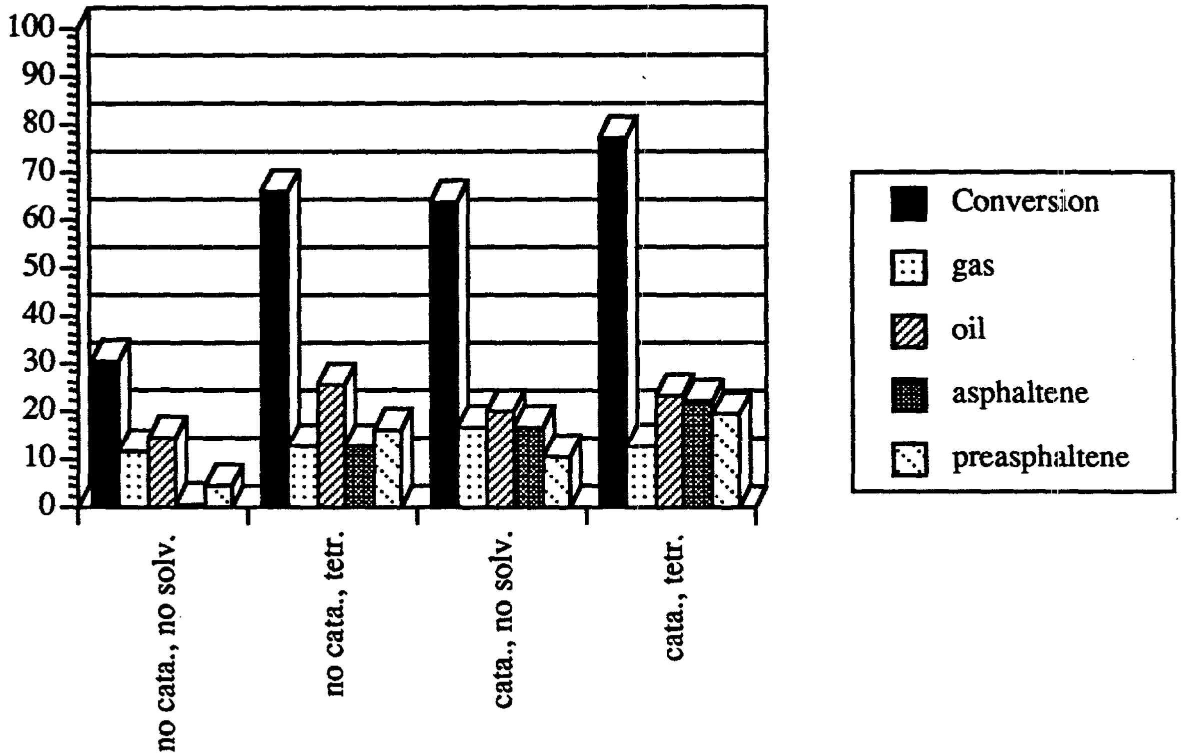


Figure 5.21 Comparison of the effects of the catalyst and donor solvent on liquefaction of the DECS-11 coal at 400°C

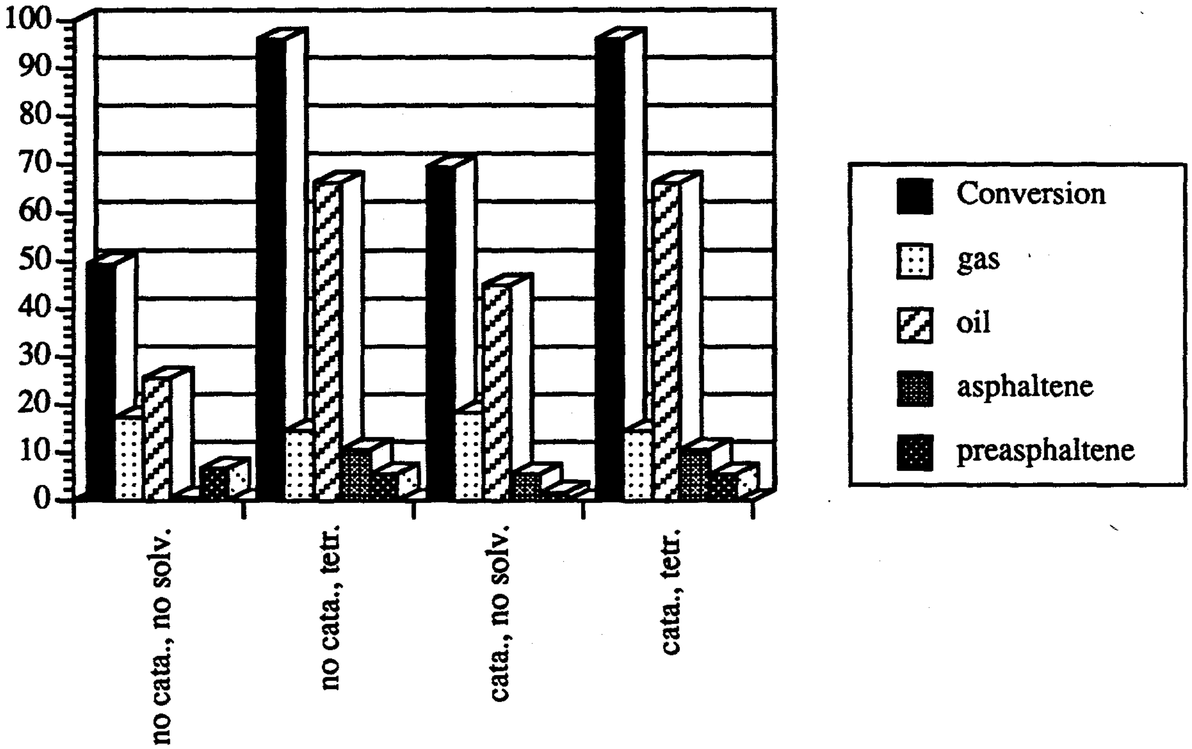


Figure 5.22 Comparison of the effects of the catalyst and the donor solvent on liquefaction of the DECS-1 coal at 450°C

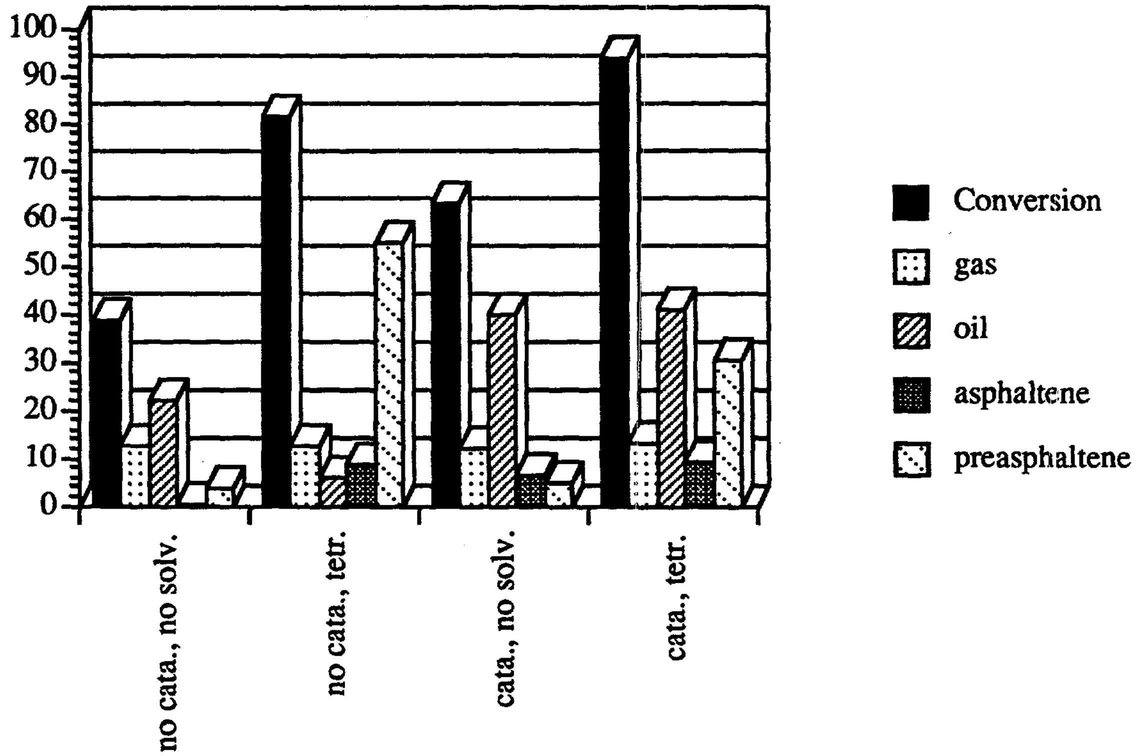


Figure 5.23 Comparison of the effects of the catalyst and the donor solvent on liquefaction of the DECS-9 coal at 450°C

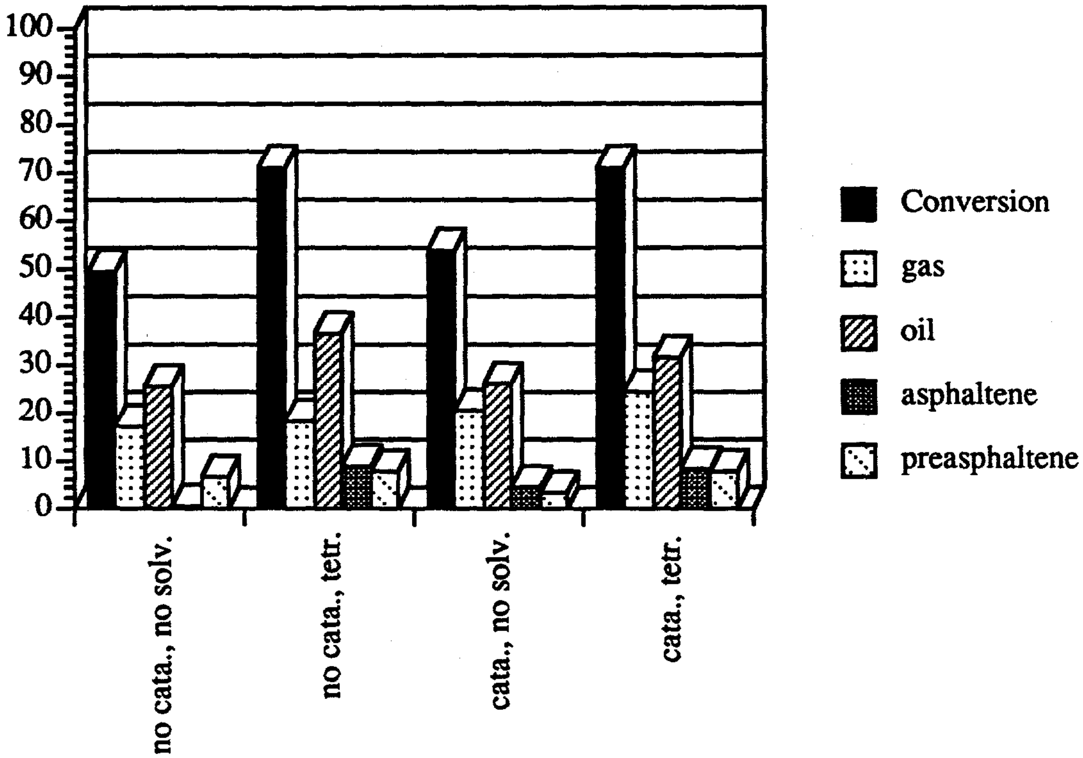


Figure 5.24 Comparison of the effects of the catalyst and the donor solvent on liquefaction of the DECS-11 coal at 450°C

Since free radicals are generated faster at this temperature than that at 400°C, it is important to enhance hydrogenation. For the DECS-1 coal, in Figure 5.22, the donor solvent seems to be able to enhance hydrogenation to a much greater extent than the catalyst. The increase of temperature from 400°C to 450°C is not beneficial to the performance of the catalyst, suggesting that the catalyst can provide a sufficient hydrogen source in this case. The reaction with both solvent and the catalyst has a similar conversion, as well as oil yield, as that in the reaction only with the solvent, indicating that the solvent provides enough hydrogen under this reaction condition. In the reaction of the DECS-9 and the DECS-11 coal, the donor solvent is more beneficial than the catalyst, and adding both the catalyst and the solvent seems to be necessary.

To summarize the observations made on the three coals under two temperatures, hydrogenation is insufficient when only the catalyst or the donor solvent is used in most of the cases. Therefore it is necessary to have both of them present in the reaction, especially when temperature is high.

5.3 Effects of Reaction Solvents and Catalysts on Gases

5.3.1 Gas Production in Reactions

The gas yields from all liquefaction experiments are plotted versus temperature in Figure 5.25-5.27 for the three coals. For the DECS-1 coal, all the gas yields are in the range from 0% to 20%; for the DECS-9 coal, they are between 2% and 14%; and for the DECS-11 coal, they are between 2% and 24%. Regardless of the solvents and the catalyst used in the reactions, all the gas yields of each coal fall on one line. Therefore, the amount of gas produced in a reaction is a function only of temperature. Since neither

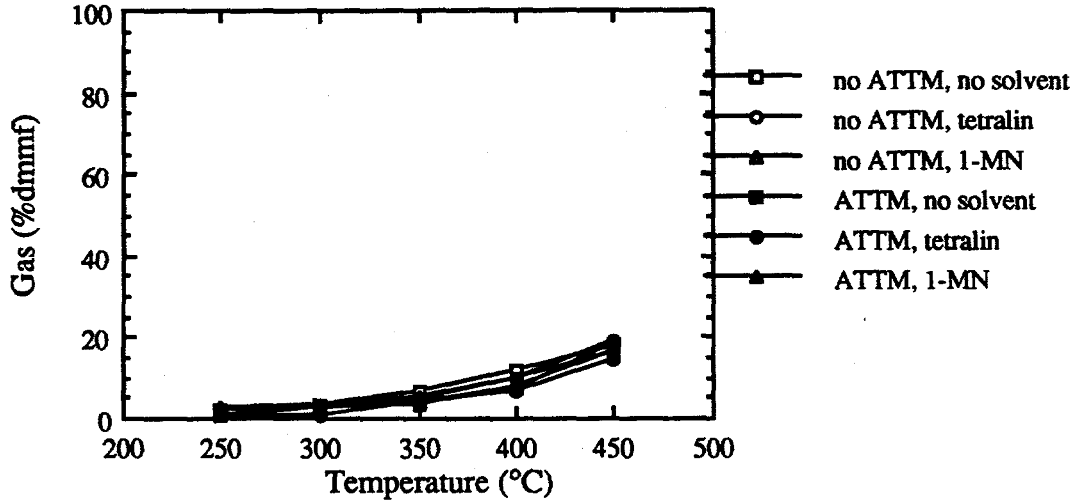


Figure 5.25 Gas yields from liquefaction of the DECS-1 coal

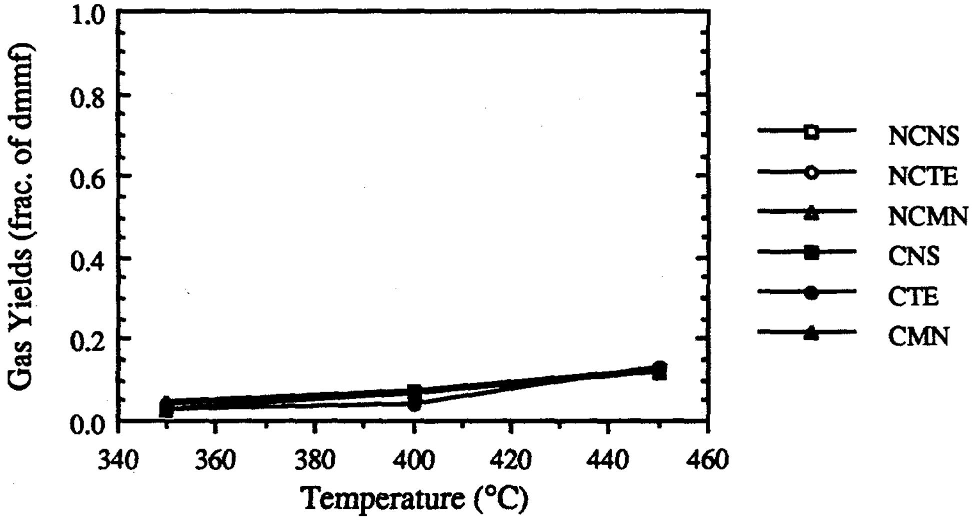


Figure 5.26 Gas yields from liquefaction of the DECS-9 coal

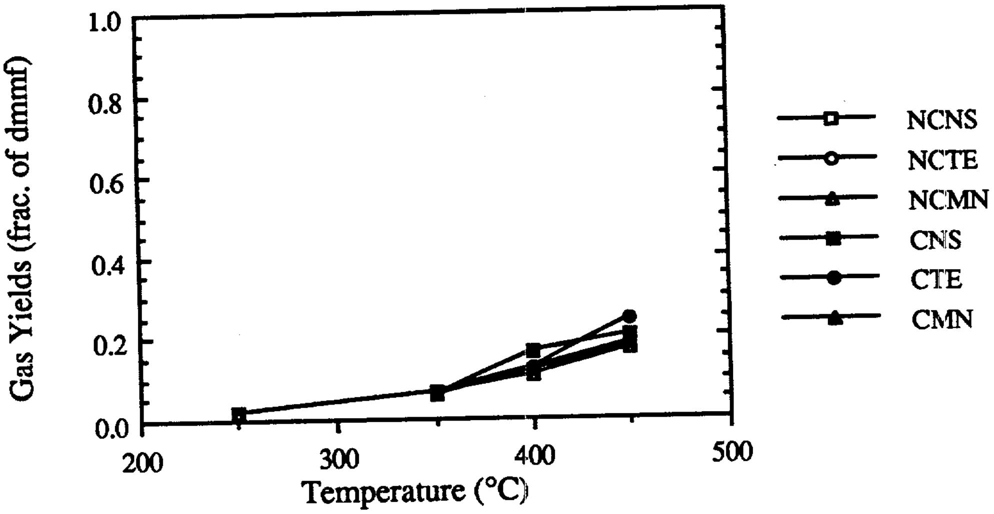


Figure 5.27 Gas yields from liquefaction of the DECS-11 coal

a solvent nor a catalyst has any effect, gas formation is a reaction driven by thermal energy.

The gas samples produced during liquefaction were collected and analyzed by gas chromatography both qualitatively and quantitatively. The amounts of hydrocarbon gases are plotted in Figure 5.28 and Figure 5.29 for the DECS-9 and DECS-11 coals under different reaction conditions. As temperature increases, the total amount of hydrocarbons increases. The majority of the gases is paraffins with number of carbons of six and less, such as methane, ethane and propane. It is interesting to notice that in the reactions with tetralin, no matter whether the catalyst is applied or not, the total amount of hydrocarbon gases is much higher than those under other conditions. This suggests that tetralin promotes the formation of paraffins with small numbers of carbons. According to the hydrogenation mechanism proposed by McMillen et al. [1985, 1987a & b, and 1991], the solvent donates a hydrogen to an aromatic site to induce a bond breaking between the aromatic ring and the side chain. The observed increases in C_1-C_3 paraffins with the presence of tetralin are possibly the results of the cleavages of the side chains. In fact, in a later discussion about the oil samples (Figure 5.35), it is observed that the oil, produced in a reaction where tetralin was present, contains less methylphenols than the ones produced in reactions where tetralin was absent, proving that the cleavage between the methyl groups and the aromatic rings are greatly enhanced by tetralin.

Figure 5.30 and Figure 5.31 show the CO_2 and CO production of the DECS-1 coal under different reaction conditions. The amount of CO_2 increases slightly when temperature increases from 350°C to 400°C, and it increases to much greater extents when temperature further increases to 450°C. The CO_2 formation is believed to be an evidence of decarboxylation reactions which could result in retrogressive reaction

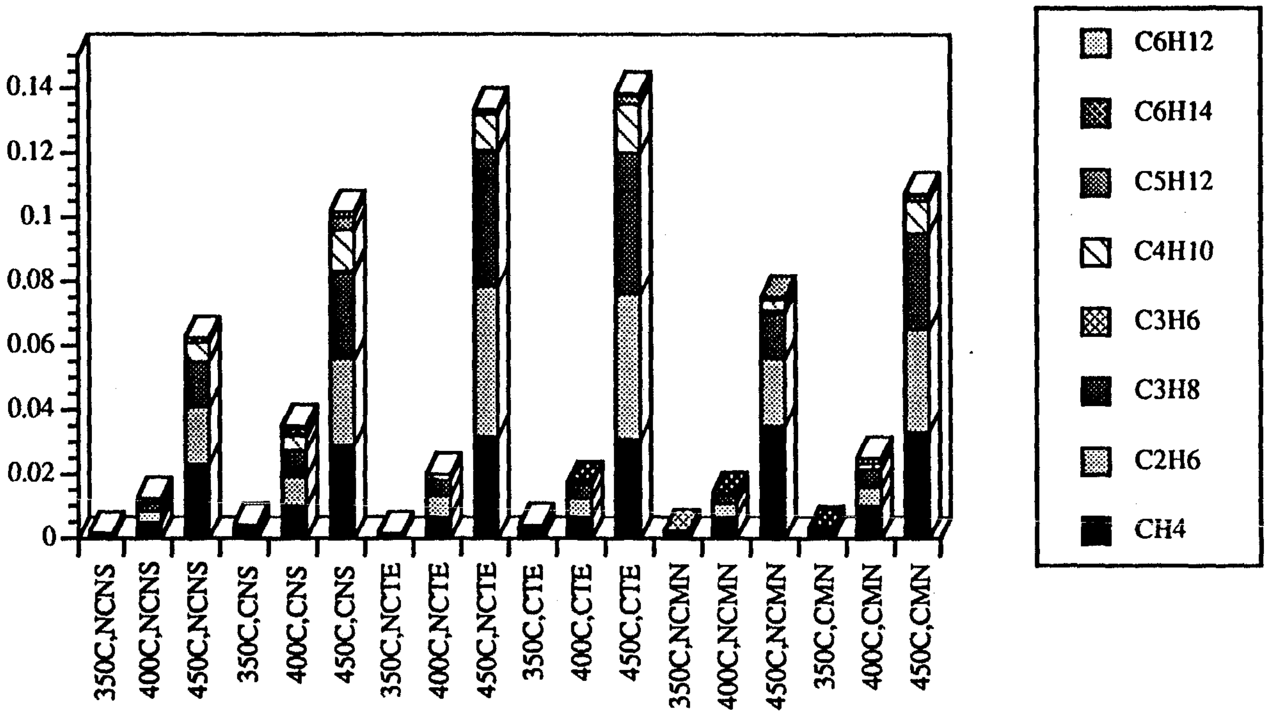


Figure 5.28 Hydrocarbon gases produced in liquefaction of the DECS-9 coal

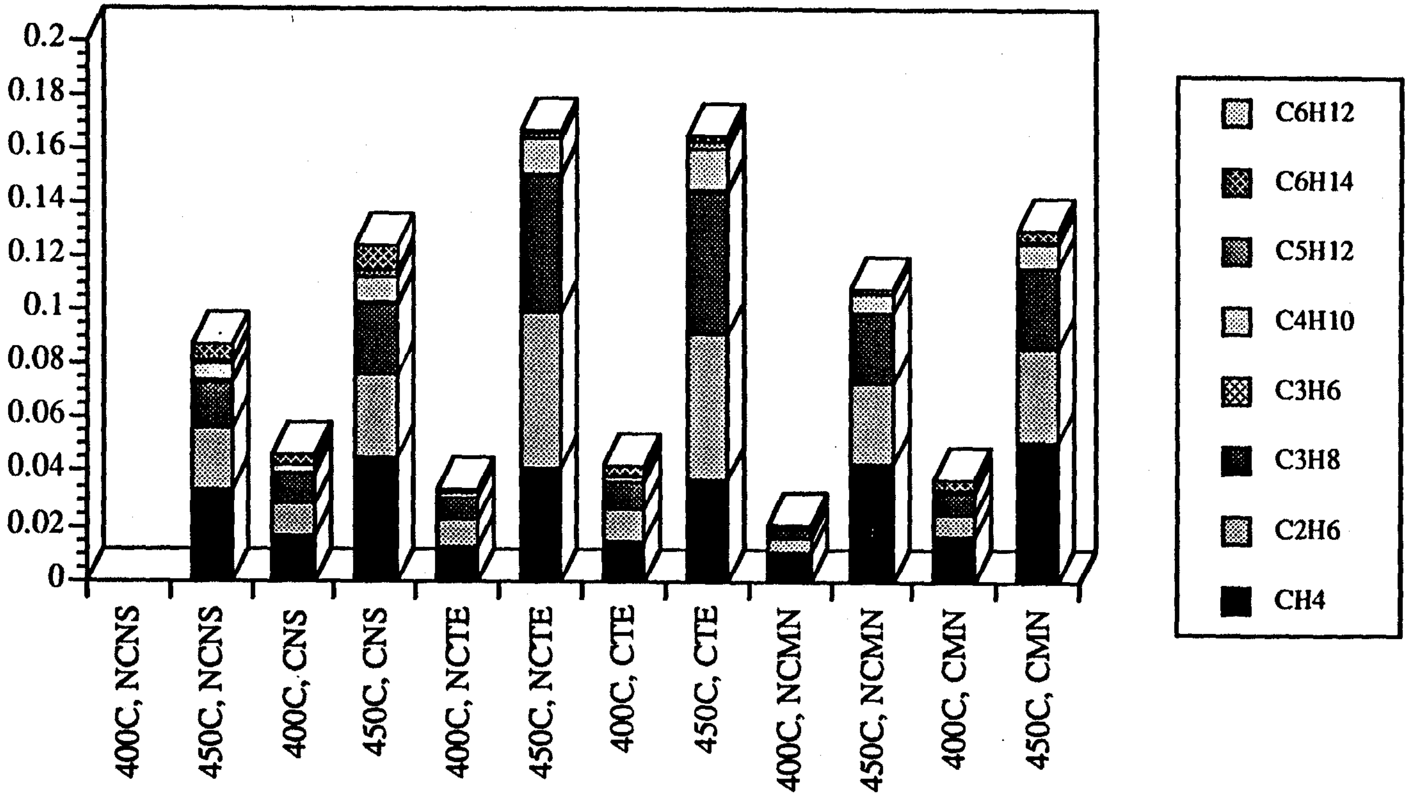


Figure 5.29 Hydrocarbon gases produced in liquefaction of the DECS-11 coal

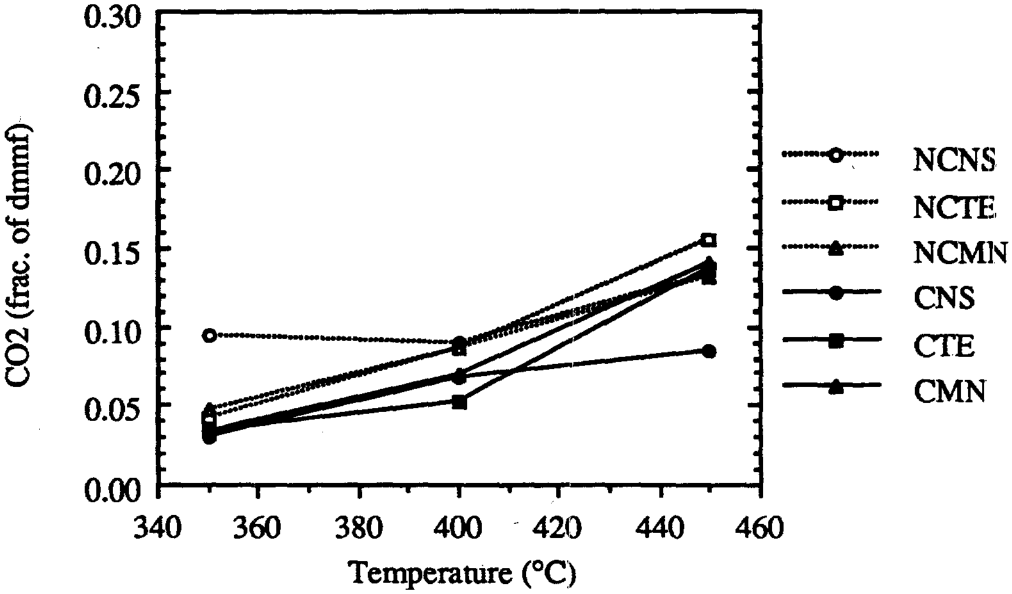


Figure 5.30 CO_2 yields in liquefaction reactions of the DECS-9 coal

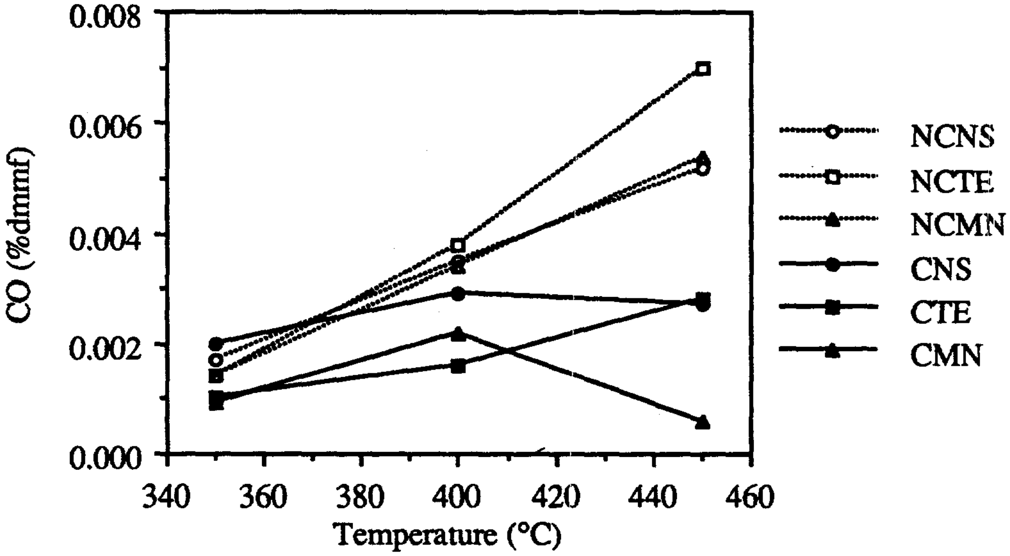


Figure 5.31 CO yields in liquefaction reactions of the DECS-9 coal

[Suuberg et al., 1987; Solomon et al., 1990; and Lynch et al., 1991], thus the increases of CO_2 when temperature increases to 450°C indicate severe retrogressive reactions at this temperature. This is in a good agreement with the earlier observation (Section 5.2) that there are considerable drops in conversions at this temperature relative to those at 400°C. The CO production, on the other hand, shows different trends upon changes in reaction condition. In the non-catalytic reactions, it increases with temperature throughout the range under study; while in catalytic reactions, the CO productions first increase when temperature increases from 350°C to 400°C then drop remarkably when temperature further increases to 450°C. The CO formation may be due to decarbonylation of ketones. The increases of CO with temperature indicate more cleavages of the bonds. When the hydrogenation catalyst (as will be discussed in the following section) is applied, the requirements for a Fischer-Tropsch reaction are satisfied, which is the co-existence of CO, a catalyst, and H_2. Therefore the Fischer-Tropsch reaction may take place and consume CO. Another postulation about the decreases in CO production in catalytic reactions is that CO insertion reactions occurred during liquefaction, which consumed CO. In a later section (Section 5.6), the CO insertion will be further discussed using evidence in FTIR spectra.

5.3.2 Hydrogen Consumption in Reactions

Earlier study by Artok et al. [1992] found that before conversion reached 100%, the more hydrogen consumed in a reaction, the higher conversion would be; and after the conversion reached 100%, any further hydrogen consumption went into converting heavy products to oils. Therefore liquefaction is indeed a task to input hydrogen into a coal. As mentioned previously, there are two hydrogen sources, one is the gas-phase hydrogen; the other is the donor solvent. The hydrogen consumption from either source can be measured by gas chromatography (GC).

To calculate the consumption of hydrogen gas, the volume of hydrogen loaded into the reactor is measured by water replacement and so is the total volume of the gas vented after reaction. Gas samples are collected and analyzed qualitatively and quantitatively by GC. The hydrocarbon contents are detected by FID, and the carbon monoxide and carbon dioxide are detected by TCD. The volume of hydrogen after reaction is calculated by subtracting the hydrocarbon and CO_x gases from the total volume of the gas after reaction. Comparing with the volume of hydrogen initially charged in the reactor, the hydrogen consumed during reaction can thus be calculated. The hydrogen consumption from the donor solvent can be calculated in a similar manner except that in this case, a capillary gas chromatography is applied to analyze the liquid sample. Tetralin consumption is calculated using the amount of naphthalene divided by the amount of tetralin loaded in the system initially. The dihydronaphthalenes appear to be less than 1% of naphthalene or tetralin and thus are neglected in the calculation. In this study, hydrogen consumption is expressed in terms of percentage of dry and mineral-matter free coal.

The hydrogen consumption from the gaseous hydrogen is plotted in Figure 5.32 for the DECS-1 coal. In the reactions without the catalyst, the hydrogen consumptions are remarkably lower than those in the catalytic reactions. It is believed that in the non-catalytic reactions, the hydrogenation undergoes the hydrogen capping mechanism, that is, the coal-derived free radicals are generated first, and then the free radicals will abstract a hydrogen radical from the H_2 molecule [Song et al., 1994]. Therefore as temperature increases, the rate of cracking also increases. More C-C bonds are broken; and more free radicals are produced thus more hydrogen will be abstracted resulting in higher hydrogen consumption. At 300°C, the hydrogen consumptions are close to zero, and even at 400°C, they are only 0.5% on the dry and mineral-matter free basis. The low hydrogen consumptions are corresponding to the low liquefactions conversions, such as those at temperatures between 200°C to 400°C without the presence of the donor solvent. The reaction at 400°C with tetralin has much higher conversion, because there is about 1% hydrogen consumption from tetralin at this temperature, Figure 5.33. When temperature is increased to 450°C, the hydrogen consumption from the gas phase is significantly enhanced to about 1.7%. However the conversions are not increased accordingly. In earlier discussion about the gases, it was observed that at 450°C there is a large jump in the amount of hydrocarbon gases produced in reaction (Figure 5.28 and Figure 5.29). It

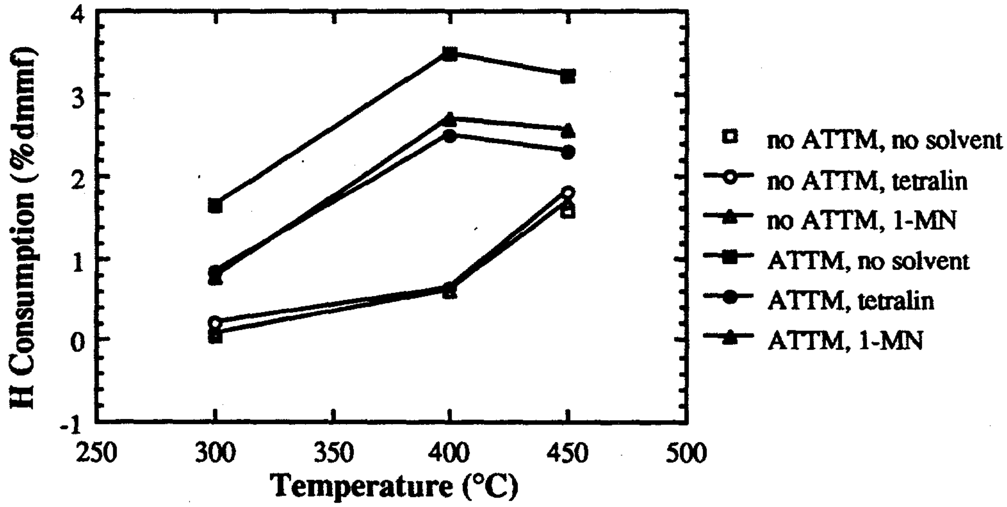


Figure 5.32 Hydrogen consumption from H_2 under various reaction conditions

is thus postulated that the gas-phase hydrogen consumed at 450°C is mainly used to produce small molecules such as C_1-C_6 paraffins. The reaction with tetralin still has a high conversion. Since tetralin donates as much hydrogen as the gas-phase hydrogen (Figure 5.33), and hydrogenation by tetralin follows a different mechanism than that of H_2 [McMillen et al., 1985, 1987a&b, and 1989; Vernon, 1980], some of the hydrogen from tetralin must have been used to crack the coal structure and form soluble product, and hence the conversion is increased.

When the catalyst is present in the reaction system, the hydrogen consumption is increased to a great extent (Figure 5.32). In catalytic reactions, the activation energy of the dissociation of H-H bond will be significantly decreased, and the hydrogenation may chose a different pathway where the hydrogen free radicals will be first generated and then stabilize the coal free radicals [Song, et al., 1994]. Generally the consumption increases when temperature increases from 300°C to 400°C, but decreases when it further increases to 450°C. Since high temperatures favors the dissociation of H_2, it is observed that hydrogen consumption increases with temperature at first. However, because hydrogenation and dehydrogenation occur simultaneously, the hydrogen consumption observed here is a net change of the hydrogen in the gas phase, that is the total amount of hydrogen consumed from the gas-phase H_2 minus the amount of hydrogen released from the coal. At 450°C, the net change of hydrogen in the gas phase decreased compared with that at 400°C, indicating that there are more dehydrogenation of the coal at 450°C. Hydrogen consumption from H_2 and tetralin in the presence of the catalyst is compared in Figure 5.34. It is found that at 400°C and below, H_2 is the main source of hydrogen, and tetralin becomes compatible only at 450°C. This observation is very interesting and in a good agreement with the conclusion made in earlier section (Section 5.2.2) that in catalytic liquefaction of the DECS-1 coal, the donor solvent has no advantage at 400°C

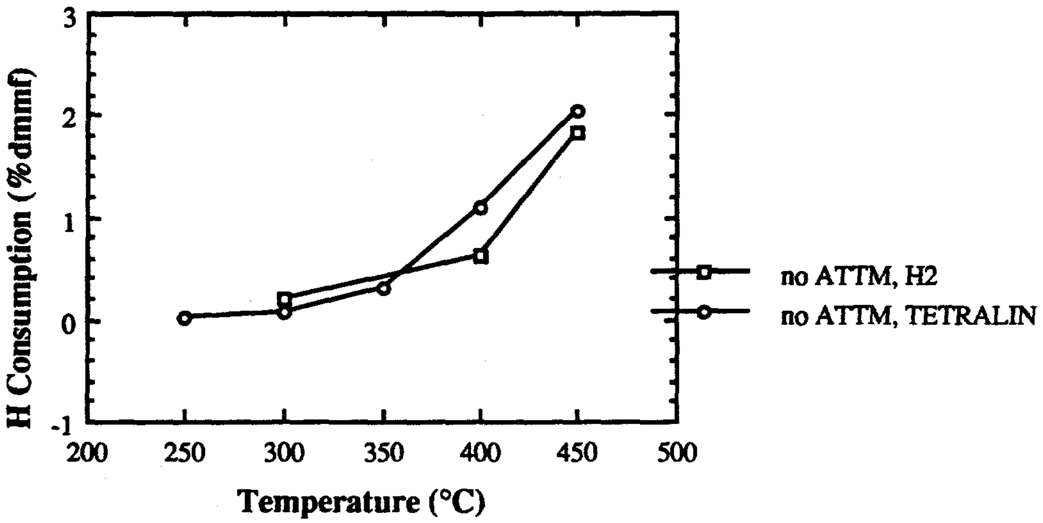


Figure 5.33 Hydrogen consumption from H_2 and tetralin in non-catalytic reactions

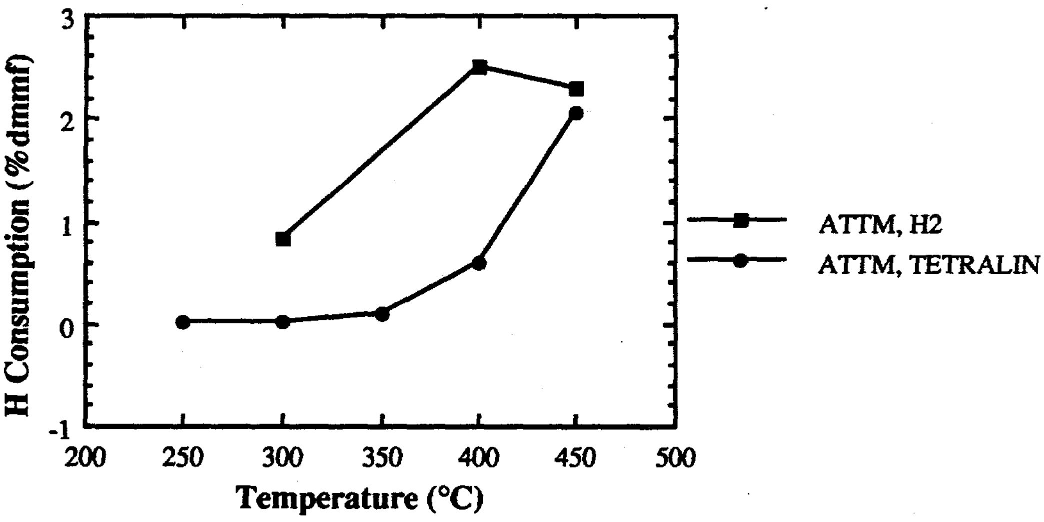


Figure 5.34 Hydrogen consumption from H_2 and tetralin in catalytic reactions

and below. At 450°C, the contribution from tetralin becomes significant, and this is why only the reaction with tetralin has a very high conversion.

It is also observed that the consumption in catalytic reactions with no solvent is higher than that in reactions with a solvent (Figure 5.32). This may be because that a solvent acts as a barrier between the catalyst and H_2. Even though at a high temperature, the solvent may be in a supercritical state, there may still some solvent molecules absorbed on the surface of the catalyst which will inhibit an intimate contact between the catalyst and H_2 molecules [Song, 1995].

Comparing reactions with the catalyst and without the catalyst in Figure 5.33 and 5.34, the hydrogen consumptions from tetralin are very close at all temperatures except 400°C. At this temperature, hydrogen is consumed more in the non-catalytic reaction. Earlier analysis of the data has found that hydrogen consumption from H_2 is close to zero at 400°C with no catalyst (Figure 5.32), and the donor solvent is the main source of hydrogen. Hence the hydrogen radicals produced by tetralin are immediately used to stabilize coal-derived free radicals. Therefore in non-catalytic reactions, there is a stronger driving force to consume tetralin than in the catalytic reactions where the main hydrogen source is H_2 at this temperature. It should be realized that the tetralin consumption is actually a net result of dehydrogenation of tetralin and hydrogenation of naphthalene or dihydronaphthalene. Therefore the values of the tetralin consumption shown in Figure 5.33 and Figure 5.44 were obtained by subtracting the amounts of naphthalene and dihydronaphthalene hydrogenated from the amounts of tetralin dehydrogenated during the reactions. In reactions with the catalyst, the hydrogenation of naphthalene is more effective than that in non-catalytic reactions, which is another reason that the tetralin appears to be consumed more in a non-catalytic reaction.

5.4 Oils Produced in Liquefaction

The hexane solubles, defined as oils, were analyzed by gas chromatography, and identified by gas chromatography/mass spectrometry. Figure 5.35 represents the oils from the DECS-9 coal without the catalyst or the donor solvent, *a*; with the catalyst but not the donor solvent, *b*; and with both the catalyst and the donor solvent, *c*. In Figure 5.35*a*, the oil contains a high proportion of long-chain alkanes, i. e. from n-C_{12} to n-C_{33}. At retention time of about 6.0 minutes, there is a very strong peak identified as toluene. In low-rank coals such as DECS-9, small aromatic clusters dominate [Song, et al, 1993; Schobert, 1990], and they are connected by aliphatic crosslinks. Once the crosslinks break, these small aromatic clusters will be released. In the DECS-9, as shown in recent work [Song et al , 1993], one-ring structural units are abundant and thus when liquefying the coal, toluene (instead of benzene) will be a major product, because the benzylic C-C bond has a much lower dissociation energy than the phenyl C-C bond [McMurry, 1984]. Relative to those of aliphatics, the amounts of aromatic compounds in the oil (with retention times from 15 minutes to 30 minutes) are much smaller (Figure 5.35*a*), indicating that this reaction condition suppresses the production of aromatic compounds in the oil. Comparing with the case without the catalyst or the donor solvent, adding ATTM into the reaction system appears to favor the yields of aromatic compounds. As shown in Figure 5.35*b*, the alkylbenzenes, phenol and alkylphenols are the major components in the oil. This observation agrees with our earlier finding that the catalyst is particularly beneficial in converting the aromatic carbons from the coal to THF solubles rather than converting the aliphatic carbons [Huang et al., 1993]. Furthermore, when tetralin is used in addition to the catalyst, the yields of phenolic compounds remain very high, Figure 5.35*c*; the one-ring aromatics seem to be in a lower proportion; and the yields of two-ring aromatics, such as indane, alkylindanes and alkylnaphthalenes, have

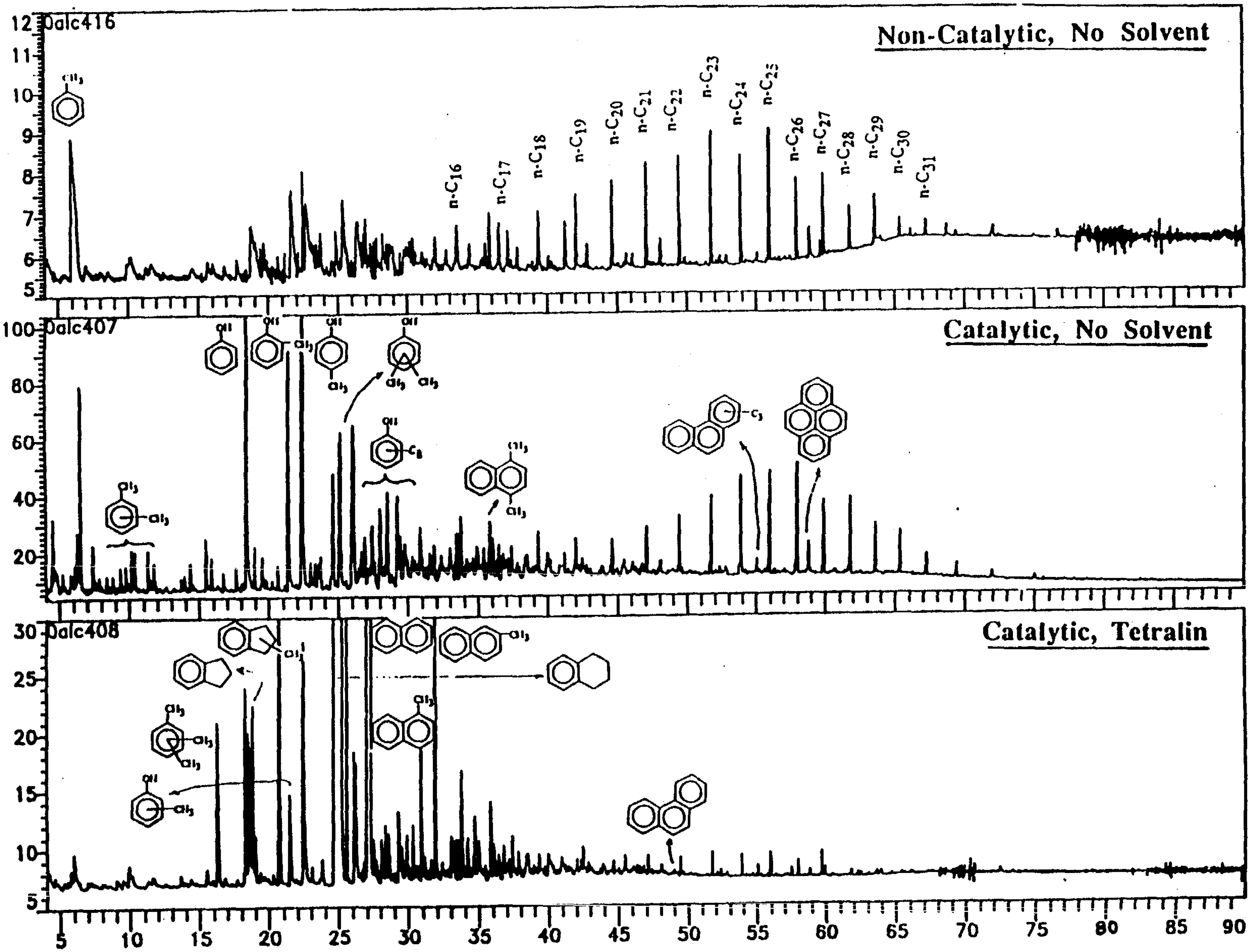


Figure 5.35 Oils produced in the liquefaction of the DECS-9 coal under various conditions

increased. The large peaks at retention times about 24.5 minutes and 27.0 minutes are due to tetralin and naphthalene, the solvent and the dehydrogenated solvent. It is likely that the increased yields of alkylindanes and alkylnaphthalenes are due, at least in part, to the use of tetralin. In the GC study, three- or four-ring compounds appear to be in small amounts and not affected by either the catalyst or the solvent. This may be because they are less abundant than the one- or two-ring structures in the coal, or because their solubilities in hexane are smaller and therefore it is hard to detect the differences in different cases.

5.5 Product Characterization Using Solid-State NMR

Examples of the spectra of CPMAS ^{13}C NMR of residues are shown in Figure 5.36-Figure 5.41 for the DECS-1 coal. The rest of the spectra of the DECS-11 and DECS-9 coals are in the appendix. All spectra were curve-fitted using the LabCalc program and the area of each peak was integrated. The aromaticities of the DECS-1 raw coal and the dried coal are both 0.48. This shows that before reaction, the aromaticity is not affected by vacuum drying at 95°C, implying that the vacuum drying does not remove any small aliphatic compounds or structural fragments from the coal. The aromaticities of residues from all runs are summarized in Table 5.21. It is observed that as temperature increases, the aromaticity increases from 0.50 to 0.94. There are two possible explanations of this increase: one is that as reaction temperature increases, more and more aliphatic carbons are cracked from the macrostructure of the coal but the aromatic carbon may not react as much; the other is that dehydrogenation and condensation reactions take place during the reaction and the amount of aromatics in the coal is increased. Comparing the aromaticities of the residues from the non-catalytic

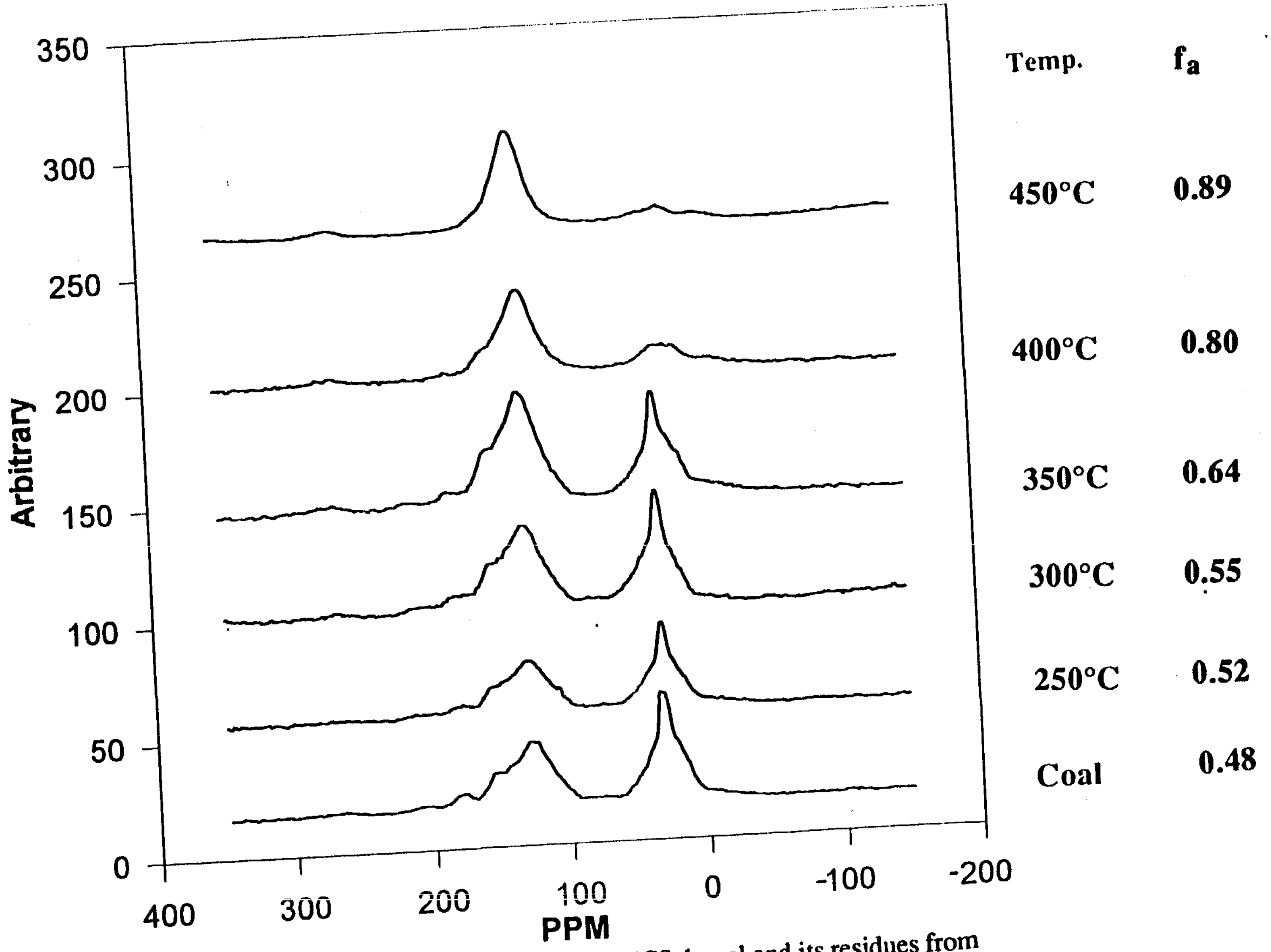


Figure 5.36 ^{13}C NMR spectra of the DECS-1 coal and its residues from reactions with no solvent or catalyst

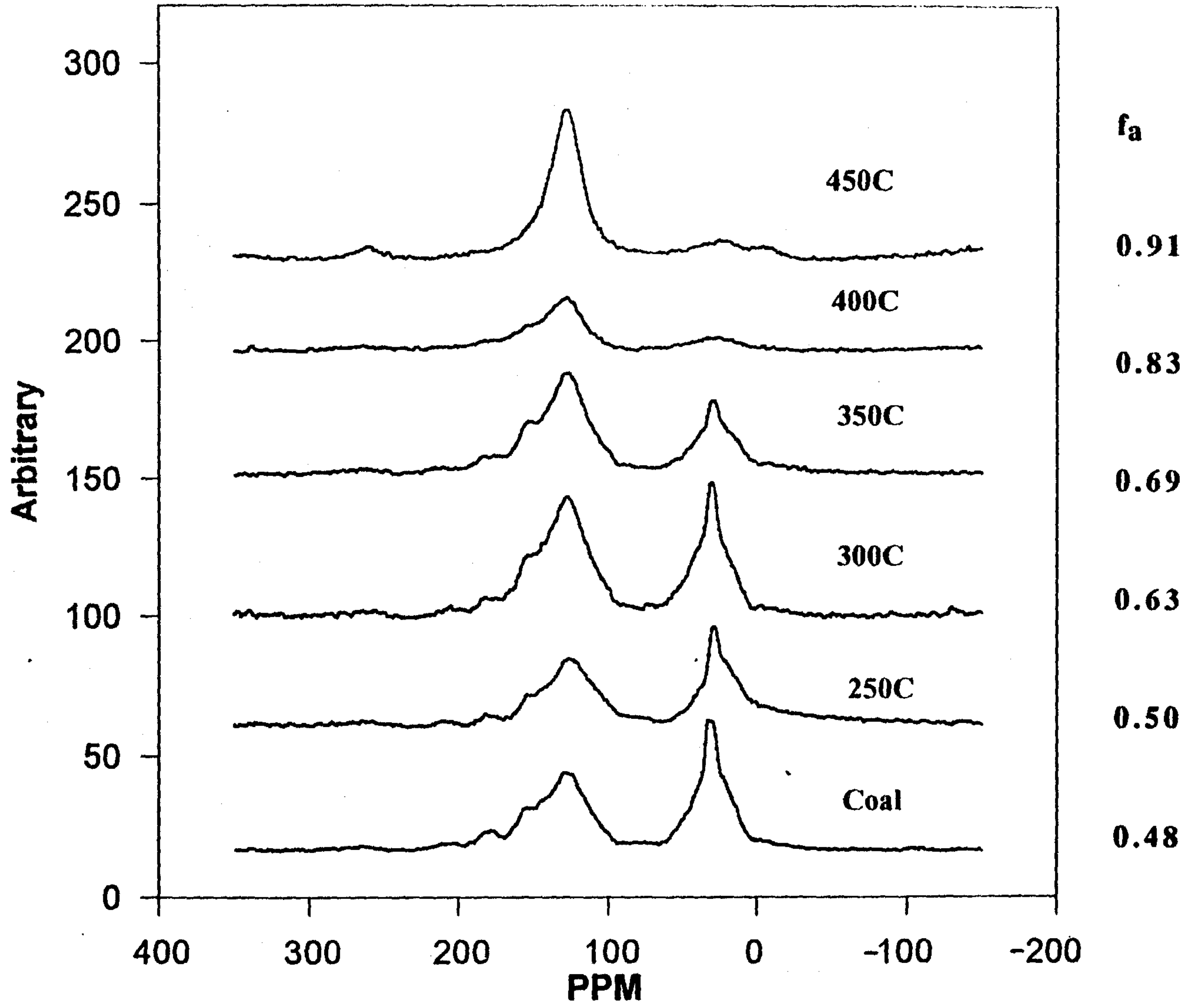


Figure 5.37 ^{13}C NMR spectra of the DECS-1 coal and its residues from reactions with tetralin but no catalyst

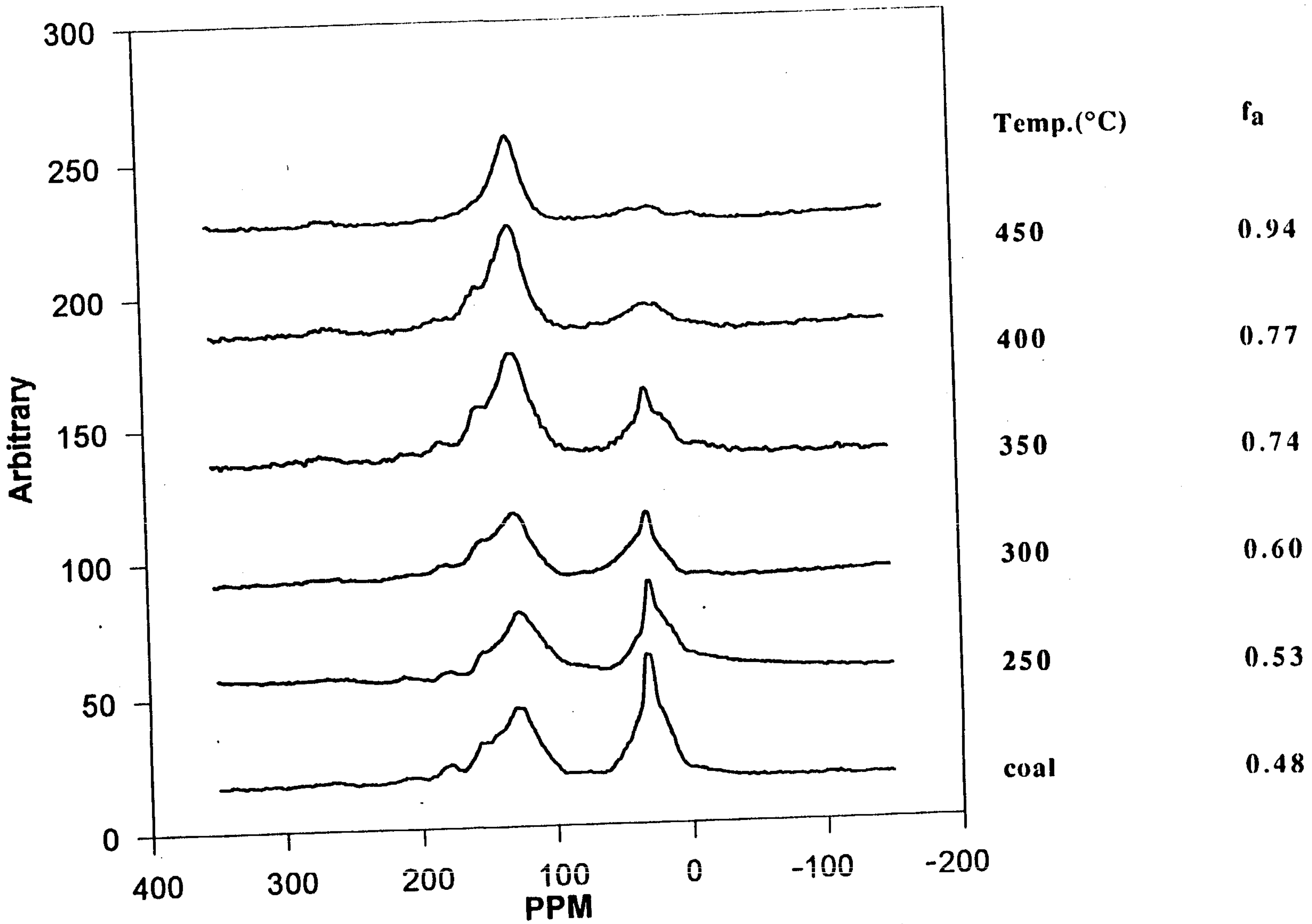


Figure 5.38 ^{13}C NMR spectra of the DECS-1 coal and its residues from reactions with 1-MN but no catalyst

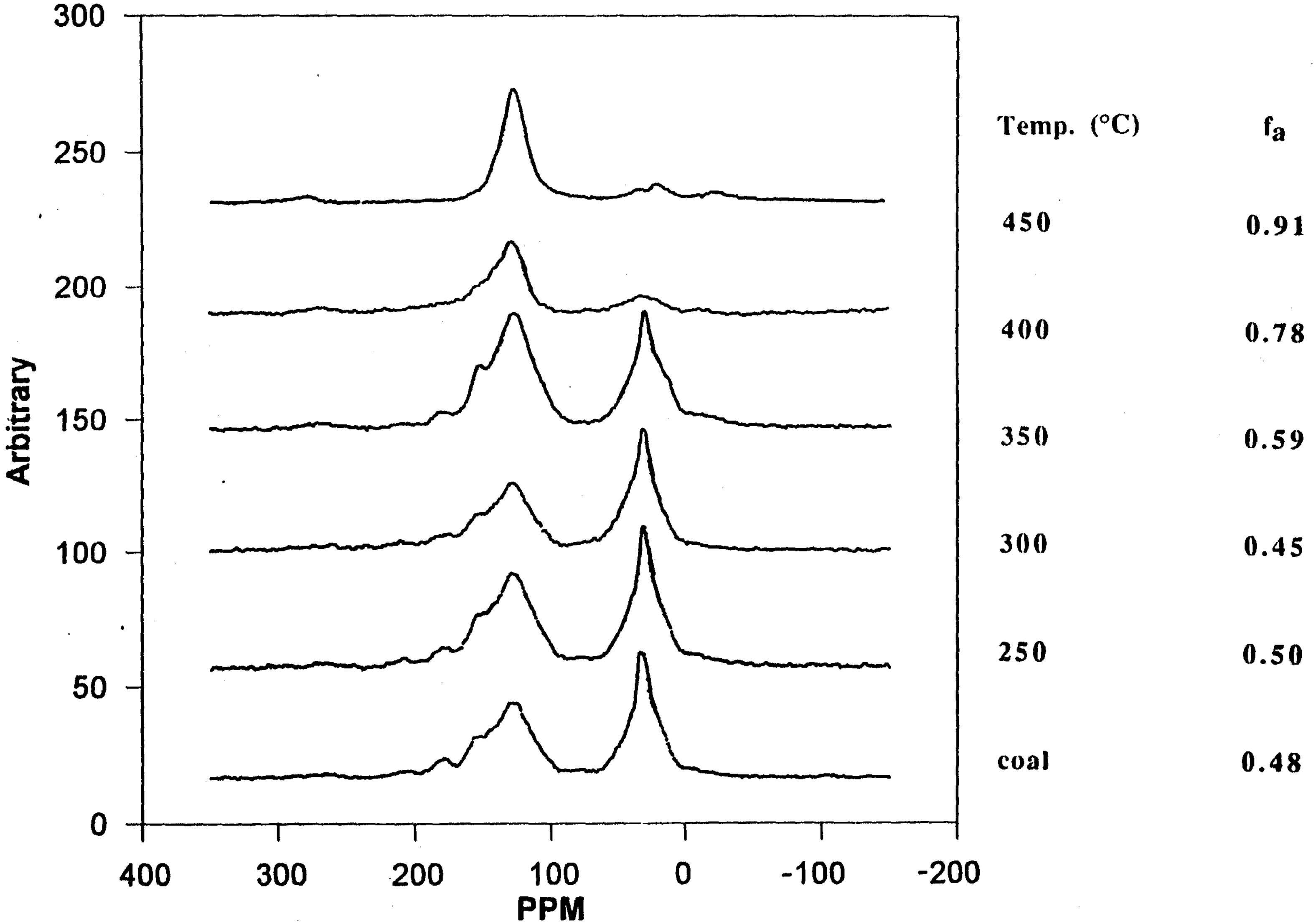


Figure 5.39 ^{13}C NMR spectra of the DECS-1 coal and its residues from reactions with ATTM but no solvent

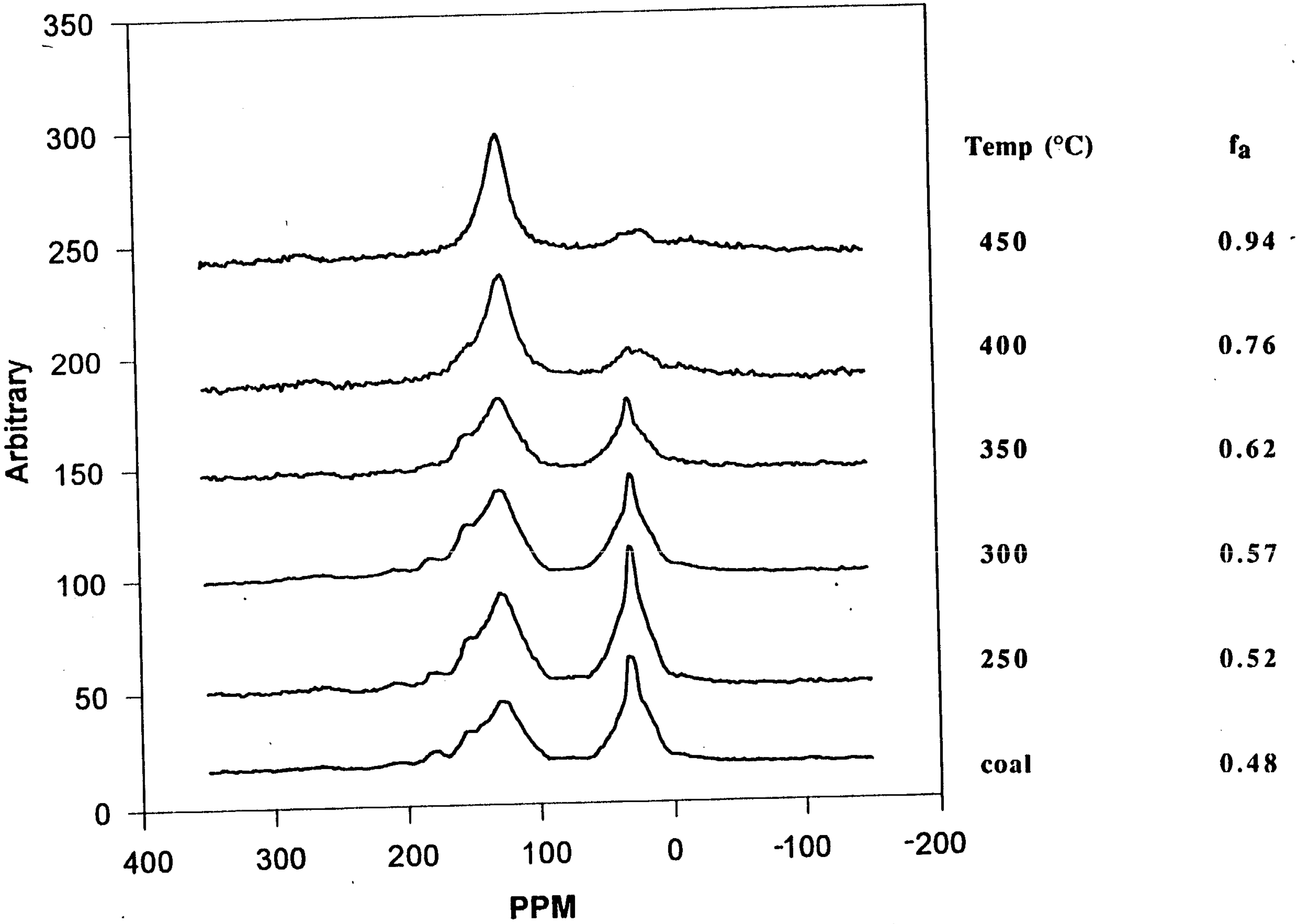


Figure 5.40 ^{13}C NMR spectra of the DECS-1 coal and its residues from reactions with ATTM and tetralin

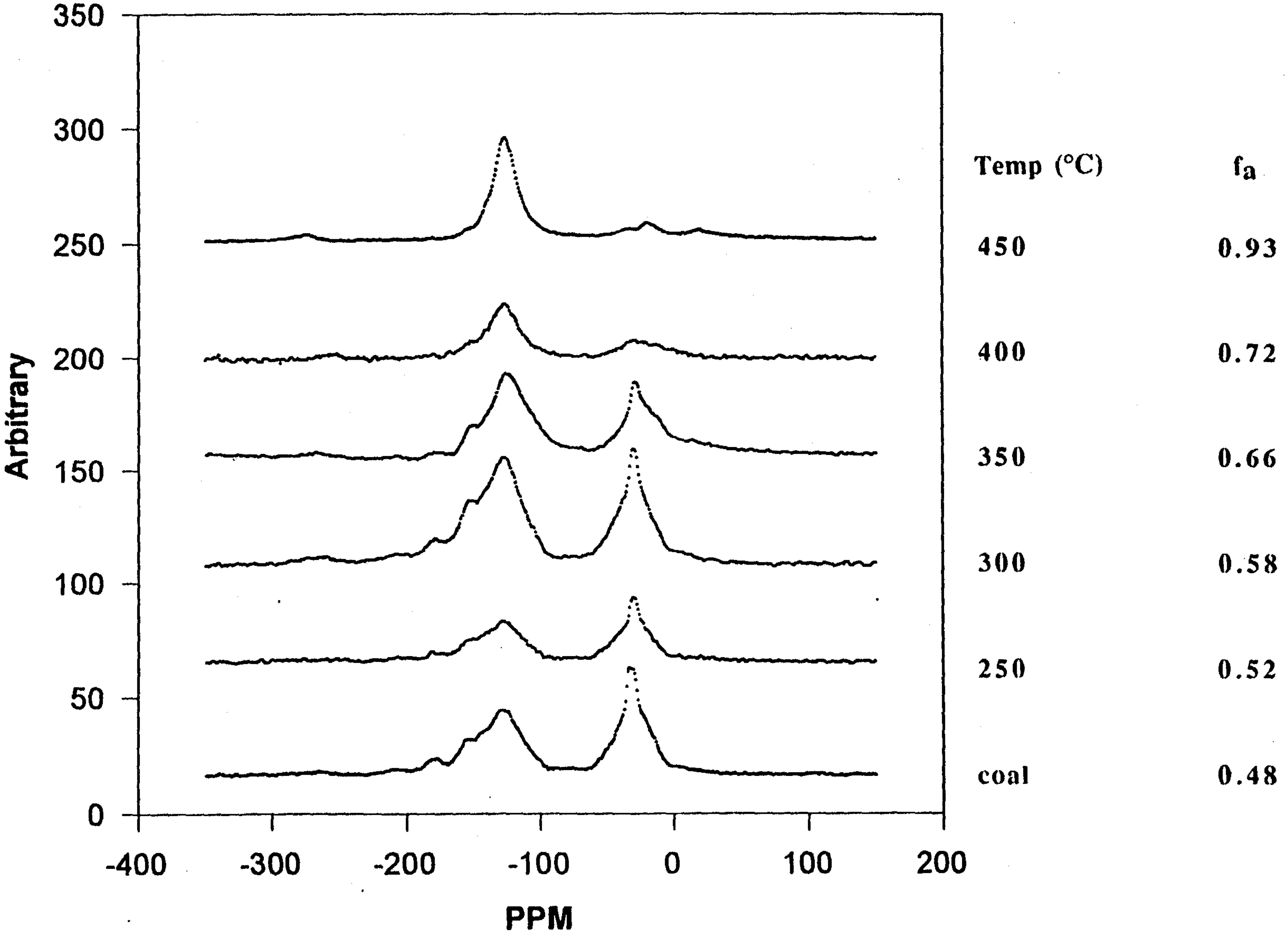


Figure 5.40 ^{13}C NMR spectra of the DECS-1 coal and its residues from reactions with ATTM and 1-MN

Table 5.21 Aromaticities of residues from liquefaction of the DECS-1 coal

	Non-Catalytic			Catalytic		
Temperature	No Solvent	Tetralin	1-MN	No Solvent	Tetralin	1-MN
250	0.52	0.5	0.53	0.5	0.52	0.52
300	0.55	0.63	0.6	0.45	0.57	0.58
350	0.64	0.69	0.74	0.59	0.62	0.66
400	0.8	0.85	0.86	0.78	0.76	0.72
450	0.89	0.91	0.94	0.85	0.94	0.93

reactions, it is found that the solvents do not have a significant effect. Furthermore, in the case of catalytic reactions, the solvents have no significant effect either. In order to determine the influence of the catalyst on the aromaticities, all the data are plotted versus conversion in Figure 5.42. A general trend is that the aromaticities of residues increase with conversion, but the data fall into two separate sets: those from reactions with and without the catalyst, regardless of the solvent used. Generally, f_a of the residue from a catalytic reaction is lower than that from a non-catalytic reaction, and the difference between the two increases with increasing conversion. At the most severe conditions, 450°C with the catalyst, the aromaticities deviate from the line of catalytic reaction. The higher aromaticities are caused by more aromatic carbon, which indicates the retrogressive reactions at this temperature. In non-catalytic reactions, the use of tetralin at 400°C and 450°C results in lower aromaticities, suggesting that tetralin helps to convert aromatic carbons from coal to THF solubles.

To achieve a general idea on what kinds of structure have been converted to THF solubles, or what kinds of reactions are actually catalyzed by the ATTM-derived catalyst during the liquefaction, the percentages of aliphatic or aromatic carbon that have been reacted (the net change in the amount of aliphatic or aromatic) are calculated based on the amounts of dry, mineral-matter-free coal charged into the reactor, aromaticity of the dried coal, the conversions, and the aromaticities of the residues. In Figure 5.43, the extent of reacted aliphatic carbon is shown as a function of temperature. At each temperature, the lowest point always corresponds to the reaction with no solvent and no catalyst. As expected, those reactions with the worst liquefaction conditions result in the lowest conversion of aliphatic carbon. Comparing the effects of the solvents, the catalyst and temperature, the latter is shown to be the most significant based on the fact that the highest conversion of aliphatic carbon at one temperature is always lower than the lowest

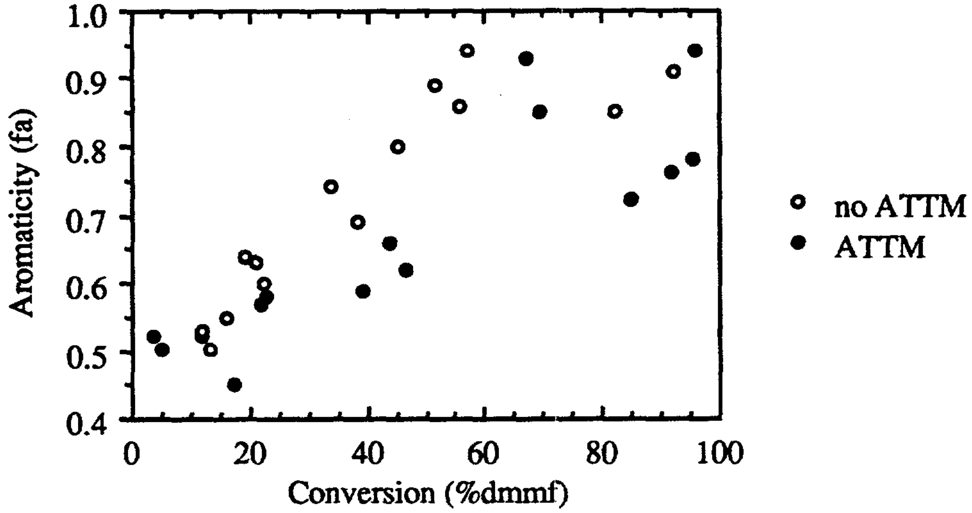


Figure 5.42 Aromaticity of residues from the catalytic and non-catalytic liquefaction of the DECS-1 coal

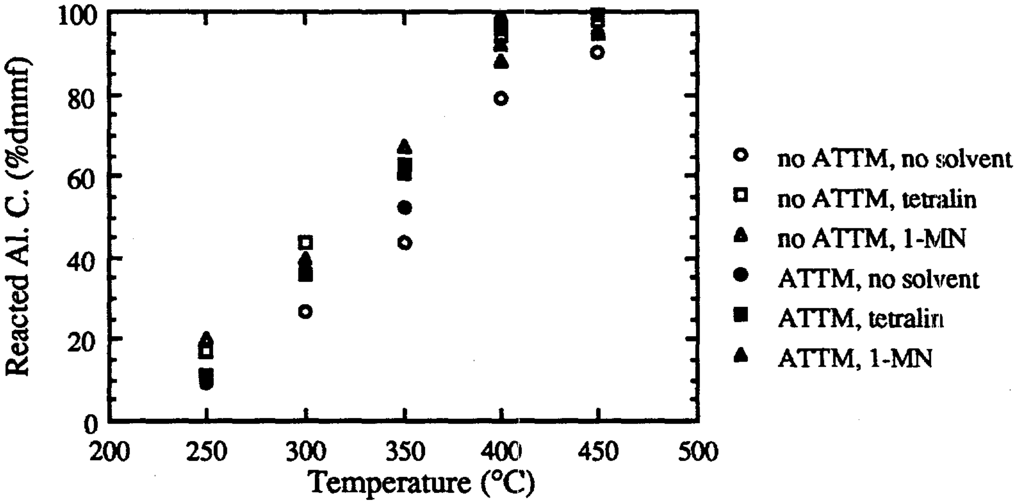


Figure 5.43 The net amount of reacted aliphatic carbon in liquefaction of the DECS-1 coal under various conditions

conversion at the next temperature (except that between 400°C and 450°C). Roughly speaking, all the points stay on one line, regardless of the use of solvent or catalyst. The amount of reacted aliphatic carbon increases nearly linearly when the temperature increases, up to 400°C. At 400°C, about 90% of the aliphatic carbon has been converted to THF solubles. When reaction temperature is further increased to 450°C, the increase of the reacted aliphatic carbon becomes insignificant, from 90% to about 95%. This study suggests that, like the yields of the gases, the conversion of aliphatic carbon from coal to THF solubles is a function mainly of temperature; neither solvent nor catalyst has any remarkable influence on it. In Figure 5.44, the amount of aromatic carbon converted to THF solubles is plotted versus the temperature. Unlike those in Figure 5.43, the data are much more scattered in Figure 5.44. In non-catalytic liquefaction reactions, tetralin made a remarkable difference from 1-MN and no solvent. When the temperature was 350°C or higher, much more of the aromatic carbon reacted in the presence of tetralin. At 450°C, the conversion of aromatics reached 86% with tetralin, but it only reached 15% and 10% with 1-MN and without solvent respectively. In catalytic liquefaction reactions, the difference caused by the solvents is diminished when the temperature increases to 400°C, indicating that the catalyst is sufficiently active in converting the aromatics into THF solubles and that solvent is no longer a major determining factor. However, when the temperature increases to 450°C with the presence of the catalyst, reactions with 1-MN or without a solvent have large decreases from 77% to 36% and from 93% to 42% respectively; while that with tetralin increased from 87% to 92%. At temperature as high as 450°C, the thermal cracking of the coal matrix is very fast, and the hydrogenation from the gaseous H_2 catalyzed by the added catalyst is no longer able to catch up. Therefore at 450°C in the presence of the catalyst, tetralin is no longer a minor factor. In fact, the only way to prevent the retrogressive reaction is to have a donor solvent, such as tetralin.

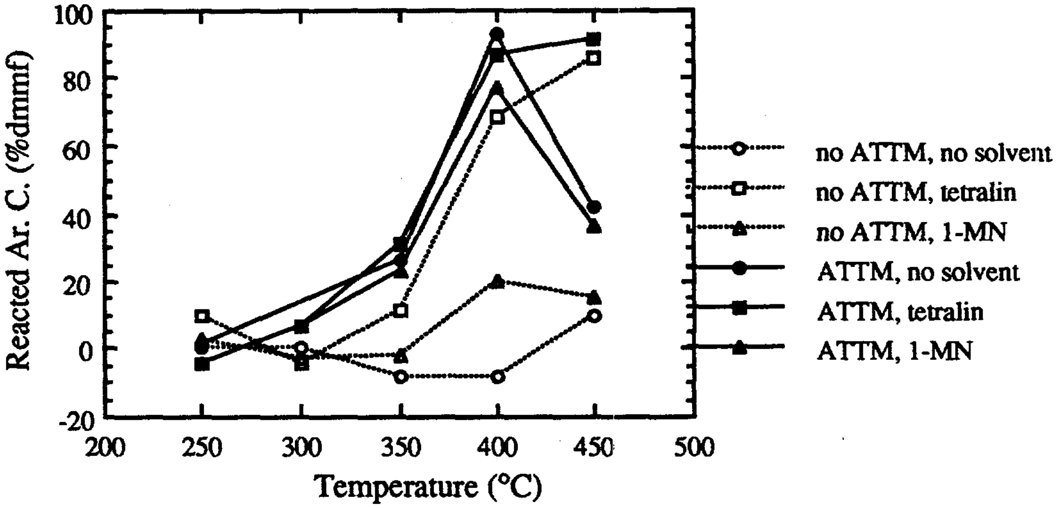


Figure 5.44 The net amount of reacted aromatic carbons in liquefaction of the DECS-1 coal under various conditions

The study of reacted aliphatic and aromatic carbon helps to explain why a non-catalytic reaction always produces residues with higher aromaticity than a catalytic reaction even though the conversion can be the same. In the former case (non-catalytic reaction), the conversion is achieved by having more aliphatic carbon reacted and in the latter case (catalytic reaction), it is achieved by having a greater proportion of aromatic carbon reacted. For example, in reaction at 400°C with no solvent or catalyst, the conversion is 44.0%, and there is -8% aromatic (implying retrogressive aromatization reactions) and 79% aliphatic carbon reacted; in reaction at 350°C with the catalyst and 1-MN, the conversion is 45%, and there is 23% aromatic and 63% aliphatic carbon reacted.

To compare the three coals, the reacted aliphatic carbons and reacted aromatic carbons are plotted in Figure 5.45 and Figure 5.46. In these figures, it is apparent that converting aliphatic carbons from the coal networks to THF solubles is much easier than converting aromatic carbons. At 400°C, even without catalyst or solvent, over 50% of aliphatic carbons are converted for all three coals. Adding the catalyst can increase the aliphatic conversions to greater extents. Furthermore, if tetralin is used in addition to the catalyst, slight increases in the aliphatic carbon conversions of DECS-9 and DECS-11 are observed; while that of DECS-1 shows almost no change, which is expected because even only with the catalyst, the conversion approaches 100%. Comparing these three coals, the aliphatic carbons in DECS-1 are the easiest to be converted; those in DECS-11 are the most difficult. This may be because that the DECS-1 coal contains much higher organic sulfur than the other two coals. The organic sulfur has two advantages in liquefaction. The first one is contributed by the sulfur linkages in the coal which are relatively easy to be cleaved. The second is due to the H_2S formation from the organic sulfur. The H_2S can further act as a hydrogen-transfer catalyst in liquefaction [Song, 1995]. In Figure 5.46, the aromatic carbons appear to be more difficult to be removed from the coal

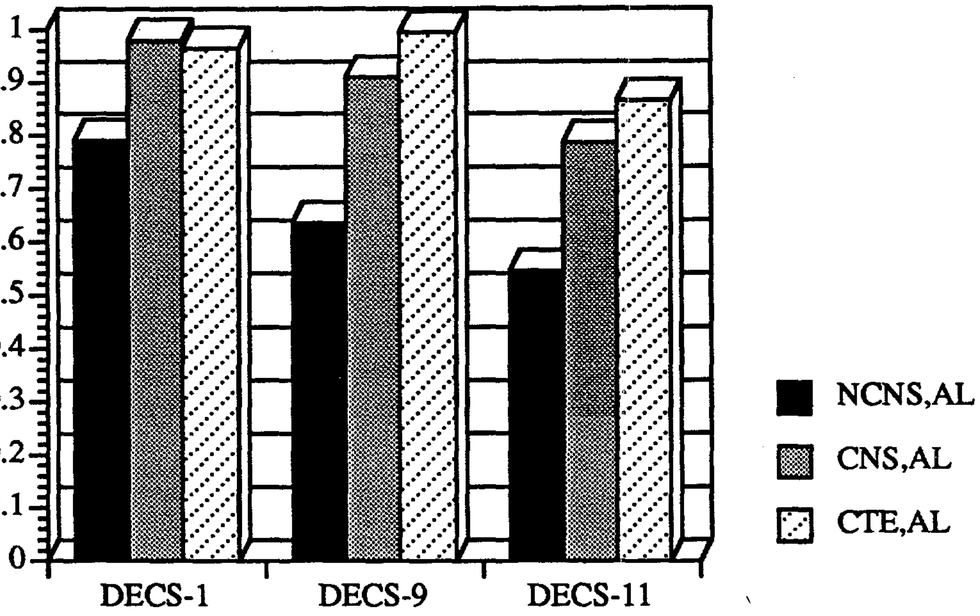


Figure 5.45 The net amount of reacted aliphatic carbons in liquefaction of the three coals at 400C

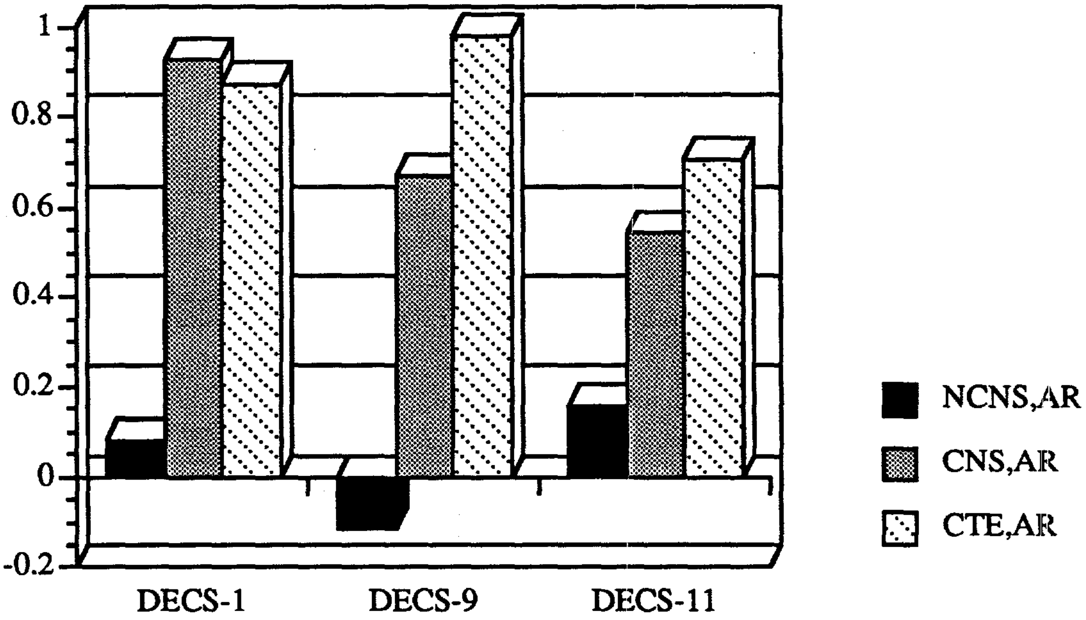


Figure 5.46 The net amount of reacted aromatic carbons in liquefaction of the three coals at 400°C

networks, and they are affected more strongly by the catalyst or the donor solvent than the aliphatic carbons. Without the presence of the catalyst or the donor solvent, less than 20% can be converted. For the DECS-9 coal, the conversion is negative, meaning that there are more aromatic carbons than we start with, and some of the aliphatic carbons have been converted to aromatic carbons during the reaction. This is a strong indication of the occurrence of retrogressive reactions. Therefore, to convert the aromatic carbons, it is crucial to use the catalyst, the donor solvent or both. For the DECS-1 coal, the catalyst is sufficient to achieve over 95% aromatic conversion; for the DECS-9 coal, with both the catalyst and the donor solvent, 98% can be obtained; for the DECS-11 coal, the least convertible coal, even with both the catalyst and the donor solvent, only about 70% aromatic conversion can be achieved.

5.6 Product Characterization Using FTIR

FTIR was used to characterize reaction products and residues qualitatively and semiquantitatively. The DECS-1 coal is selected to be discussed here. The spectra of the DECS-9 and the DECS-11 coals will be shown in the appendix. All spectra were normalized to 1 mg of organic matter. Figure 5.47 - Figure 5.50 are the spectra of residues of reactions with no solvent and no catalyst, with tetralin but no solvent, with ATTM but no solvent and with both tetralin and ATTM, respectively. To see the subtle differences between the residues and the coal, the spectrum of the coal is subtracted from those of residues, Figure 5.51 - Figure 5.54.

The broad band between 3550 to 3200 cm^{-1} is due to water absorbed on the pellet, based on the fact that it is consistent throughout the temperature range and under different reaction conditions. The bands at 2920 cm^{-1} and 2853 cm^{-1} are methylene stretchings

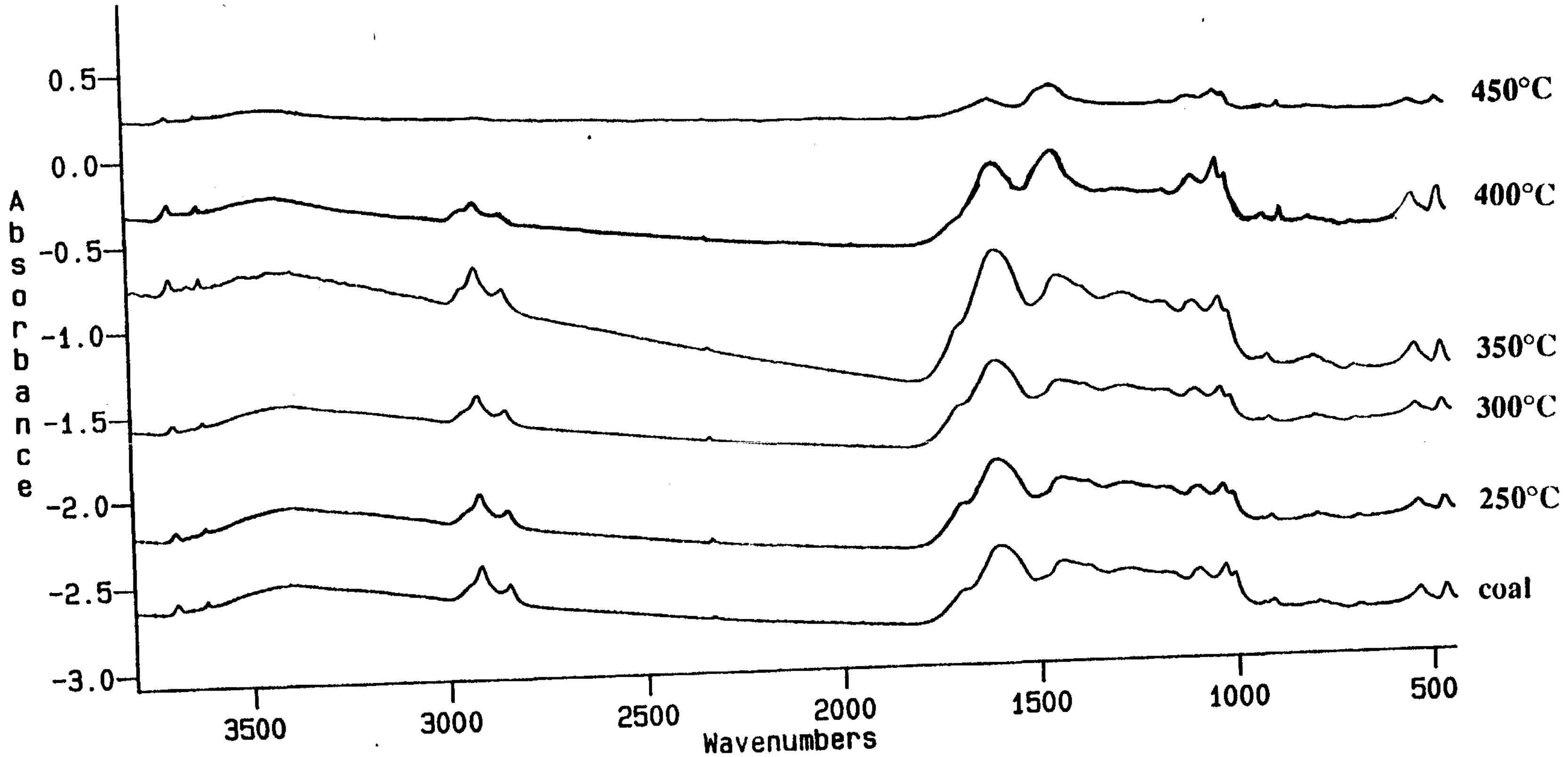


Figure 5.47 FTIR spectra of the DECS-1 coal and its residues from non-catalytic liquefaction with no solvent at various temperatures. The spectra were normalized to 1 gram of organic material.

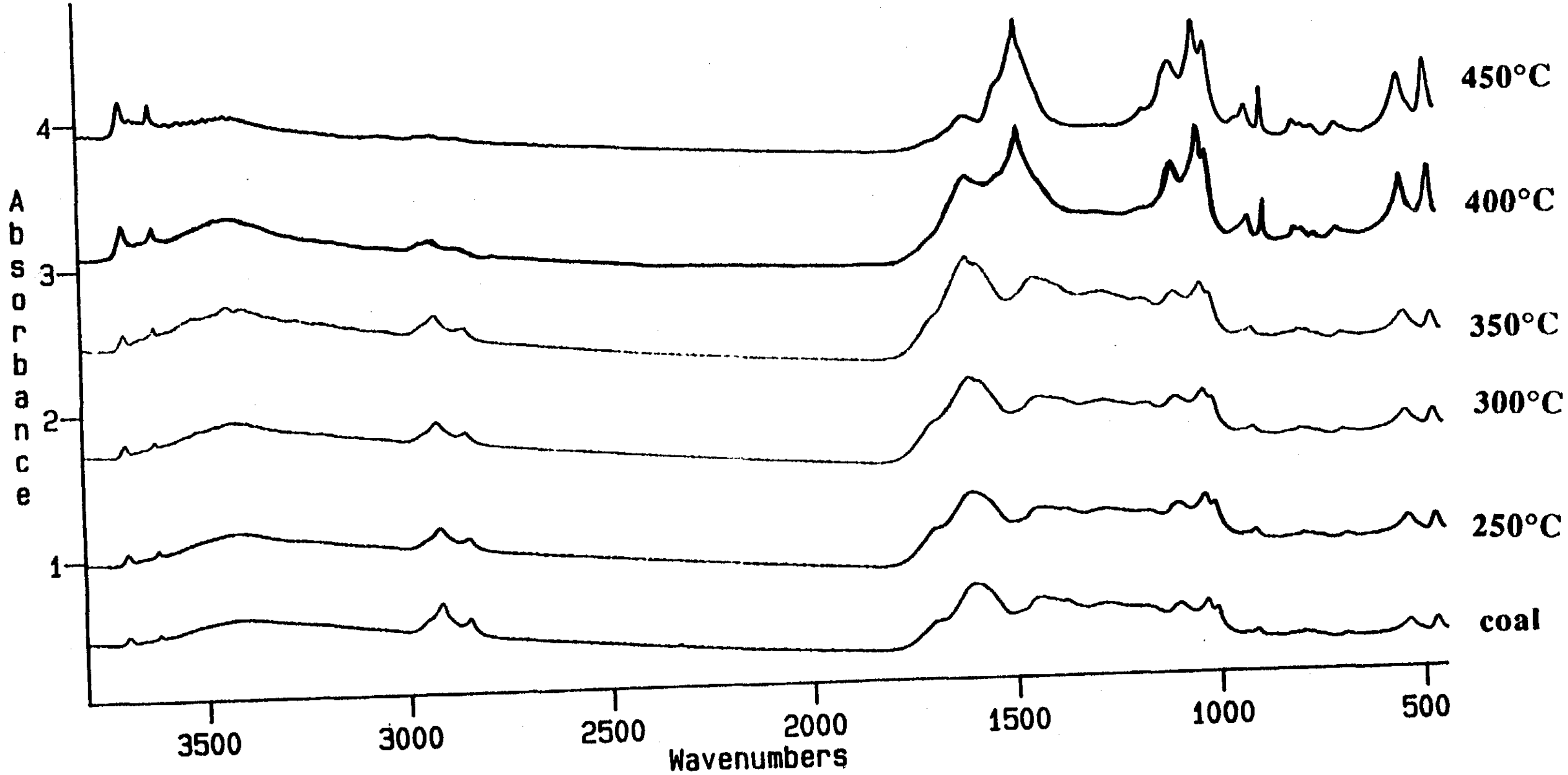


Figure 5.48 FTIR spectra of the DECS-1 coal and its residues from non-catalytic liquefaction with tetralin at various temperatures. The spectra were normalized to 1 gram of organic material.

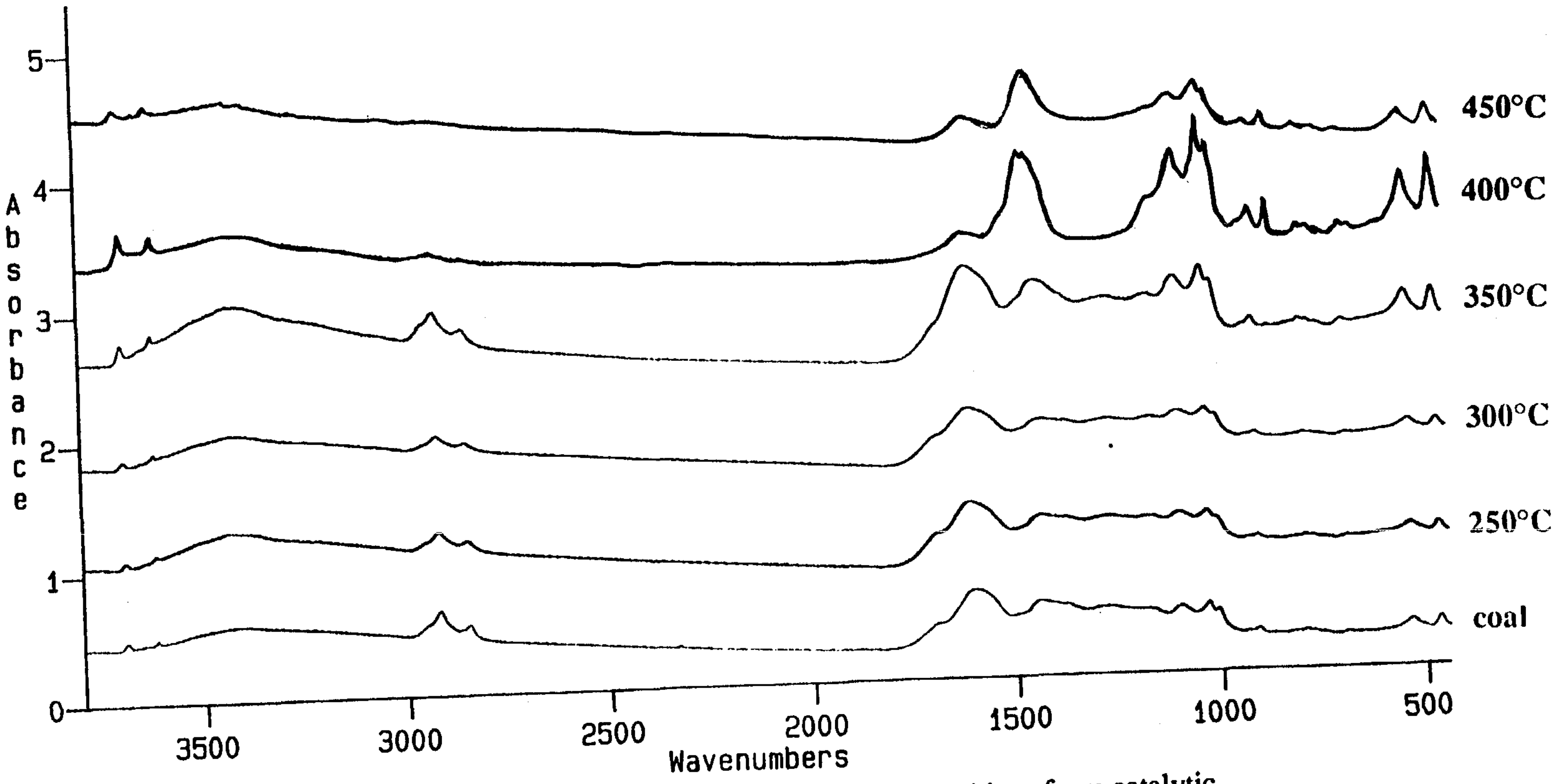


Figure 5.49 FTIR spectra of the DECS-1 coal and its residues from catalytic liquefaction with no solvent at various temperatures. The spectra were normalized to 1 gram of organic material.

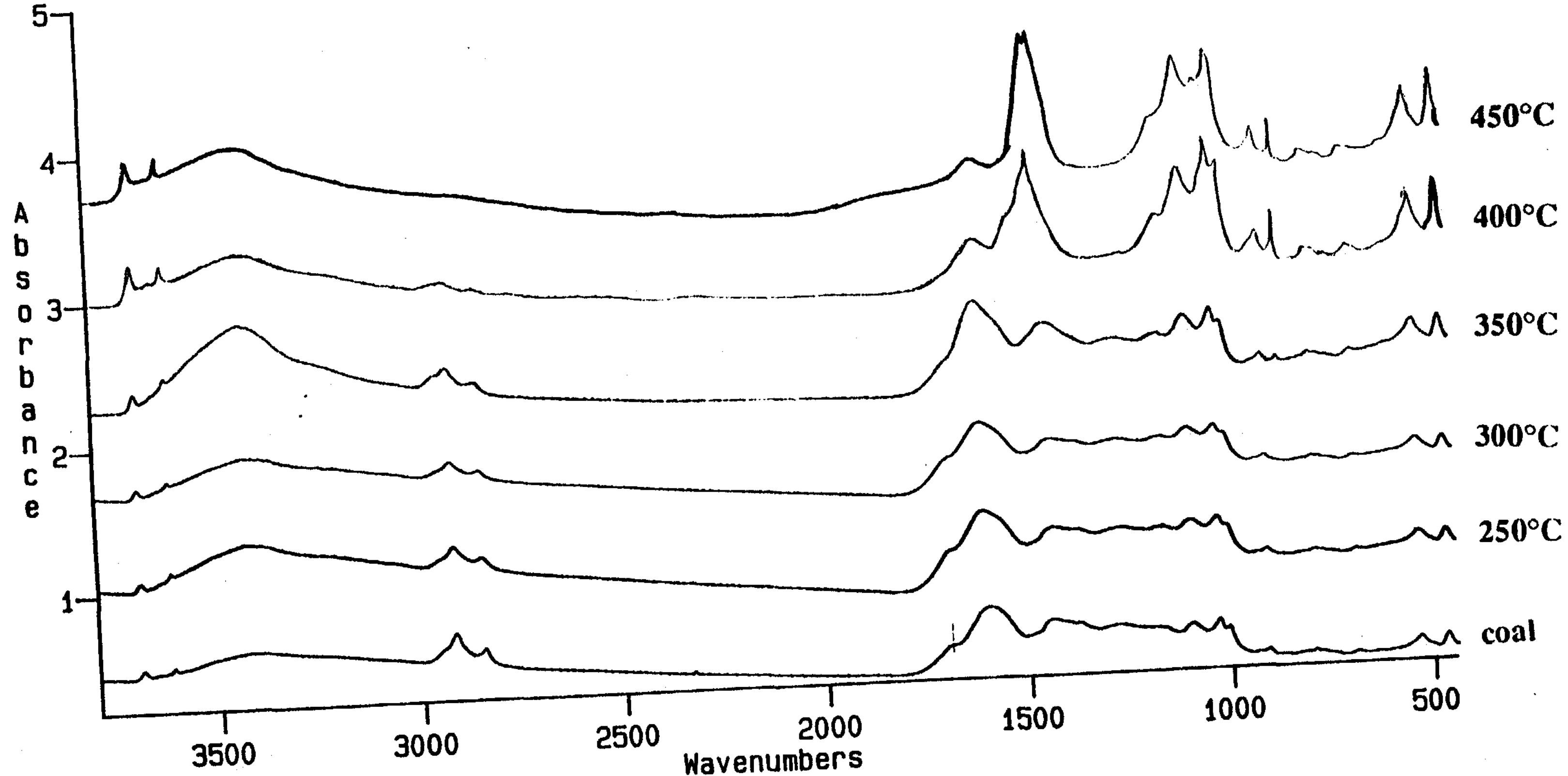


Figure 5.50 FTIR spectra of the DECS-1 coal and its residues from catalytic liquefaction with tetralin at various temperatures. The spectra were normalized to 1 gram of organic material.

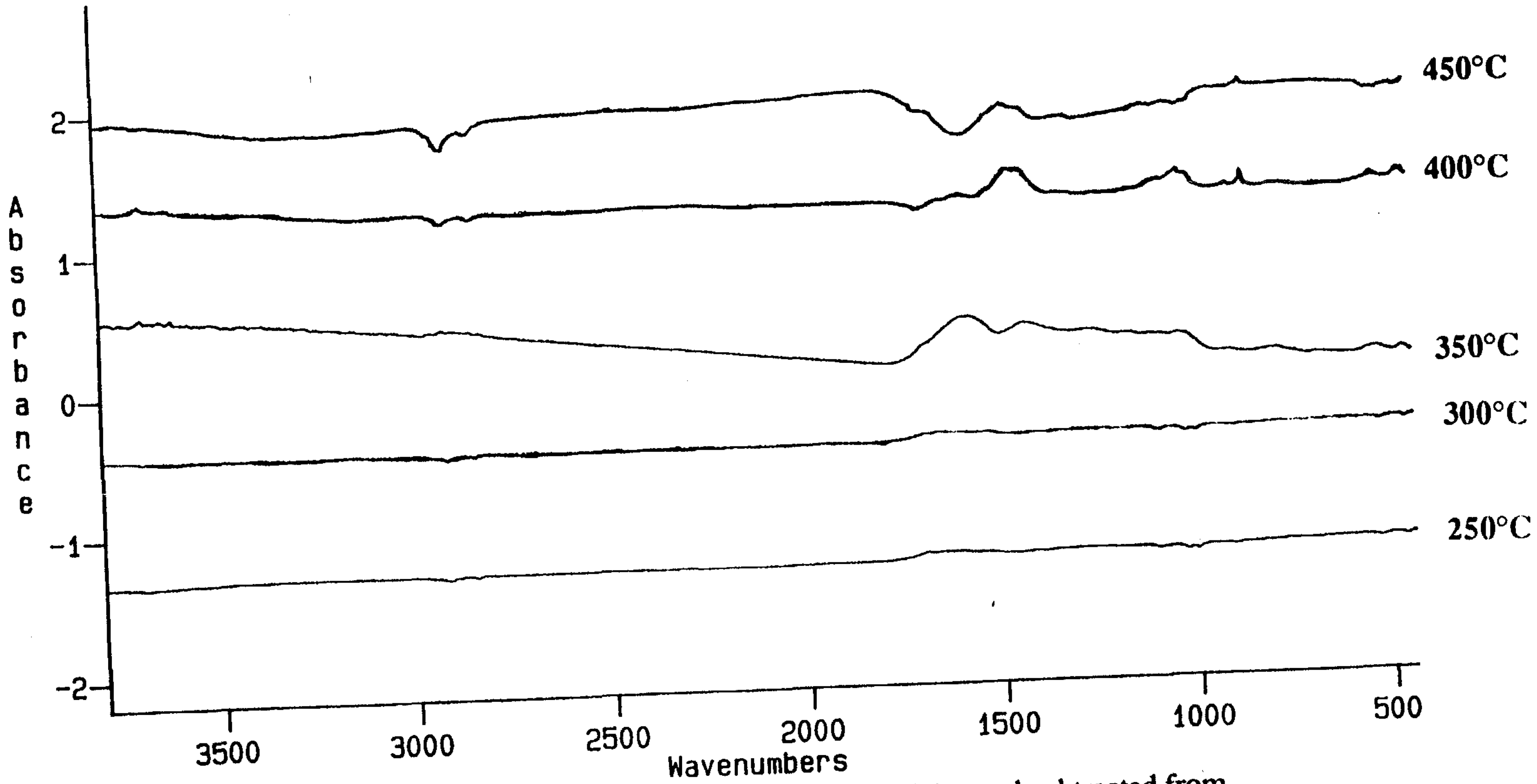


Figure 5.51 The difference spectra (the spectrum of the coal subtracted from those of residues) of residues from non-catalytic liquefaction with no solvent at various temperatures

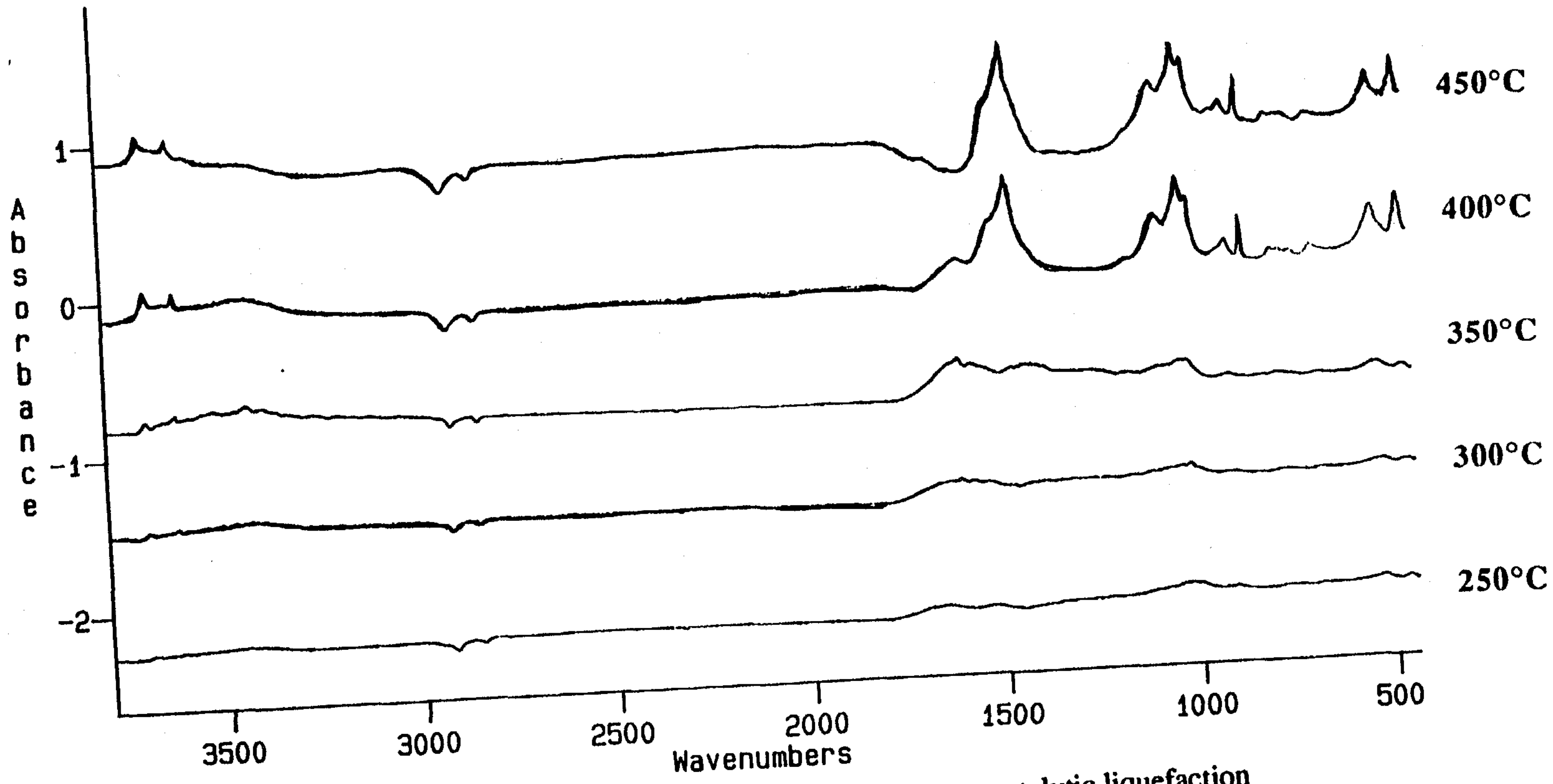


Figure 5.52 The difference spectra of residues from non-catalytic liquefaction with tetralin at various temperatures

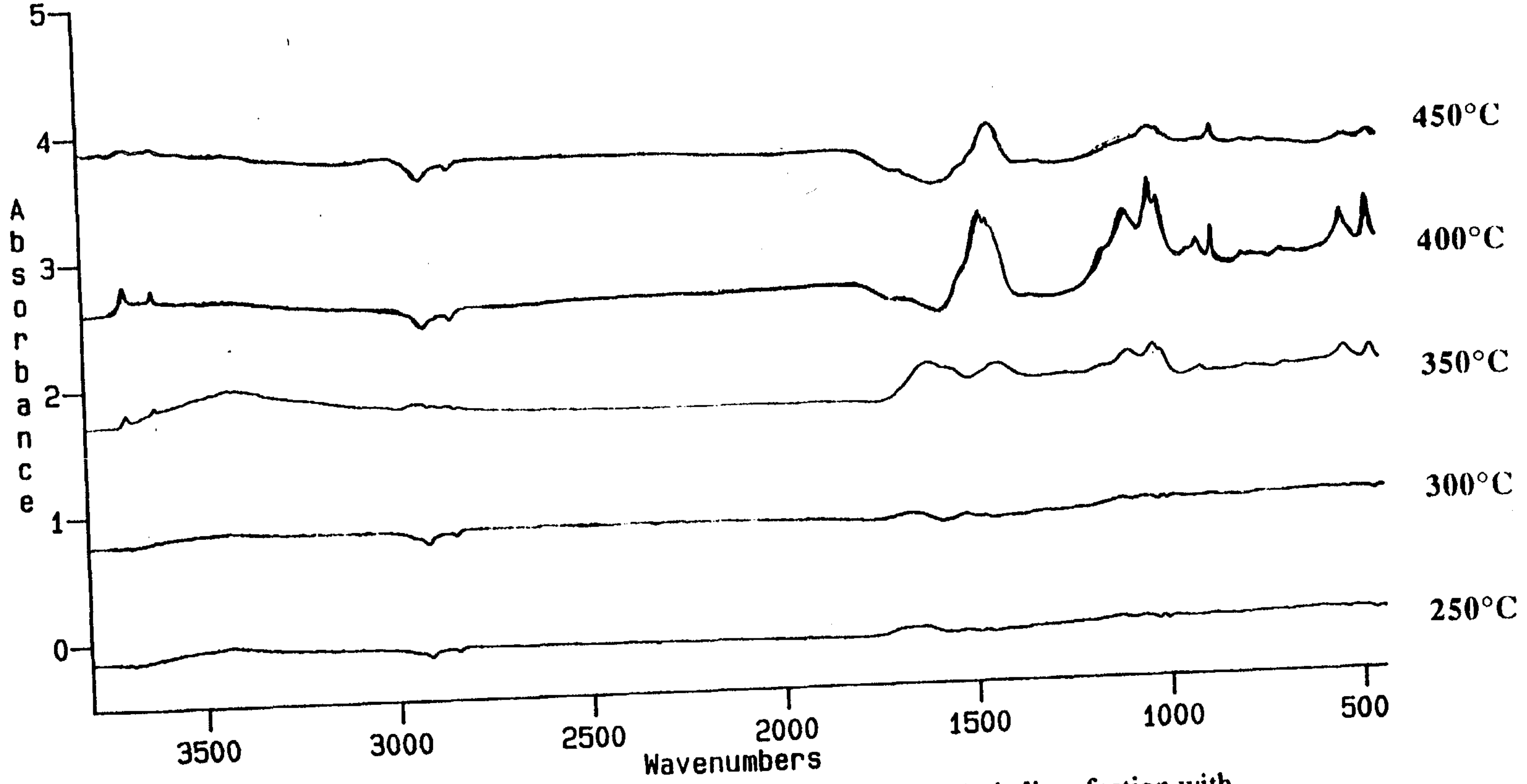


Figure 5.53 The difference spectra of residues from catalytic liquefaction with no solvent at various temperatures

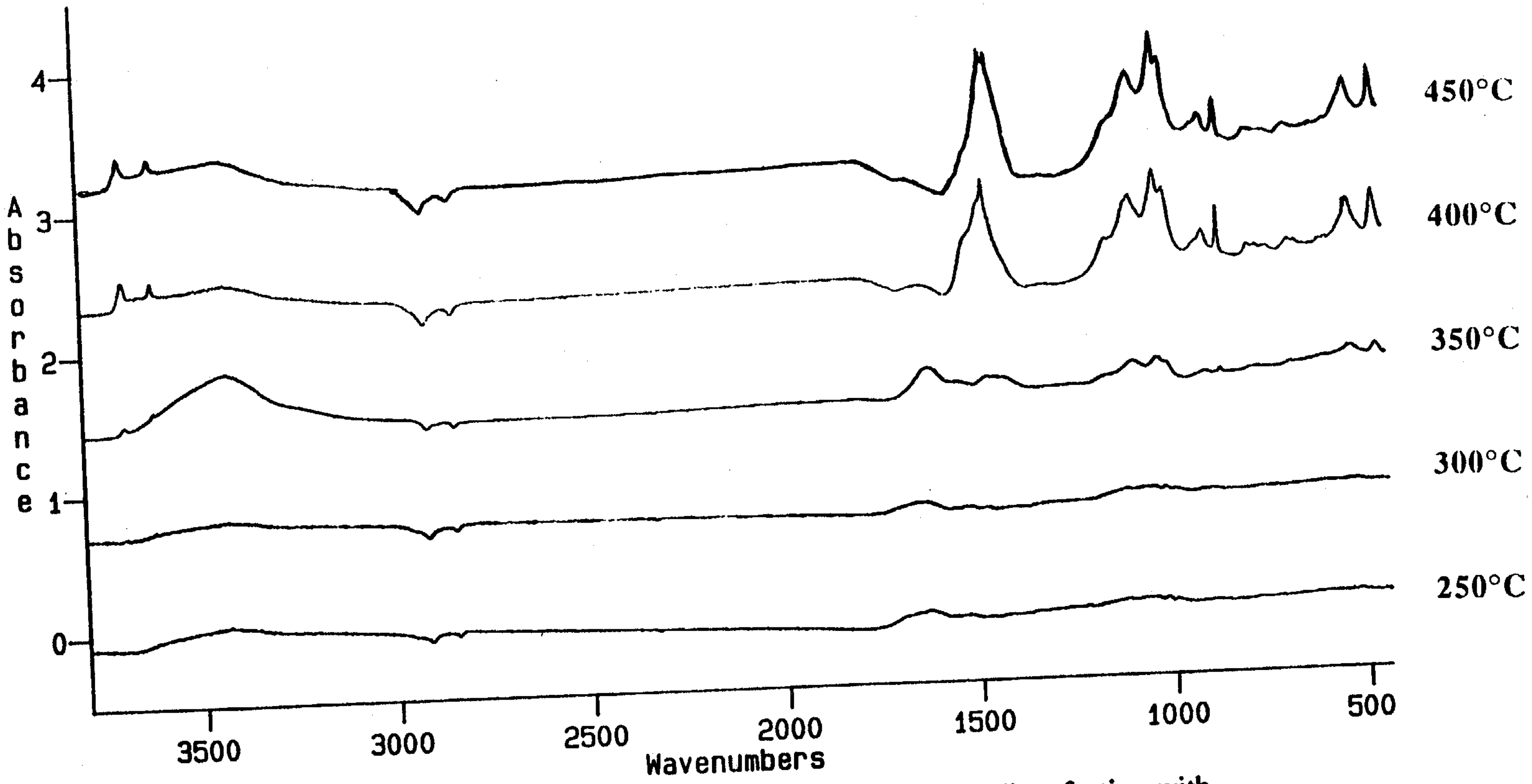


Figure 5.54 The difference spectra of residues from catalytic liquefaction with tetralin at various temperatures

[Van Krevelen, 1993]. It has been suggested by Painter et al. [1985] that the area covered by these bands can be used as an indication of the amount of aliphatic carbons in the sample. It is observed that the intensities of the bands decreases with temperature. For reactions with no solvent and catalyst, the area under these bands reduced to about half of that of the coal at 400°C. In reactions with tetralin, with catalyst, or with both of them, the bands almost disappear at this temperature. This observation suggests that at 400°C there is a significant amount of aliphatic carbons converted to THF solubles, and that either the donor solvent or the catalyst can enhance the conversion. At 450°C, the aliphatic carbons responsible for the bands at 2920 cm^{-1} and 2853 cm^{-1} are all converted to THF solubles under all reaction conditions applied.

The shoulder around 1700 cm^{-1} is due to C=O in ketone, aldehyde and COOH [Painter, 1985]. The intensity of this shoulder decreases with temperature and disappears at 450°C. Comparing the catalytic reactions and non-catalytic reactions, the catalyst has managed to remove the C=O functional groups quite effectively, based on the fact that the residues of the catalytic reactions contain less C=O groups than those of non-catalytic reactions.

It is interesting to note that the relative intensities of the bends at 1612 cm^{-1} and 1500 cm^{-1} change with temperature. The former is assigned to aromatic C-H stretching; and the latter is assigned to aromatic C-C stretching. In the parent coal and the residues from reactions at low temperatures, the peak at 1612 cm^{-1} is much stronger than that at 1500 cm^{-1}, implying that the aromatic ring is less substituted and less condensed. However when temperature increases to 400°C and higher, the relationship between the two peaks reverses. The peak at 1612 cm^{-1} almost disappears and the one at 1500 cm^{-1} becomes dominant. The observation indicates that more hydrogenated aromatic carbons are removed from the coal during reactions at high temperatures, though there is a possibility that these aromatic rings could be condensed too. The organic phase left behind in the reactions are highly condensed rings, which could be the portion inherent in the coal, or it could also be a result of condensation reactions due to lack of hydrogenation. It was found in the NMR study that retrogressive reactions occurred in the experiments without a donor solvent but not in those where the donor solvent was present. Therefore the observed increases in the peak located at 1500 cm^{-1} in residues of non-solvent reactions are a result of condensation; while those in the reactions with tetralin are due to the large aromatic rings in the parent coal.

With the increase of temperature there is another change, which is the increase in intensity of bands at 1096 cm^{-1} and 1036 cm^{-1}, especially in the reactions where the catalyst is involved. According to the assignment by Van Krevelen [1993], these bands are due to phenolic and alcoholic C-O bending. The observation indicates that there is an increase in the amount of C-O bonds. Recall that in the discussion about gases produced in liquefaction, it was found that the CO yield decreased in the catalytic reaction compared with that in the non-catalytic reaction (Section 5.3.1). It is therefore believed that carbonyl insertion reactions occur during liquefaction, which lead to a high content of C-O bonds in residues.

The soluble products, such as asphaltene and preasphaltene, are also studied by FTIR. Some examples are presented in Figure 5.55 - Figure 5.57 for the DECS-1 coal, with the rest in the appendix. Asphaltenes produced in catalytic reactions with tetralin are compared in Figure 5.55. The marked differences among these spectra are the appearance of the band at 3040 cm^{-1} and the disappearance of the band at 1700 cm^{-1}. The 3040 cm^{-1} band is assigned to aromatic C-H stretching mode [Painter, 1985]. The

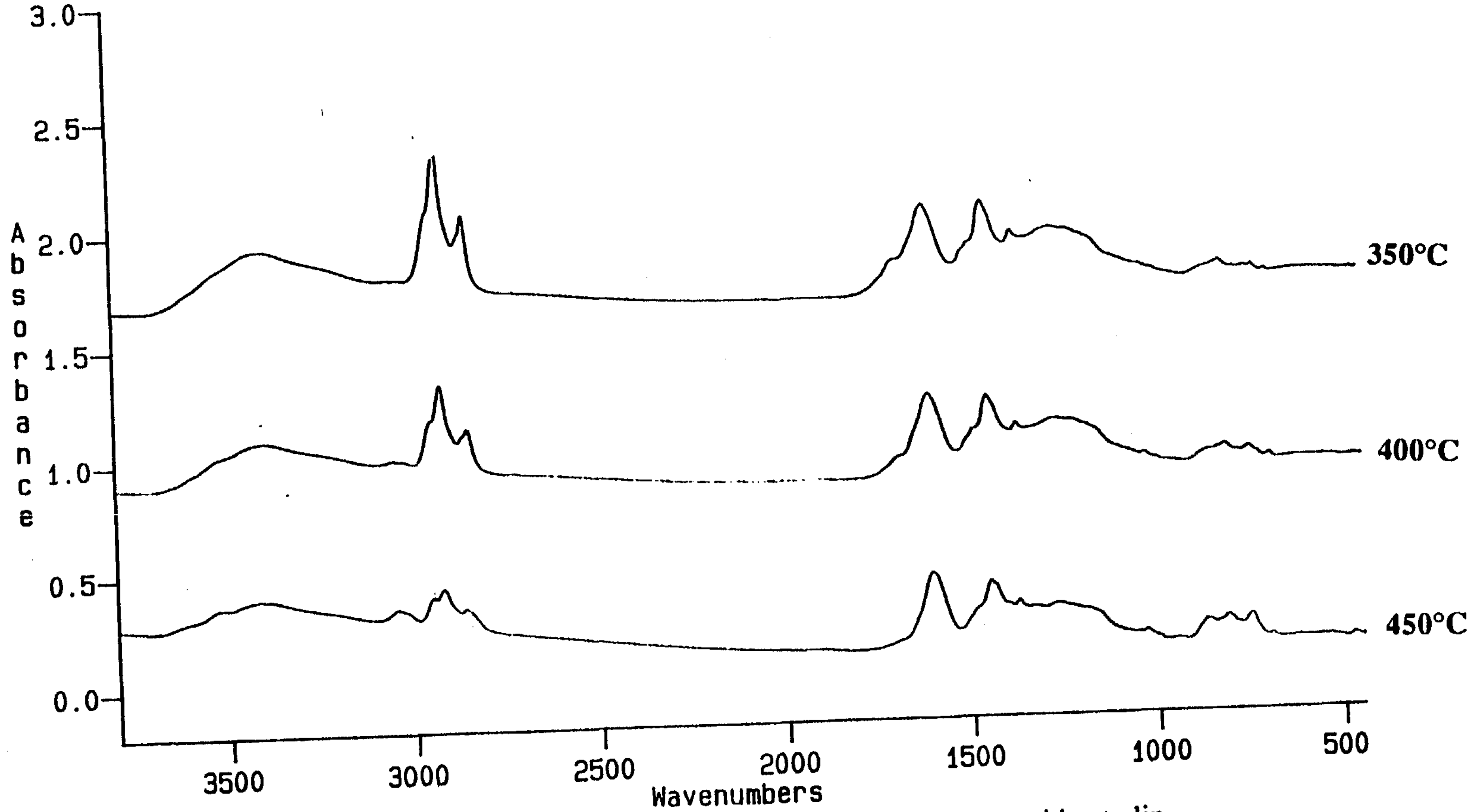


Figure 5.55 FTIR spectra of asphaltenes from catalytic reactions with tetralin at three temperatures

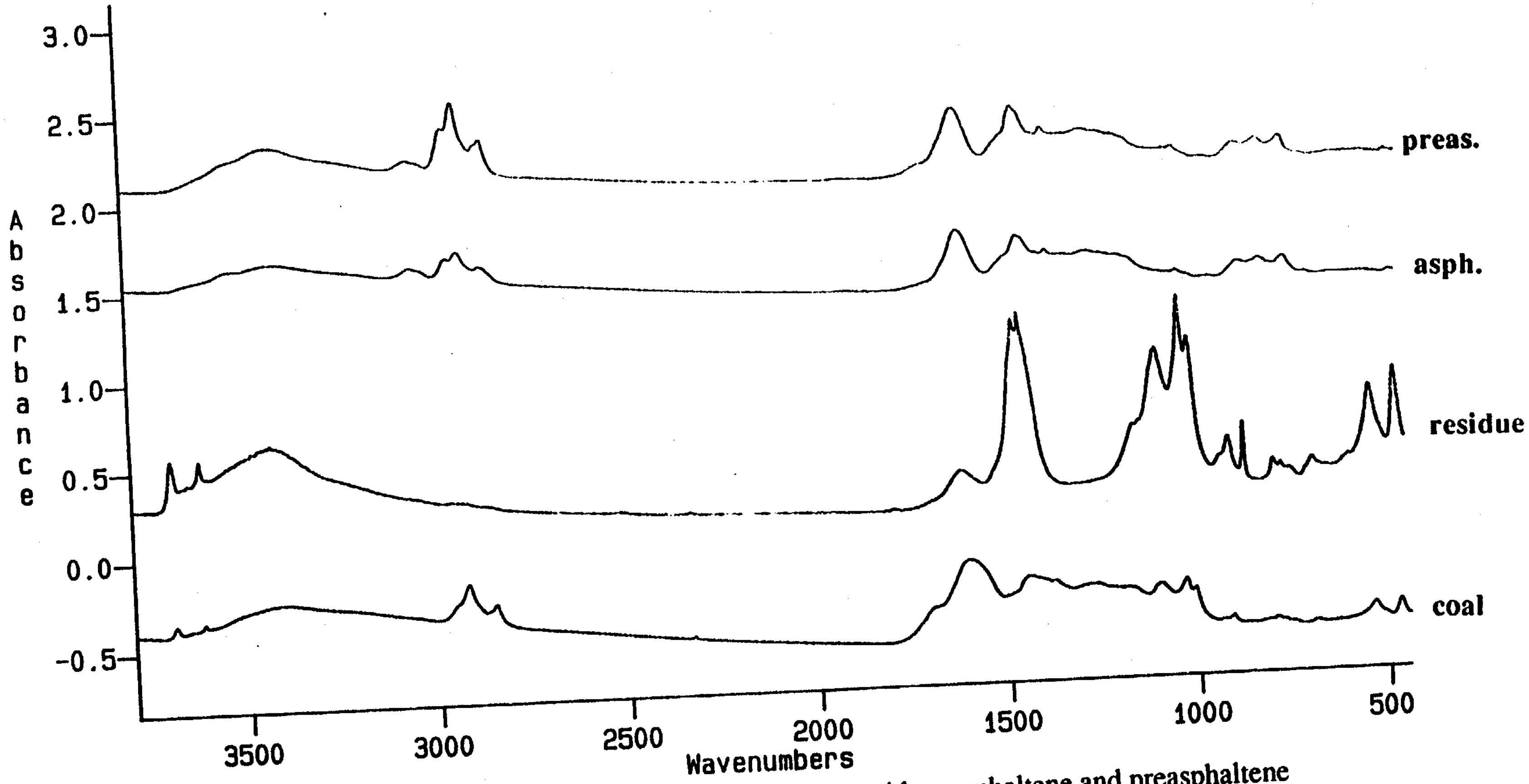


Figure 5.56 FTIR spectra of the DECS-1 coal, residue, asphaltene and preasphaltene from catalytic reaction with tetralin at 450°C

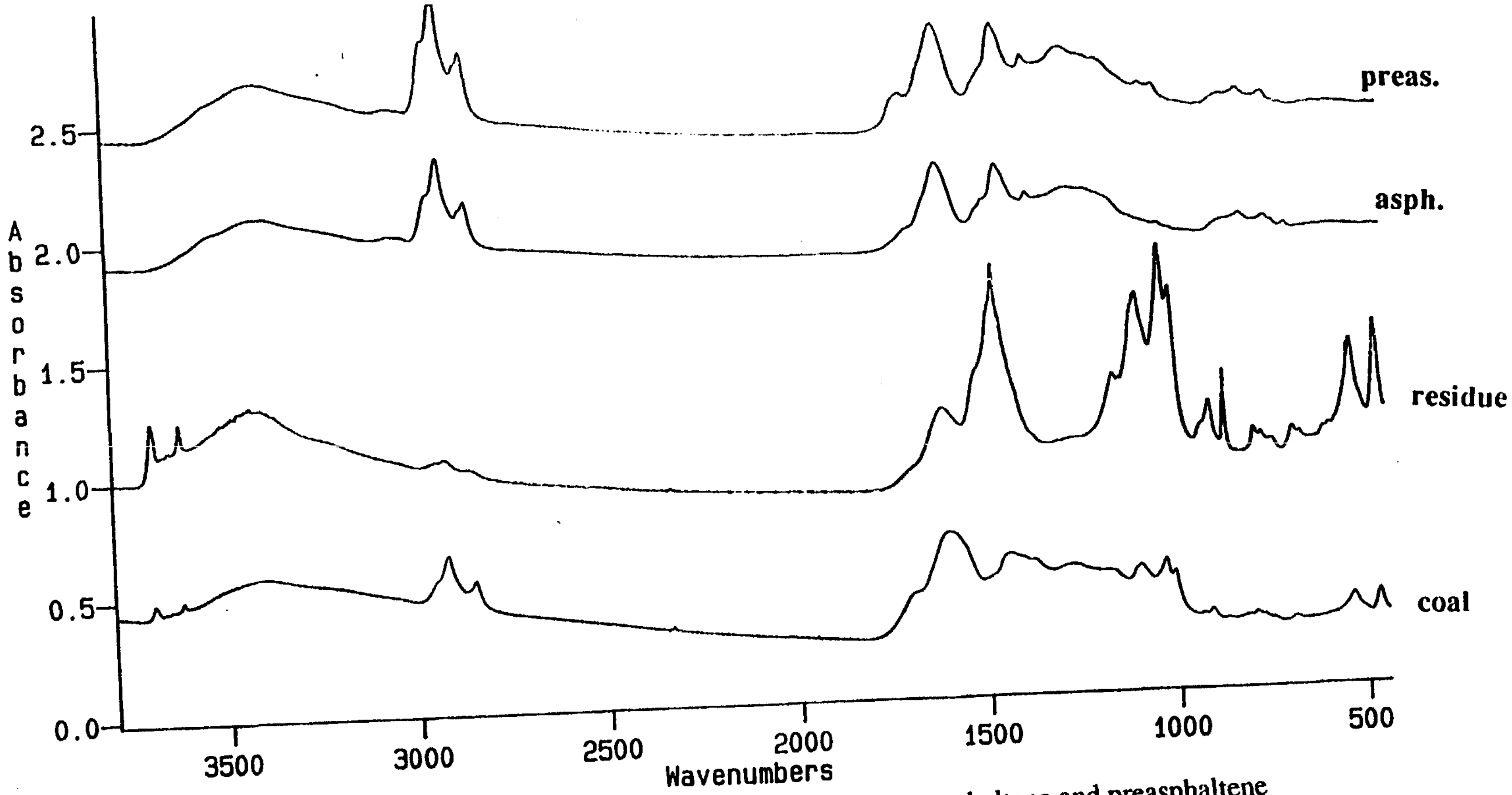


Figure 5.57 FTIR spectra of the DECS-1 coal, residue, asphaltene and preasphaltene from catalytic reaction with tetralin at 400°C

increases in the intensity of this band suggest that only at a high temperature can more aromatic carbon be released from the coal to the toluene-solubles (asphaltene). The 1700 cm^{-1} band, as is well known, is due to C=O bond. Figure 5.56 has the spectra of asphaltene, preasphaltene and residue produced in the catalytic reaction at 450°C with tetralin. It is observed that none of them has the band at 1700 cm^{-1}, strongly suggesting that the fragments containing C=O bonds are further broken down to oils which are first extracted from the product mixture. The products of the catalytic reaction at 400°C with tetralin are also compared, Figure 5.57. As other samples, the spectra are normalized to 1 gm of organic material. Therefore, according to the spectra, there are much more aliphatic carbons in asphaltene and preasphaltene than in the parent coal and the residue. This is expected because the earlier study has suggested that the aliphatic carbons in a coal are much easier to be converted to soluble product, such as asphaltene and preasphaltene. The preasphaltene (recalling that the preasphaltene is THF soluble but toluene insoluble) contains more C=O bonds than the asphaltene. According to the law that "like dissolves like", THF is a polar organic solvent, thus it favors the dissolution of compounds containing C=O groups, which are obviously polar. The intense bands at 1600 cm^{-1} (aromatic C-H stretching) of the preasphaltene and asphaltene imply that bond breaking to reduce molecular weight is very effective under this condition. The residue has a sharp peak at 1500 cm^{-1}, which indicates that the unreacted part of the coal contains large aromatic ring systems.

CHAPTER 6

CONCLUSIONS AND COMMENTS ON POSSIBLE FURTHER WORK

6.1 Conclusions

In this section, we have organized the major conclusions in terms of the specific objectives of the work as originally described in the Project Management Plan.

Study the effects of pretreatment temperature.

Although a low-temperature pretreatment seems beneficial compared to using a single-stage reaction, there is little, if anything, to be gained by raising the pretreatment temperature above 200°C. This effect is summarized for DECS-9 coal in Figure 4.7.

Study the effects of catalyst type.

The work reported in this Volume used only ATTM as a catalyst precursor, and therefore does not address this issue.

Study the effects of coal rank

The three coals, though all of low rank, appear to be quite different to convert to THF solubles. DECS-1 seems to be easiest. Having used only three coals in this portion of the work, a statistical analysis relating liquefaction performance to coal characteristics is not warranted. The reactivity data that highlight only the effects of the coals themselves are reactions in absence of solvent and catalyst (Tables 5.15–5.17). The main effect observed by ranking those results with characteristics of the coals is that conversions and oil yields at 400° and 450°C vary with organic sulfur, the coal with highest organic sulfur giving the highest oil yield. It is postulated that the organic sulfur has two advantages in liquefaction.

The first is contributed by the sulfur linkages in the coal which are relatively easy to cleave. The second is due to the H_2S formed from the organic sulfur further acting as a hydrogen transfer catalyst [Song, 1995].

Study the influence of solvent.

Solvents have two major effects on non-catalytic coal liquefaction: one involves physical processes, and other involves chemical processes. One of the physical processes is to dissolve coal-derived radicals to dilute their local concentration, to prevent recombination. The other is to "loosen" the coal structure so that hydrogen radicals carried by a solvent can reach the reaction sites. The chemical processes include dehydrogenation of the solvent and hydrogenation of the free radicals. Comparative study under the temperature-programmed condition yields the same conclusions as those under the single-staged condition. At low temperatures (350°C and below), using a solvent will enhance liquefaction to a noticeable extent. However, different types of solvents do not show significant differences, indicating that the advantages of the solvents at these temperatures are mainly due to physical processes. At medium temperatures, 350°C up to 450°C, both physical and chemical processes are involved. Physical ones can be seen based on the fact that reactions with the non-donor solvent have higher conversions than those without solvent. Reactions with a donor solvent, on the other hand, have even higher conversion than those with the non-donor solvent, indicating that hydrogen donation plays a role. At 450°C, physical processes are no longer important, from the observation that the non-donor solvent has no advantage in terms of providing a high conversion compared with the solvent-free reactions. At high temperatures, a large portion (if not all) of the solvents are in vapor phase, which eliminates the advantage that the solvent can dissolve some radicals and products and thus minimize recombination. The donor solvent, however, still shows its beneficial effects on all the three coals. In fact, use of a donor solvent is the most effective way to prevent retrogressive reactions, which are observed at this temperature. In the reactions with both a solvent and a catalyst, hydrogen consumption from the gas-phase H_2 indicates that the ATTM-derived catalyst is very effective. For a coal that is easy to convert to THF solubles, such as DECS-1, the catalyst has a stronger influence than the solvent on conversion and product distribution at 400°C and below, which is why the donor solvent shows no beneficial effect. For a coal that is less easily converted, however, the donor solvent can provide some "extra" conversion as well as oil yield.

Identify changes in coal structure induced by catalytic and thermal pretreatment

^{13}C NMR and FTIR provided useful information. Asphaltene and preasphaltene ^{13}C NMR spectra appeared to be very similar to those of the coals. Therefore further characterization was done by FTIR. The spectra of asphaltenes showed that more aromatic materials reacted and were extracted by toluene at a high temperature. In reactions with both donor solvent and the catalyst, compounds containing C=O bonds were not observed in asphaltene, preasphaltene or residue, suggesting that they were further broken down and appeared as oils. Residues were studied by solid-state ^{13}C NMR to determine their aromaticities. As reaction temperature increased the aromaticity increased, indicating that more aliphatic carbons were removed from the coal, or that more aromatic carbons were produced via retrogressive reactions. Further calculation on the net reacted aliphatic carbons and aromatic carbons shows that the reactions of aliphatic carbons are not significantly affected by the solvents or the catalyst applied; those of aromatic carbons are determined by the use of solvents and the catalyst, that is, the donor solvent or the catalyst must be used in order to liquefy those aromatics in the coal structure. This again shows that at a high temperature, such as 450°C, the only way to prevent retrogressive reaction is to use donor solvent, and that the catalyst is not fully effective. The FTIR study results in similar conclusions. The reactions of aliphatic carbons are determined mainly by temperature; and at 400°C, most aliphatic carbons are removed from the coals. Neither the solvents nor the catalyst have strong effects on the aliphatic reactions. However, the catalyst is very effective in removing C=O groups from the coal. The observations on aromatic C–H and C–C reveal that most of the hydrogenated aromatic carbons are removed from the coals in reactions at high temperatures, and the aromatic rings are more condensed, in good agreement with conclusions from NMR.

Examine reactivity of catalytically and thermally treated coals for liquefaction

Hydrogen consumption suggests that conversion is a function of the amount of hydrogen input into the coal, in agreement with earlier work by Artok et al. [1994]. In non-catalytic reactions, the amount of hydrogen consumed from H_2 increases drastically when temperature increases from 400°C to 450°C, and is comparable with that from tetralin. Reactions (non-catalytic) with tetralin have much higher conversions than those without tetralin, because in the former cases there is twice as much hydrogen consumed as those in the latter cases. In catalytic reactions, however, the hydrogen consumed from H_2 is greatly enhanced and becomes the dominant hydrogen source at temperatures of 400°C or below (which explains the fact that the donor solvent shows no advantage in catalytic reactions at a low temperature). At high temperature, it is quite different. Hydrogen consumption from the donor solvent becomes comparable with that from H_2, and thus can not be neglected. Therefore in catalytic reactions at 450°C with donor solvent, the total amount of hydrogen consumed is much higher than in reactions without donor solvent. In fact, using donor solvent is an efficient way to prevent retrogressive reactions at this temperature.

Examine pretreatment-induced changes in coal structure

Comparative study at different temperatures reveals that the coal structures can be readily broken down at 350°C and higher. Analysis of the products also results in some interesting findings. The studies on gas samples show that the amount of gas produced is a function of temperature, and that neither the catalyst nor the solvents have any significant impact. They, however, can influence the composition of the gases. The oils were analyzed by gas chromatography/mass spectrometry. In a non-catalytic reaction with no solvent, the oils contain mainly long-chain alkanes. Adding the catalyst appears to favor the production of aromatic compounds, mainly alkylbenzenes, phenol and alkylphenols. This suggests that the catalyst is particularly beneficial in converting the aromatic carbons from the coal to THF solubles rather than converting the aliphatic carbons. When donor solvent is used in addition to catalyst, the yields of phenolic compounds remain very high; and two- and three-ring aromatic compounds start to appear in the gas chromatogram.

Clarify impacts of pretreatment on liquefaction

The dried samples yielded higher conversions and more desirable products at 400°C without the presence of the catalyst. Moisture in the raw coal samples seemed to be able to enhance the conversion from preasphaltene to oil or asphaltene. (For this study, all coal samples were dried before reaction to compare the results on the same basis.) Studies on impregnation methods concluded that the binary solvent (THF/H_2O 1:1) had an advantage over H_2O in loading the catalyst onto a coal sample. This may be because an organic solvent has a higher affinity towards the coal surface than water. Therefore the THF/H_2O mixture was used as the impregnation solvent throughout this research. In the investigation of impregnation methods, it was found that for DECS-1 coal, the order of the impregnation methods in terms of the total conversion is swelling > incipient wetness > slurrying. For the DECS-11 and the DECS-9 coals, no clear trend was observed. Reactions under a less severe condition, such as single-staged with a non-donor solvent, were also carried out to minimize the effects of reaction condition and solvent. However, a similar behavior was observed. Therefore it is concluded that the impregnation methods applied here do not play a significant role, at least for these coals. Since the slurrying method was simplest, it was selected to be the standard impregnation method.

Three reaction conditions, single-staged, temperature-staged and temperature-programmed, were compared. The latter two were especially interesting to maximize conversion and minimize retrogressive reactions. The temperature-staged and temperature-programmed conditions are beneficial, particularly for the coals which are less easily converted. It was postulated that the advantages of these two conditions relied on the both chemical and physical processes related to reaction solvents and catalyst, based on the fact that the beneficial effects are more significant when both solvent and catalyst were present in the reaction. The chemical processes include the slow-down of the free-radical formation by slow heat-up, and, possibly, the activation of the catalyst precursor. Physical processes include the better mixing between a reaction solvent and the coal and the redistribution of the catalyst for a better dispersion.

Identify structures responsible for retrograde reactions

Retrogressive reactions take place immediately when the temperature reaches 450°C. The catalyst can help to reduce the retrogressive reactions, but only to a small extent. The best way is to use a donor solvent, which almost prevents the retrogressive reactions. We saw no clear evidence for retrogressive reactions at the lower temperatures. The present work shows that, at temperatures up to 400°C, retrogressive reactions are not an obvious problem provided that one uses either a good donor solvent or a good hydrogenation catalyst. Presumably one or the other of these would be present in any likely process configuration. Retrogressive reactions become significant at temperatures higher than 400°C. Because we worked at intervals of 50°C, we did not identify a specific temperature above which retrogressive reactions are certain to occur (and we speculate that such a limiting temperature may vary from one coal to another). Clearly retrogressive reactions are not a problem at 400° and are potentially a serious problem at 450°. The key to avoiding retrogressive reactions at high temperature is to use both a good donor solvent and a good hydrogenation catalyst. At these high temperatures most of the readily reactive material in the coal is converted to liquid, and the unreacted portion is highly aromatic. Although we did not identify specific functional groups or structures responsible for retrogressive reactions, it seems very likely that such reactions arise from ring coupling or ring condensation in or among aromatic systems.

Additional findings of this portion of the project

Using solid-state ^{13}C NMR and FTIR, it was found that all of the coals contain significant amounts of long-chain aliphatic structures, with the DECS-1 coal having the most. The oxygen appears to be in phenolic, catechol, carboxyl, carbonyl and methoxyl groups. The reaction time was investigated and it was noted that the conversion from the coal to THF solubles was a fast process. Within 10 minutes, high conversions can be achieved. However the conversion within the THF solubles, such as from preasphaltene to oil or from asphaltene to oil, was a much slower one. The comparative study concluded that 30 minutes was the optimum reaction time, and thus it was used as the standard time in this research. Several factors have impacts on conversion and product distribution. Examples are donor solvents, catalysts, and reaction conditions. In this study it was found that these factors influence the reactions to various extents. Qualitatively, Figure 6.1 summarizes their relationships to conclude this study.

6.2 Comments on Possible Further Work

When this project was originally planned, one of the aims had been to develop structure-reactivity relationships associated with catalyst type, coal rank, and solvent. It was envisioned that, for example, these relationships might be presented in the form of some sort of three-dimensional surface in which some liquefaction parameter of interest (e.g. conversion or oil yield) is expressed as a function of, say, coal rank and solvent

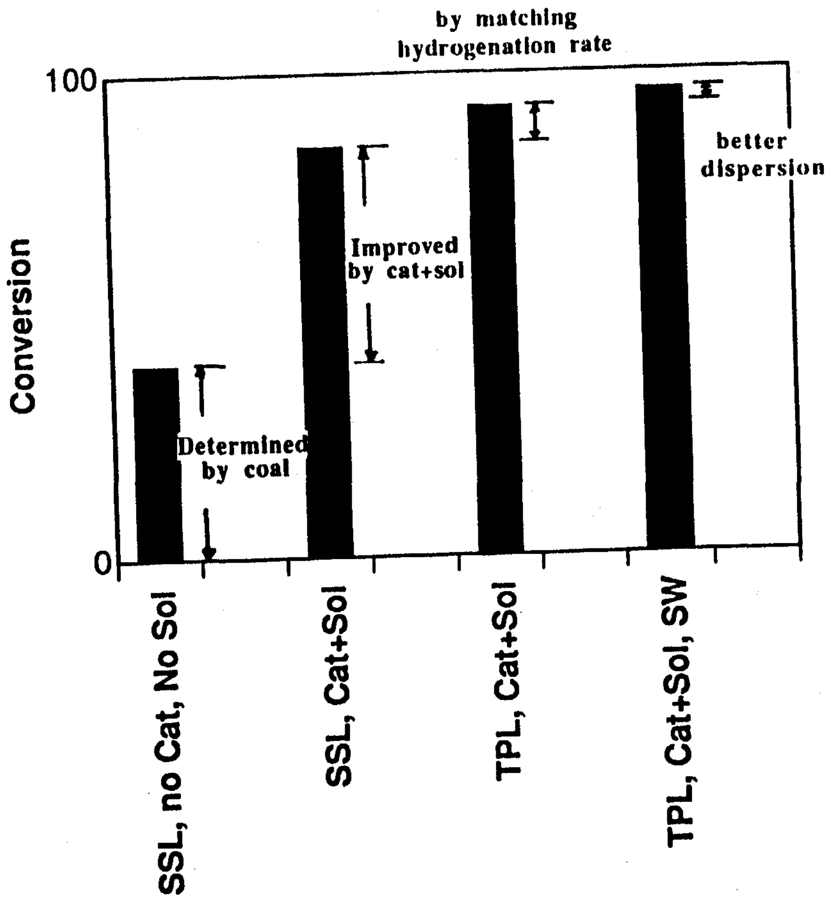


Figure 6.1 Comparison of the effects of solvents, catalysts, temperature conditions and impregnation methods on liquefaction of the low-rank coals

quality.. As the work progressed it became apparent that there were two problems standing in the way of this.

First, even with the full suite of six project coals (the three discussed in this volume and the three other coals), this is not a large enough data base for statistical manipulation, particularly multivariate statistics. That in itself is not an insuperable problem, since we estimate that, as a result of previous and collateral liquefaction projects in our laboratory, we now have in hand the results from at least 1,000 liquefaction tests, involving ≈20 coals (including some from overseas), ≈10 solvents, ≈15 catalyst precursors, and 3 reaction strategies (i.e., single staged, temperature staged, and temperature programmed). These data can be collected and put into a spread sheet format for statistical analysis.

The second, and much more formidable, problem is that there seems to be no good way to express numerically the catalyst activity and selectivity and solvent quality. The development of a numerical structure-reactivity relationship requires the ability to assign numbers—if only comparative ranks—that describe the role of the catalyst and the solvent.

If would be very useful if DOE/PETC could organize, via its own in-house research and the various extramural contractors, some agreed-upon tests for catalyst activity, selectivity, and solvent quality. These might, for example, use certain "standard" model compounds or selected coals from the DECS or Argonne sample sets. Even if the resulting numerical scales were in arbitrary units, rather than in fundamental kinetic or thermodynamic parameters, they would still represent a major step forward and would allow organizing and analyzing the very large amounts of data that have been generated over the past decade.

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APPENDIX A

SUMMARY OF CONVERSION AND PRODUCT YIELD DATA OF ALL LIQUEFACTION EXPERIMENTS

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
101, P6	9	400C, NC, WIMD, SSL	54.3		3.2	9.2	41.9
102, P19	9	400C, NC, WIMD, TPL	62.1		35.4	14.7	12.0
103, P21	9	400C, Ni, WIMD, TPL	82.6		45.9	22.3	14.4
104, P33	9	400C, Ni, WIMD, SSL	86.2		51.9	19.0	15.3
105, P36	9	400C, ATTM, WIMD, TPL	90.5		50.1	26.8	13.6
106, P39	9	400C, ATTM, WIMD, SSL	85.9		43.1	32.7	10.1
107, P41	9	400C, Ni, WIMD, SSL	76.8		35.5	20.8	20.6
108, P44	9	400C, NC, WIMD, TPL	55.1		25.2	19.8	10.2
109, P47	9	400C, NC, WIMD, SSL					
110, P49	9	400C, ATTM, WIMD, TPL	91.3		52.8	21.1	17.4
111, P52	9	400C, ATTM, WIMD, SSL	82.9		42.4	25.0	15.5
112, P55	9	400C,Ni,WIMD, TPL	73.6		35.6	19.9	18.1
113, P58	9	400C, NC, WIMD, SSL	52.2		30.2	12.5	9.6
114, P64	9	300/400°C, ATTM, WIMD, TPL	92.0		47.3	26.2	18.5

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
115, P67	9	250/400C, ATTM, WIMD, TPL	88.0		47.9	25.5	14.6
116, P70	9	200/400C, ATTMWIMD,TSL	91.2		47.6	25.9	17.7
117, P73	9	300/400C, ATTM, WIMD,TSL	86.4		42.8	27.4	16.2
118, P76	9	300/400C, ATTM, WIMD, TPL	87.3		53.9	19.1	14.3
119, P79	9	250/400C, ATTM, WIMD, TPL					
120, P86	9	200/400C, ATTM/H2O, WIMD, TPL					
121, P89	9	400C, ATTM/H2O, WIMD, TPL	83.2		39.0	19.5	24.8
122, P92	9	200/400C, ATTM/H2O, WIMD, TPL	80.6		41.2	23.4	15.4
123, P94	9	400C, ATTM/H2O, WIMD, SSL	65.8		37.6	21.5	6.6
124, P97	9	250/400C, ATTM/WIMD, TPL	85.1		45.8	22.3	17.0
125, P100	9	200/400C, ATTM, WIMD, TSL	87.7		40.3	29.3	18.0
126, P103	9	300/400C, ATTM, WIMD, TSL	89.4		42.6	29.3	17.6
127, P106	9	200/425C, ATTM, WIMD, TPL	93.3		62.4	15.5	15.5
128, P111	9	200/400C, ATTM, WIMD, TPL	81.8		58.4	18.0	5.4

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
129, P114	9	200/425C, ATTM, WIMD, TPL	89.1		58.1	20.1	10.8
130, P117	9	200/450C, ATTM, WIMD, TPL	85.1		66.3	12.5	6.4
131, P120	9	200/400C, ATTM, NS, TPL	71.8		42.4	19.8	9.6
132, P123	9	EXTRACTION	7.1		3.1	0.2	3.5
201, P3	1	EXTRACTION					
202, P4	11	EXTRACTION					
203, P10	1	200/400C, NC, WIMD, TPL	73.9		28.5	13.9	31.6
204, P12	11	200/400C, NC,WIMD, TPL	67.1		38.6	15.4	13.1
205, P16	1	200/400C, ATTM, WIMD, TPL	92.7		62.4	14.4	15.9
206, P18	11	200/400C, ATTM, WIMD, TPL	85.0		49.4	19.9	15.7
207, P28	1	200C, ATTM, WIMD, SSL,15MIN	0.8			3.4	3.9
208, P30	11	200C, ATTM, WIMD, SSL,15MIN	2.8				
209, P32	1	300C, ATTM, WIMD, SSL,15MIN	4.2			6.5	5.1
210, P34	11	300C, ATTM, WIMD, SSL,15MIN	4.9			3.9	2.3

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
211, P36	1	200C,15MIN->400C, ATTM, WIMD	45.8		20.5	12.5	12.8
212, P38	11	200C,15MIN->400C, ATTM, WIMD	37.8		15.5	12.7	9.6
213, P40	9	200C,15MIN->400C, ATTM, WIMD	59.2	3.5	19.8	19.6	19.8
214, P44	9	200C, ATTM, WIMD, SSL, 15MIN	0.3				
215, P46	9	300C, ATTM, WIMD, SSL, 15MIN	7.2			3.3	7.4
216, P52	1	200/400C, ATTM, TE, TPL					
217, P54	11	200/400C, ATTM, TE, TPL	86.3	8.0	43.5	10.5	24.3
218, P56	9	200/400C, ATTM, TE, TPL	94.0	5.4	46.0	12.4	30.1
219, P60	1	400C, ATTM, TE, SSL	83.5	4.0	44.8	13.7	21.0
220, P62	11	400C, ATTM, TE, SSL	78.7	9.0	25.0	15.7	29.0
221, P64	9	400C, ATTM, TE, SSL	85.9	5.8	32.2	18.6	29.4
222, P78	1	200/400C, ATTM, SW, WIMD, TPL	94.2	5.2	51.9	21.1	16.0
223, P80	11	200/400C, ATTM, SW, WIMD, TPL	83.2	9.7	42.0	16.7	14.7
224, P82	9	200/400C, ATTM, SW, WIMD, TPL	91.8	7.6	35.1	23.0	26.0

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
225, P84	1	200/400C, ATTM, SW, WIMD, TPL	97.2	8.9	40.5	19.4	28.5
226, P86	11	200/400C, ATTM, SW, WIMD, TPL	84.0	10.4	37.9	18.6	17.0
227, P88	9	200/400C, ATTM, SW, WIMD, TPL	90.0	7.0	37.4	26.1	19.5
228, P90	1	200/400C, NC, TE, TPL	76.5		40.0	13.7	22.8
229, P92	11	200/400C, NC, TE, TPL	72.6		38.7	16.4	17.5
230, P94	9	200/400C, NC, TE, TPL	75.2	11.2	24.7	21.6	17.7
231, P96	1	200/400C, NC, TE, TPL	78.1	9.2	35.5	18.0	15.3
232, P98	11	200/400C, NC, TE, TPL	73.6	12.4	28.0	15.0	18.4
233, P100	9	200/400C, NC, TE, TPL	76.3	18.0	14.3	21.7	22.2
234, P108	1	200/400C, ATTM, DE, TPL	86.6		61.2	17.9	7.5
235, P110	11	200/400C, ATTM, DE, TPL	68.7		47.9	7.1	13.7
236, P112	9	200/400C, ATTM, DE, TPL	77.8	4.6	38.9	21.9	12.5
237, P114	1	200/400C, ATTM, DE, TPL	86.0		57.6	20.6	7.9
238, P116	11	200/400C, ATTM, DE, TPL	69.7	11.3			6.0

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
239, P118	9	200/400C, ATTM, DE, TPL	77.1	5.0	39.8	19.9	12.5
240, P122	1	200/400C, ATTM, SL,WIMD, TPL	89.3		55.3	19.6	14.4
241, P124	11	200/400C, ATTM, SL,WIMD, TPL	79.9		47.1	20.5	12.3
242, P126	9	200/400C, ATTM, SL,WIMD, TPL	93.5		51.4	26.0	16.1
243, P128	1	200/400C, ATTM, SL,WIMD, TPL	87.2	9.2	46.2	16.8	15.0
244, P130	11	200/400C, ATTM, SL,WIMD, TPL	82.6	15.8	39.1	17.7	9.9
245, P132	9	200/400C, ATTM, SL,WIMD, TPL	90.3	8.7	41.3	24.3	15.9
246, P134	1	350C, ATTM, SL,WIMD, SSL	37.1	7.4	12.4	12.0	5.3
247, P136	11	350C, ATTM, SL,WIMD, SSL	42.8	8.0	12.4	11.4	11.0
248, P138	9	350C, ATTM, SL, WIMD, SSL	53.3	4.1	16.3	16.0	16.9
249, P140	1	350C, ATTM, SW, WIMD, SSL	34.4	6.8	12.8	11.8	3.1
250, P142	11	350C, ATTM, SW, WIMD, SSL	37.5	8.4	13.5	11.2	4.4
251, P144	9	350C, ATTM, SW, WIMD, SSL	44.0	4.7	0.6	17.2	21.5
252, P146	1	350C, ATTM, IW, WIMD, SSL	33.6	3.2	13.3	11.0	6.1

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
253, P148	11	350C, ATTM, IW, WIMD, SSL					
254, P150	9	350C, ATTM, IW, WIMD, SSL	45.5	3.3	4.3	14.9	23.3
255, P152	1	350C, ATTM, SL, WIMD, SSL	27.9	5.3	9.0	10.2	3.5
256, P154	1	350C, ATTM, SW, WIMD, SSL	44.5	3.7	22.0	11.2	7.6
257, P156	11	350C, ATTM, IW, WIMD, SSL	36.0	7.7	12.4	6.8	8.4
258, P158	1	350C, NC, WIMD, SSL	28.6	5.8	10.0	6.2	6.7
259, P160	11	350C, NC, WIMD, SSL	25.5	8.6	9.7	3.6	3.6
260, P162	9	350C, NC, WIMD, SSL	26.8	4.7	4.0	8.8	9.3
261, P164	1	350C, ATTM, SL, WIMD, SSL	44.2	4.3	22.7	10.6	6.6
262, P166	11	350C, ATTM, SL, WIMD, SSL	47.4	7.2	27.7	6.9	5.6
263, P168	9	350C, ATTM, SL, WIMD, SSL	56.5	3.5	25.0	14.4	13.6
264, P170	1	200/400C, NC, DE, TPL	49.4	10.3	25.3	9.5	4.3
265, P172	11	200/400C, NC, DE, TPL	38.0	17.0	14.7	2.7	3.6
266, P174	9	200/400C, NC, DE, TPL	37.3	9.4	17.4	5.9	4.7

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
267, P176	1	350C, ATTM, SW, 1-MN, SSL	54.5	4.3	33.9	14.5	12.7
268, P178	1	350C, ATTM, IW, 1-MN, SSL	47.4	4.7	19.6	13.1	10.0
269, P180	1	350C, ATTM, SL, 1-MN, SSL	49.7	4.6	20.7	13.9	10.5
270, P182	1	200/400C, NC, WIMD, TPL	67.1	10.3	18.3	15.8	22.8
271, P184	1	200/400C, NC, DE, TPL	44.7	9.7	20.9	8.9	5.2
272, P186	1	200/400C, NC, 1-MN, TPL	47.1	10.2	15.0	9.5	12.5
273, P188	1	200/400C, NC, 1-MN, TPL	45.4	10.3	14.0	10.7	10.6
301, P4	11	200/400C, NC, WIMD, TPL	57.1	12.8	19.2	15.2	10.0
302, P6	9	200/400C, NC, WIMD, TPL	56.6	9.6	18.9	15.4	12.7
303, P8	1	350C, NC, TE, SSL	33.4	4.2	12.1	9.0	8.0
304, P10	1	350C, NC, DE, SSL	24.7	6.8	8.4	4.8	4.7
305, P12	1	350C, NC, 1-MN, SSL	29.0	4.9	7.6	9.1	7.6
306, P14	1	350C, NC, WIMD, SSL	30.7	4.7	12.7	8.4	4.9
307, P16	1	350C, NC, TE, SSL	38.2	4.4	18.2	8.3	7.4

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
308, P18	1	350C, NC, DE, SSL	29.5	5.0	17.1	4.8	2.7
309, P20	1	350C, NC, 1-MN, SSL	33.8	5.0	14.8	7.4	6.7
310, P22	11	350C, NC, WIMD, SSL	25.6	9.4	8.6	5.1	2.5
311, P24	9	350C, NC, WIMD, SSL	29.0	5.0	6.3	11.3	6.5
312, P26	1	350C, ATTM, SW, WIMD, SSL	46.4	3.7	25.7	11.8	5.7
313, P30	6	275/425C, NC, PHE,TSL	49.6	3.8	22.3	14.0	9.5
314, P32	6	275/425C, NC, PHE,TSL	52.9	5.4	20.9	13.8	12.9
315, P34	6	275/425C, ATTM, NC, PHE,TSL	57.5	4.6	29.3	14.6	9.0
316, P36	6	275/425C, ATTM, NC, PHE,TSL	54.7	3.7	25.8	13.4	11.8
317, P40	1	250C, NC, NS, 250C, SSL	11.7	1.9	8.2	0.8	0.8
318, P42	1	250C, NC, TE, SSL	13.3	0.6	6.0	3.7	3.1
319, P44	1	250C, NC, 1-MN, SSL	11.9	2.8	5.6	2.4	1.2
320, P48	1	350C, NC, NS, SSL	19.1	6.5	7.4	1.1	4.1
321, P50	1	EXTRACTION	7.6				

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
322, P52	1	250C, ATTM(SL), NS, SSL	14.3	0.9	6.5	3.1	3.8
323, P54	1	250C, ATTM(SL), TE, SSL	3.8	0.9		2.3	1.7
324, P56	1	250C, ATTM(SL), 1-MN, SSL	3.6	0.6		2.3	2.5
325, P60	1	350C, ATTM(SL), NS, SSL	39.4	4.0	23.2	6.2	6.0
326, P62	1	350C, ATTM(SL), TE, SSL	46.6	3.7	23.9	11.4	7.6
327, P64	1	350C, ATTM(SL), 1-MN, SSL	44.0	3.4	18.5	9.9	12.2
328, P66	1	400C, ATTM(SL), NS, SSL	95.5	7.4	58.9	24.0	5.2
329, P68	1	400C, ATTM(SL), TE, SSL	92.0	6.8	44.3	19.3	21.6
330, P70	1	400C, ATTM(SL), 1-MN, SSL	84.8	8.1	41.6	16.4	18.7
333, P77	1	EXTRACTION	4.9			2.3	4.3
331, P82	1	400C, NC, NS, SSL	45.0	11.6	19.8	3.4	10.2
332, P84	1	400C, NC, TE, SSL	82.0	9.5	36.7	16.6	19.2
334, P86	1	400C, NC, TE, SSL	55.5	9.7	24.4	10.4	11.0
335, P90	1	300C, NC, NS, SSL	16.2	3.5	7.9	0.9	3.9

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
336, P92	1	300C, NC, TE, SSL	20.8	3.5	9.8	3.5	4.0
337, P94	1	300C, NC, 1-MN, SSL	22.2	3.5	10.2	2.0	6.5
338, P96	1	300C, ATTM, NS, SSL	17.2	2.5	9.3	1.8	3.6
339, P98	1	300C, ATTM, TE, SSL	22.0	0.9	12.4	5.5	3.2
340, P100	1	300C, ATTM, 1-MN, SSL	22.9	2.4	10.2	6.0	4.3
341, P104	11	350C, NC, NS, SSL	15.4	6.5	8.4	0.3	0.2
342, P106	11	350C, NC, TE, SSL	28.1	6.6	19.9	5.0	3.2
343, P108	11	350C, NC, 1-MN, SSL	23.3	6.8	11.3	3.9	1.3
344, P114	11	250C, NC, NS, SSL	4.7	2.0	1.3	0.2	1.2
345, P116	11	250C, NC, TE, SSL	4.6	1.7		1.2	1.7
346, P118	11	250C, NC, 1-MN, SSL	5.3	2.0	1.5	1.2	0.6
347, P122	1	400C, ATTM, NS, SSL	92.0	10.3	59.8	13.1	8.8
349, P126	1	450C, NC, NS, SSL	51.5	17.6	28.8	0.9	4.2
350, P128	1	450C, NC, TE, SSL	92.2	19.2	49.0	8.4	15.6

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
351, P130	1	450C, NC, 1-MN, SSL	57.0	16.3	31.8	4.3	4.6
352, P134	1	450C, ATTM, NS, SSL	69.4	18.0	44.6	5.2	1.6
353, P136	1	450C, NC, TE, SSL	95.8	14.2	66.1	10.4	5.1
354, P138	1	450C, NC, 1-MN, SSL	67.2	16.1	37.4	5.3	8.4
355, P148	11	350C, ATTM, NS, SSL	17.1	6.2	5.7	2.2	3.0
356, P146	11	350C, ATTM, TE, SSL	29.8	5.7	12.0	5.5	6.7
357, P150	11	350C, ATTM, 1-MN, SSL	28.6	6.0	8.3	8.0	6.3
358, P156	1	400C, ATTM, NS, SSL, 60MINS	81.0	13.0	47.6	14.2	6.2
359, P158	1	400C, ATTM, TE, SSL, 60MINS	94.8	7.4	57.1	8.9	21.3
360, P160	1	400C, ATTM, 1-MN, SSL, 60 MINS	87.3	7.1	52.6	19.4	8.2
361, P162	1	400C, ATTM, NS, SSL, 10MINS	84.1	7.4	45.2	22.8	8.6
362, P164	1	400C, ATTM, TE, SSL, 10MINS	67.4	8.3	24.5	8.1	26.5
363, P166	1	400C, ATTM, 1-MN, SSL, 10MINS	61.5	8.6	22.3	10.8	19.8
364, P168	11	450C, ATTM, NS, SSL, 30MINS	53.6	20.3	26.0	4.0	3.4

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
365, P170	11	450C, ATTM, TE, SSL, 30MINS	71.1	24.2	31.7	7.9	7.3
366, P172	11	450C, ATTM, 1-MN, SSL, 30MINS	54.6	18.4	26.9	5.2	4.1
367, P176	11	400C, ATTM, NS, SSL	63.5	16.6	20.0	16.4	10.5
368, P178	11	400C, ATTM, TE, SSL	76.8	12.3	23.2	21.8	19.5
369, P180	11	400C, ATTM, 1-MN, SSL	65.5	11.7	18.6	14.7	20.5
370, P182	11	450C, NC, NC, SSL	49.1	16.8	25.3	0.6	6.4
371, P184	11	450C, NC, TE, SSL	70.9	18.4	36.4	8.5	7.6
372, P186	11	450C, NC, 1-MN, SSL	46.7	16.8	23.5	3.4	3.1
401, P4	11	400C, NC, NS, SSL	30.6	11.7	14.3	0.4	4.2
402, P6	11	400C, NC, TE, SSL	65.9	12.5	25.3	12.3	15.7
403, P8	11	400C, NC, 1-MN, SSL	37.7	10.6	16.2	4.0	6.9
404, P12	9	450C, ATTM, NS, SSL	62.9	12.0	39.8	6.2	4.9
405, P14	9	450C, ATTM, TE, SSL	93.8	13.2	41.0	9.2	30.5
406, P16	9	450C, ATTM, 1-MN, SSL	61.7	11.5	35.9	11.2	3.0

Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
407, P18	9	400C, ATTM, NS, SSL	78.5	6.3	34.1	23.5	14.6
408, P20	9	400C, ATTM, TE, SSL	98.5	3.7	40.5	27.6	26.6
409, P22	9	400C, ATTM, 1-MN, SSL	76.5	7.2	30.2	14.3	24.9
410, P24	9	350C, ATTM, NS, SSL	47.1	2.9	8.7	12.5	23.1
411, P26	9	350C, ATTM, TE, SSL	57.9	2.9	14.6	20.2	20.3
412, P28	9	350C, ATTM, 1-MN, SSL	47.7	2.9	10.8	13.9	20.0
413, P32	9	450C, NC, NS, SSL	38.5	12.5	21.9	0.3	3.8
414, P34	9	450C, NC, TE, SSL	81.6	12.5	6.0	8.5	54.7
415, P36	9	450C, NC, 1-MN, SSL	38.9	11.7	21.9	3.9	1.4
416, P40	9	400C, NC, NS, SSL	24.2	7.1			4.6
417, P42	9	400C, NC, TE, SSL	74.2	6.9	26.6	18.9	21.8
418, P44	9	400C, NC, 1-MN, SSL	37.6	7.1	13.8	8.8	8.0
419, P46	9	350C, NC, NS, SSL	19.4	2.5	8.8	2.5	5.7
420, P48	9	350C, NC, TE, SSL	42.8	3.6	15.7	12.1	11.4

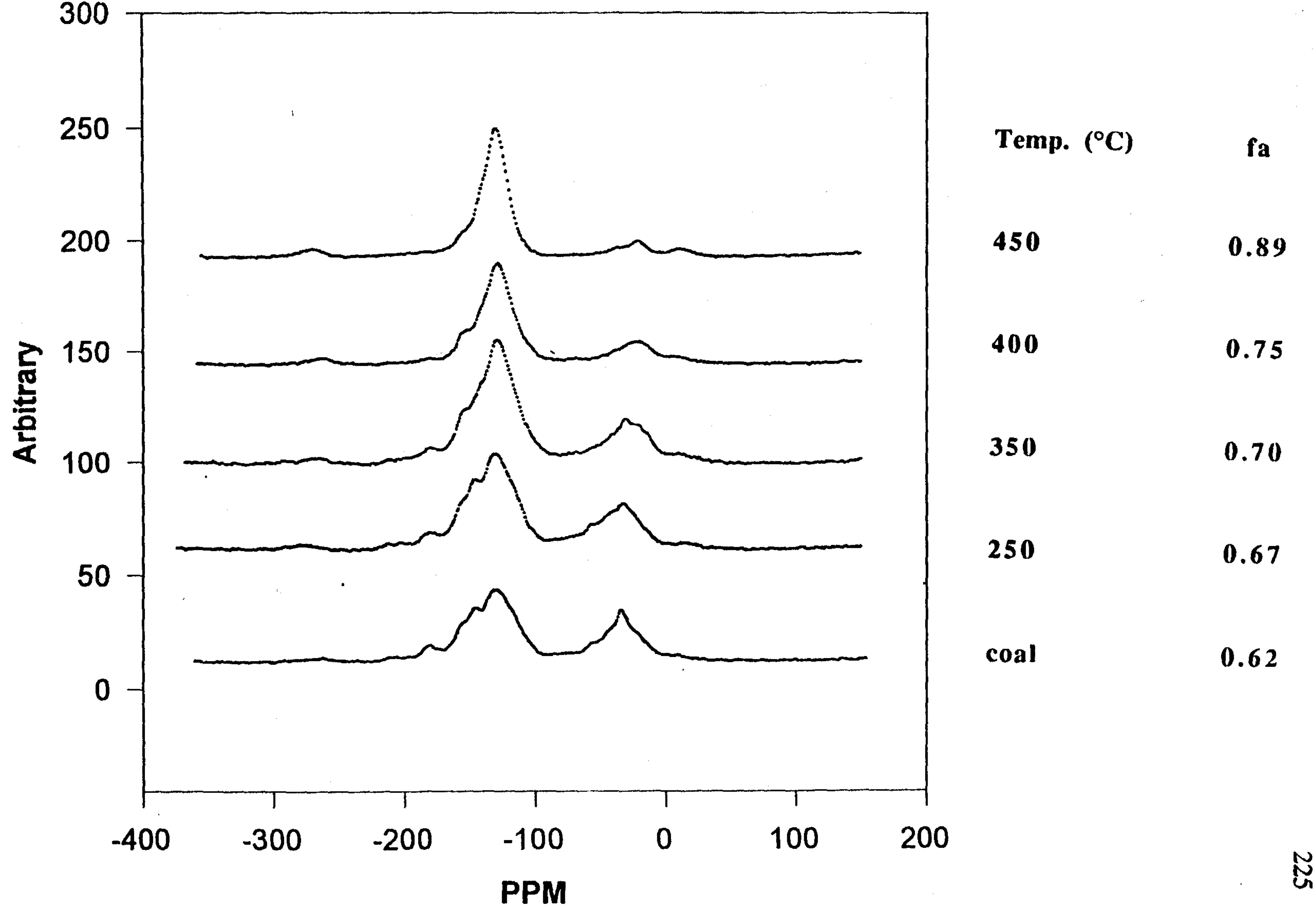
Expt. # Page #	DECS # of the coal	Reaction Condition	Conv.	Gas	Oil	Asph.	Preasph.
421, P50	9	350C, NC, 1-MN, SSL	29.6	4.7	7.0	10.3	7.7

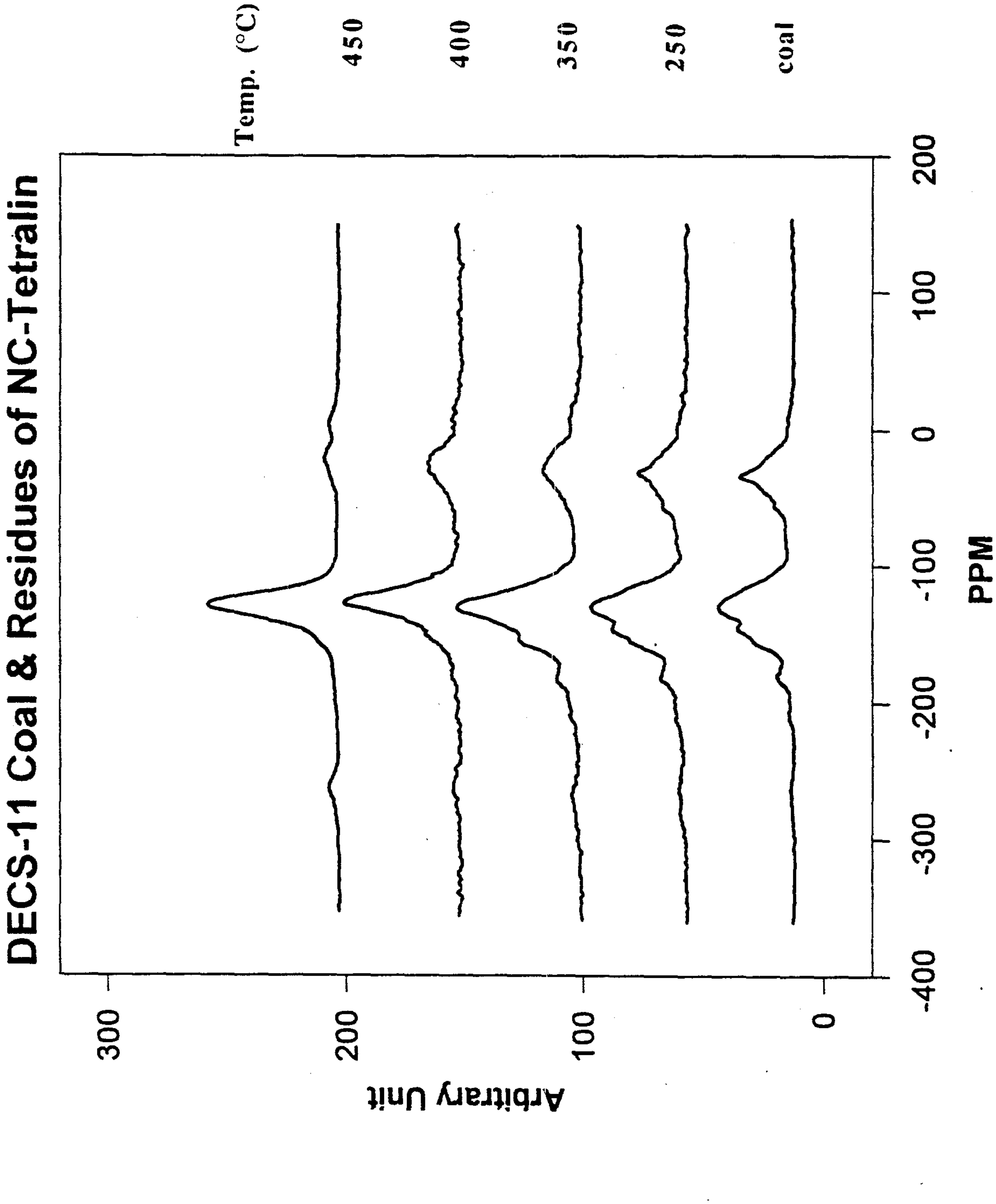
* Expt. # and Page #: The first digit of the experiment number is the laboratory notebook number; the second and the third number are the experiment number in that book. The "Page #" is the page on which the experiment was recorded. For example, "220, P62" is the experiment # 20 in the second notebook, on page 62.

APPENDIX B

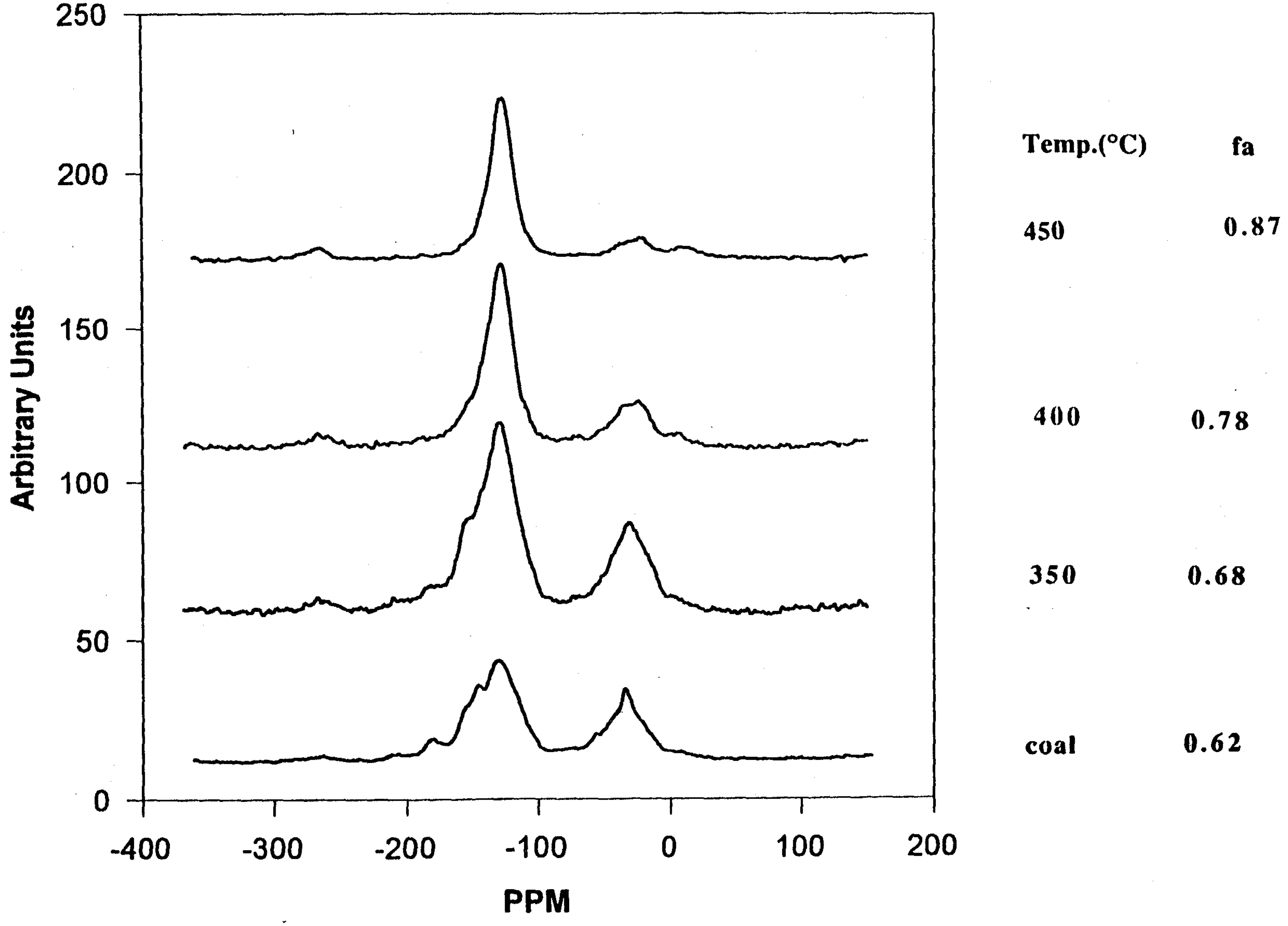
SOLID-STATE ^{13}C NMR SPECTRA OF COALS AND THEIR LIQUEFACTION PRODUCTS

DECS-11 Coal & Residues of NC-No Solvent



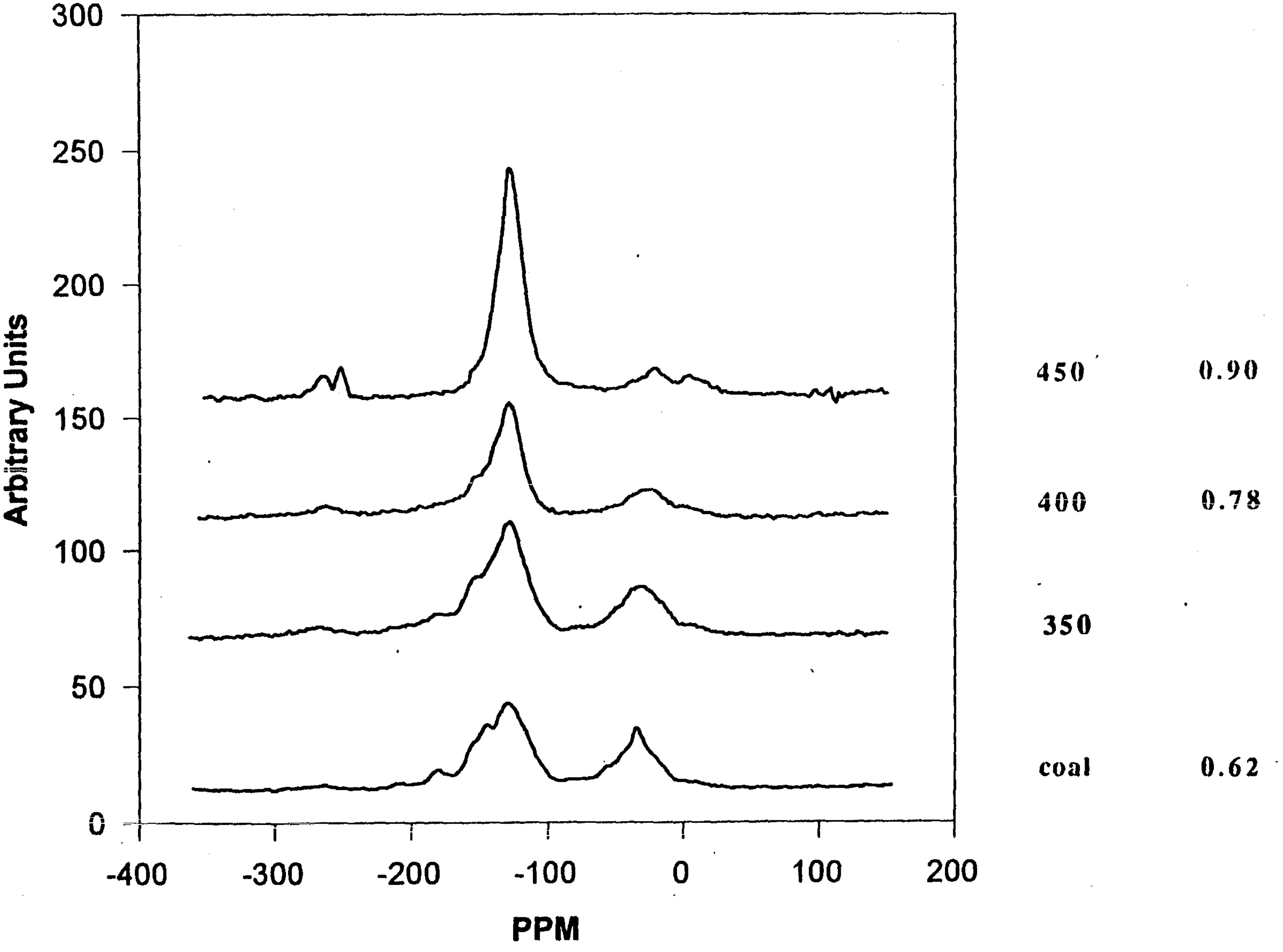


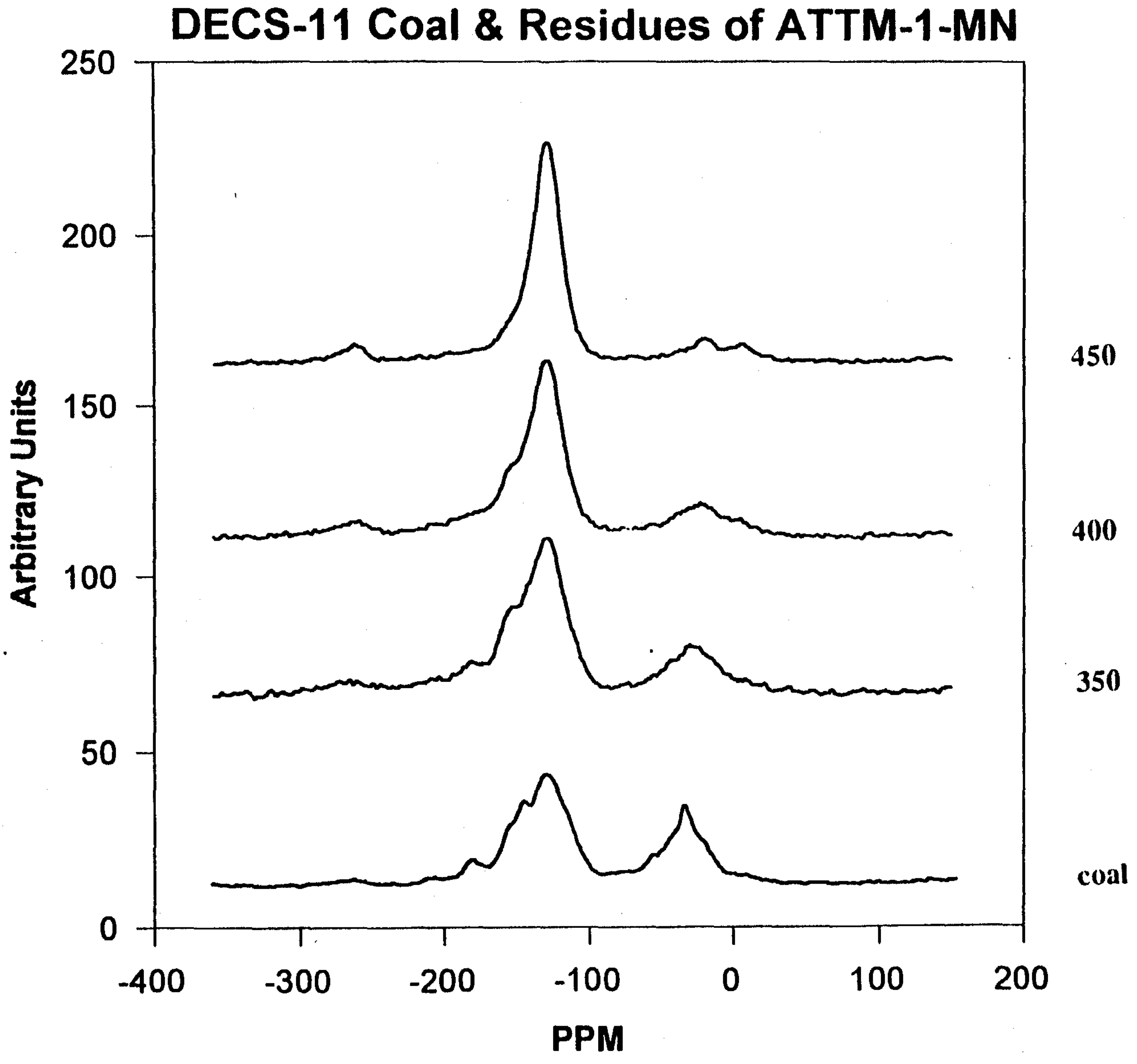
DECS-11 Coal & Residues of NC-Tetralin

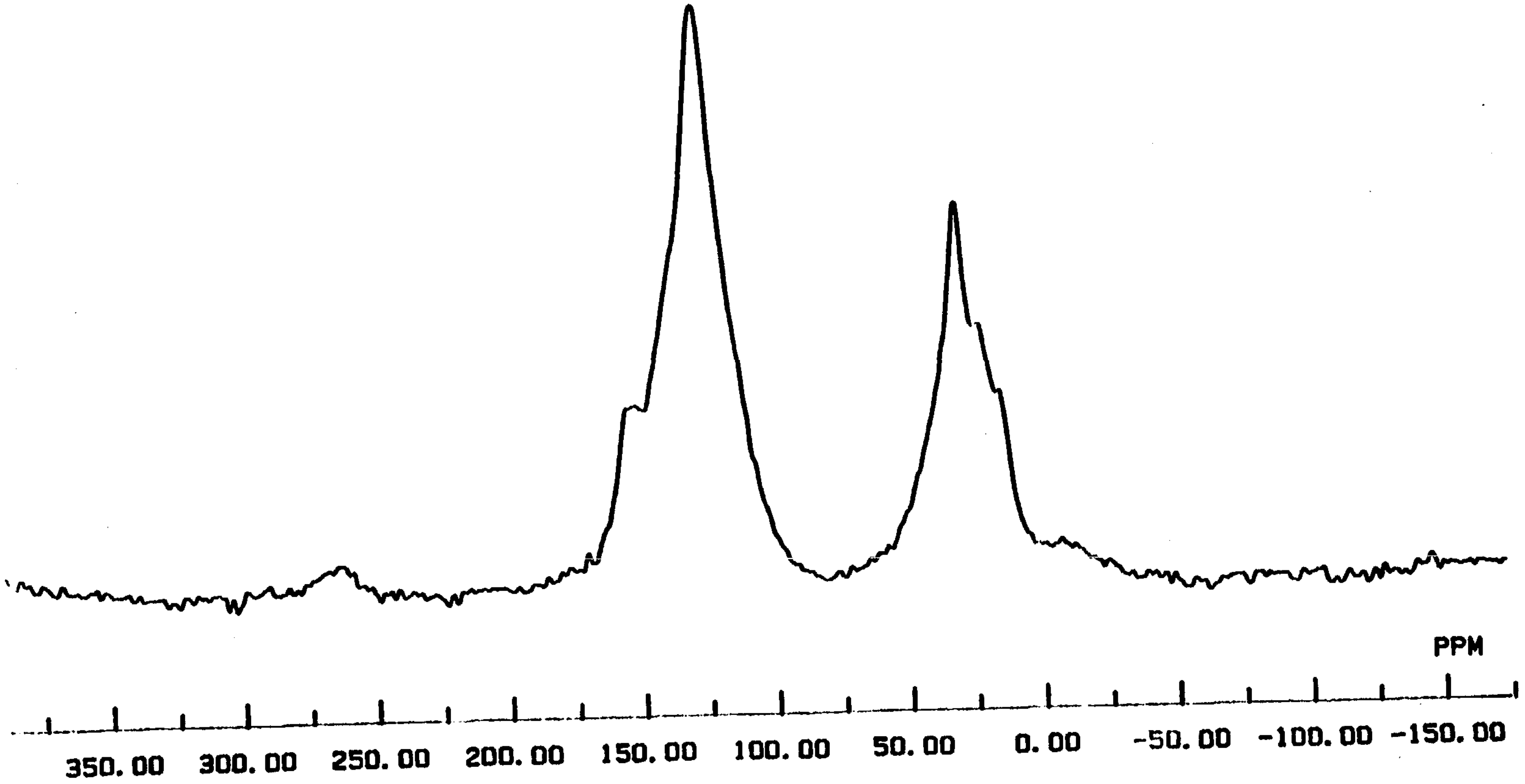


DECS-11 Coal & Residues of ATTM-No Solvent

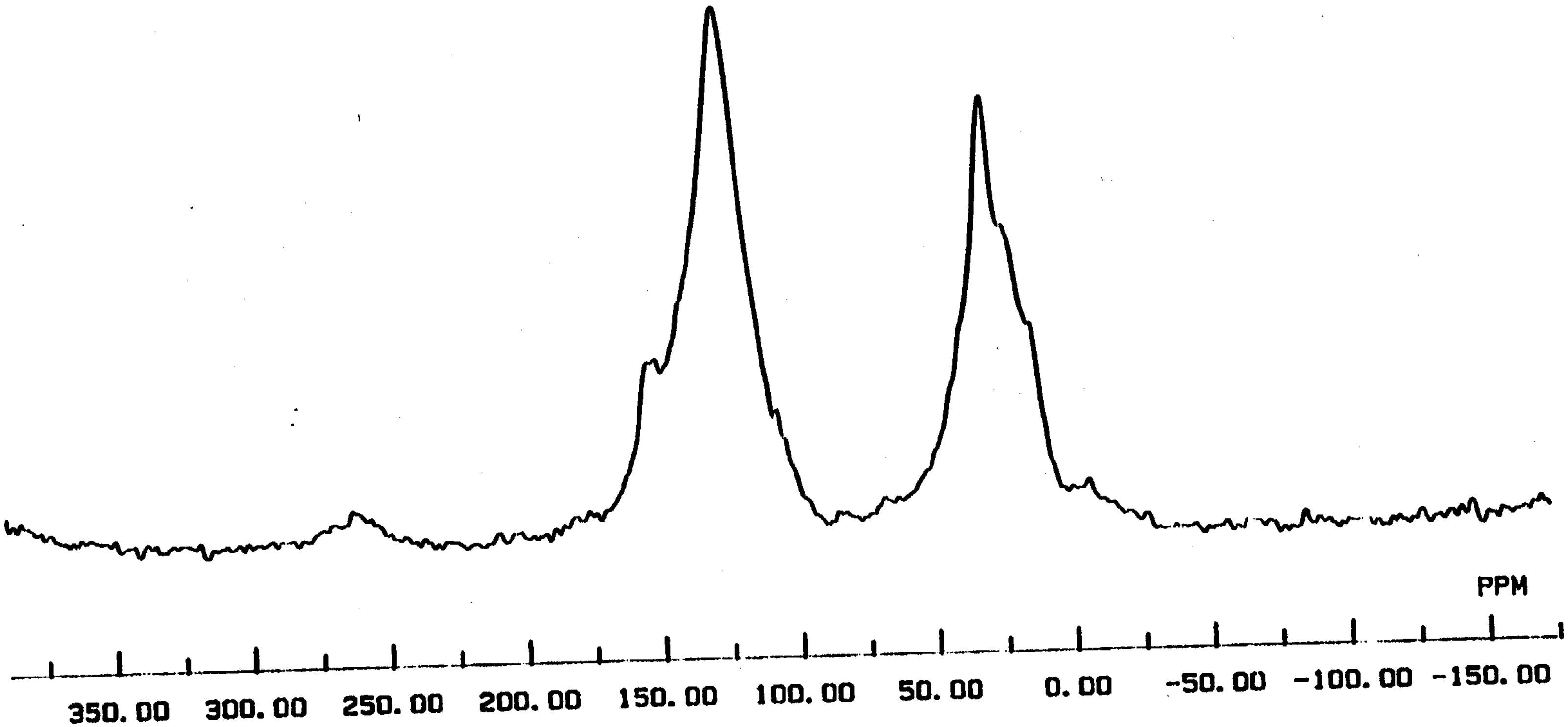
DECS-11 Coal & Residues of ATTM-Tetralin




DECS-11 Coal & Residues of ATTM-1-MN
Arbitrary Units
250
200
150
100
50
0
-400
-300
-200
-100
0
100
200
PPM
450
400
350
coal



CPMAS ^{13}C NMR spectrum of asphaltene produced in liquefaction of the DECS-1 coal at 400°C with ATTM and tetralin

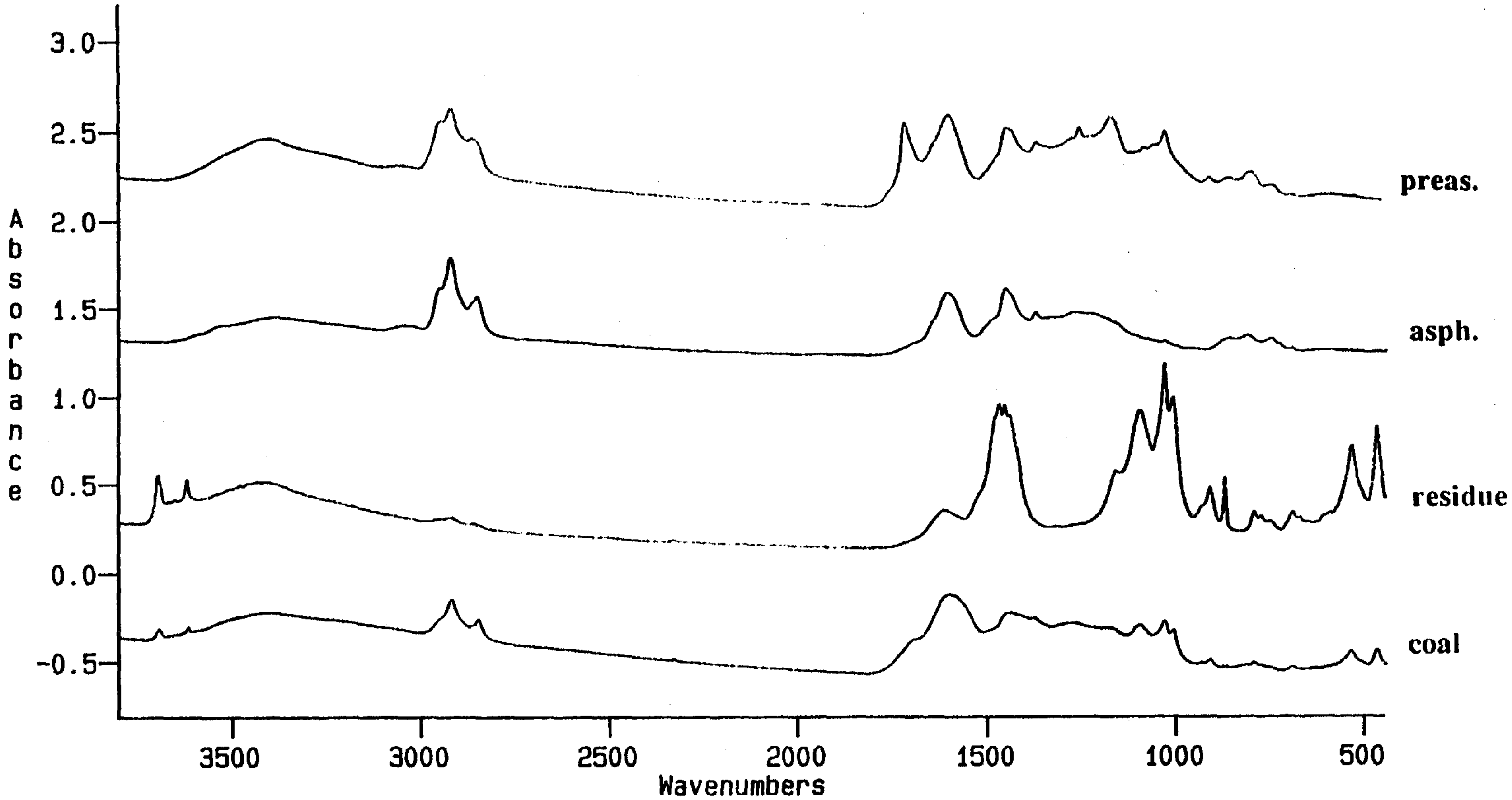


CPMAS ^{13}C NMR spectrum of preasphaltene produced in liquefaction of the DECS-1 coal

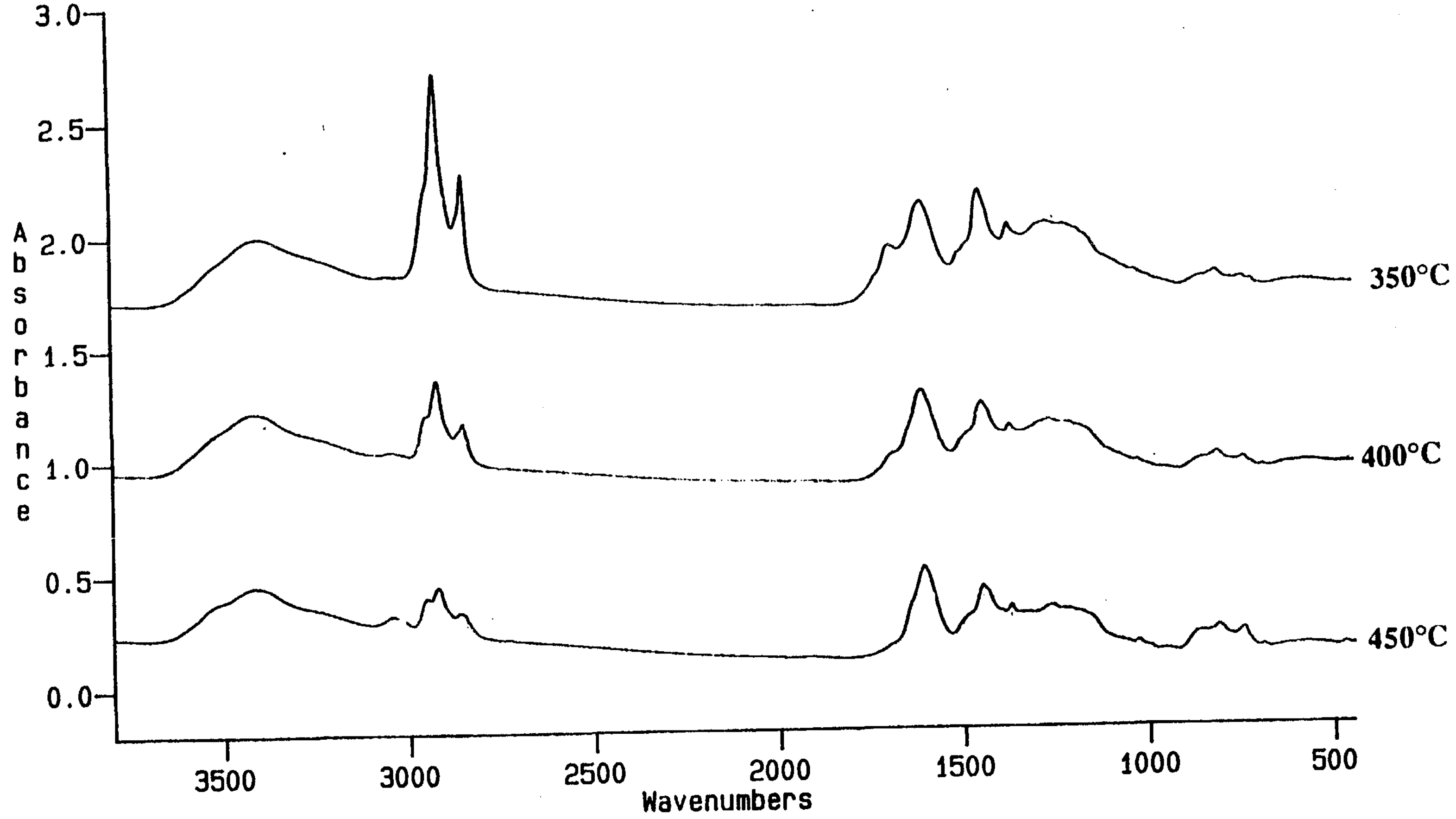
at 400°C with ATTM and tetralin

APPENDIX C

FTIR SPECTRA OF THE THREE COALS AND THEIR LIQUEFACTION PRODUCTS

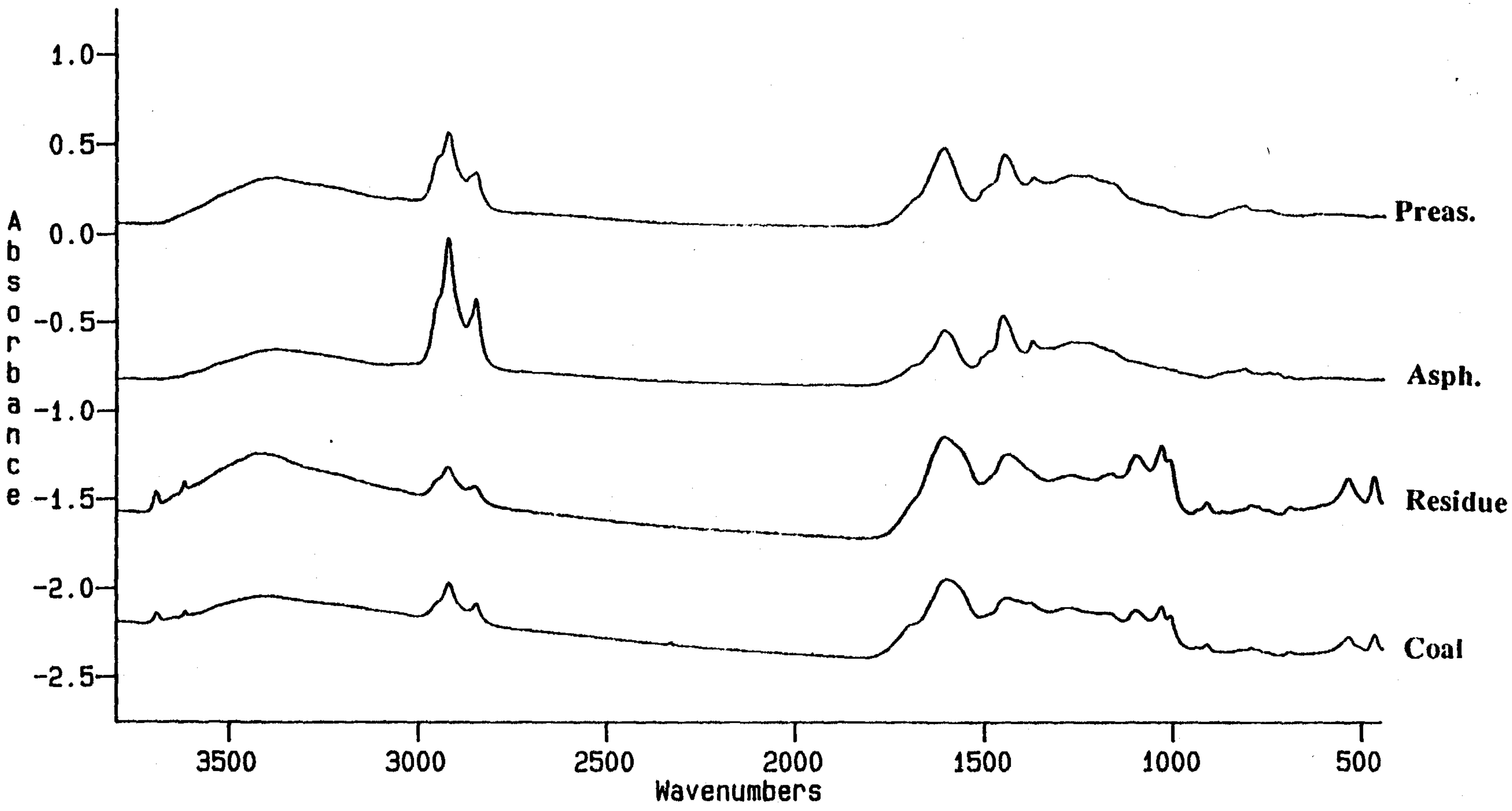


FTIR spectrum of the preasphaltene, asphaltene and residue produced in liquefaction of the DECS-1 coal at 400°C with ATTM but no solvent.

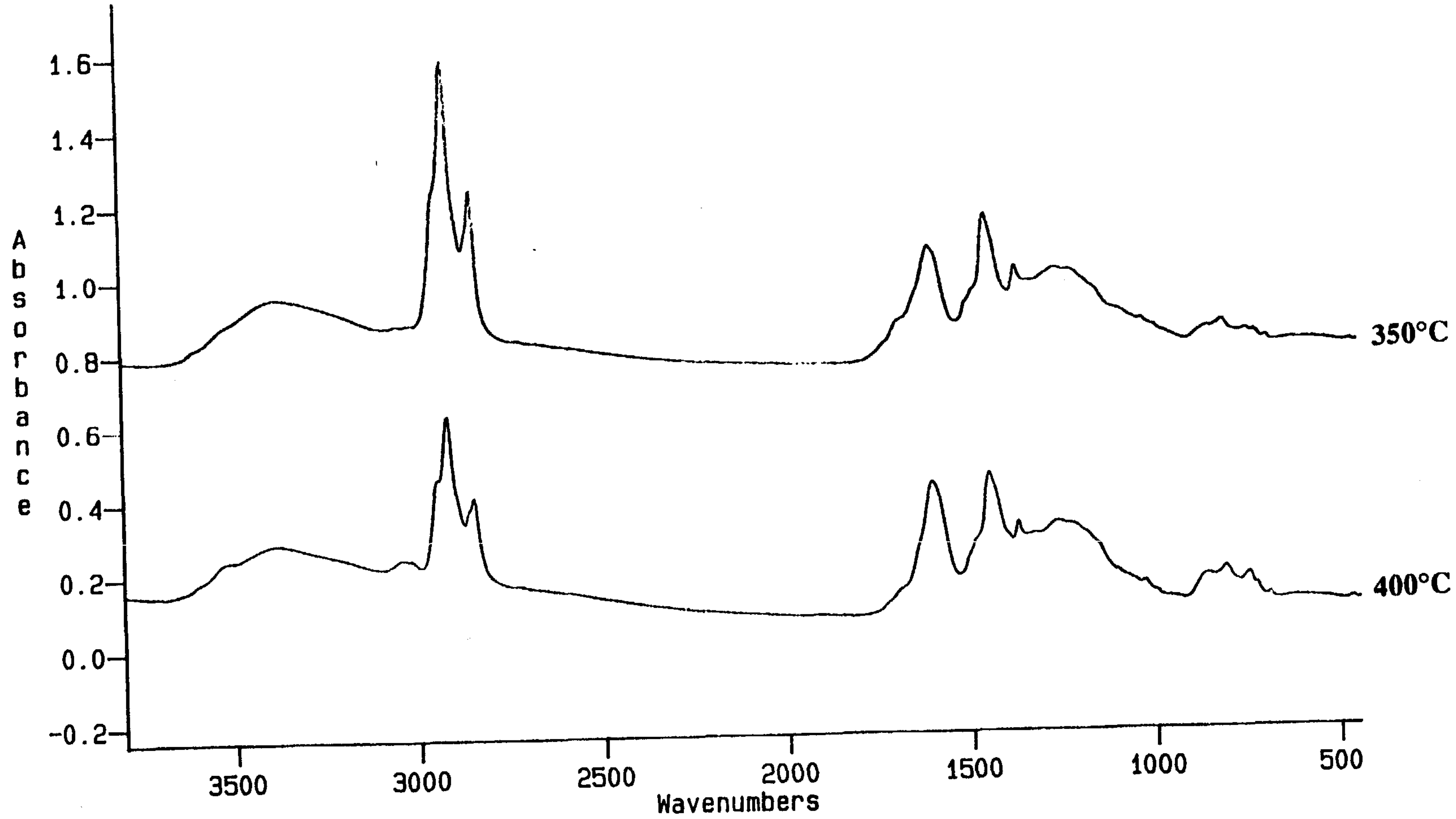


FTIR spectrum of the asphaltene produced in liquefaction of the DECS-1 coal with tetralin

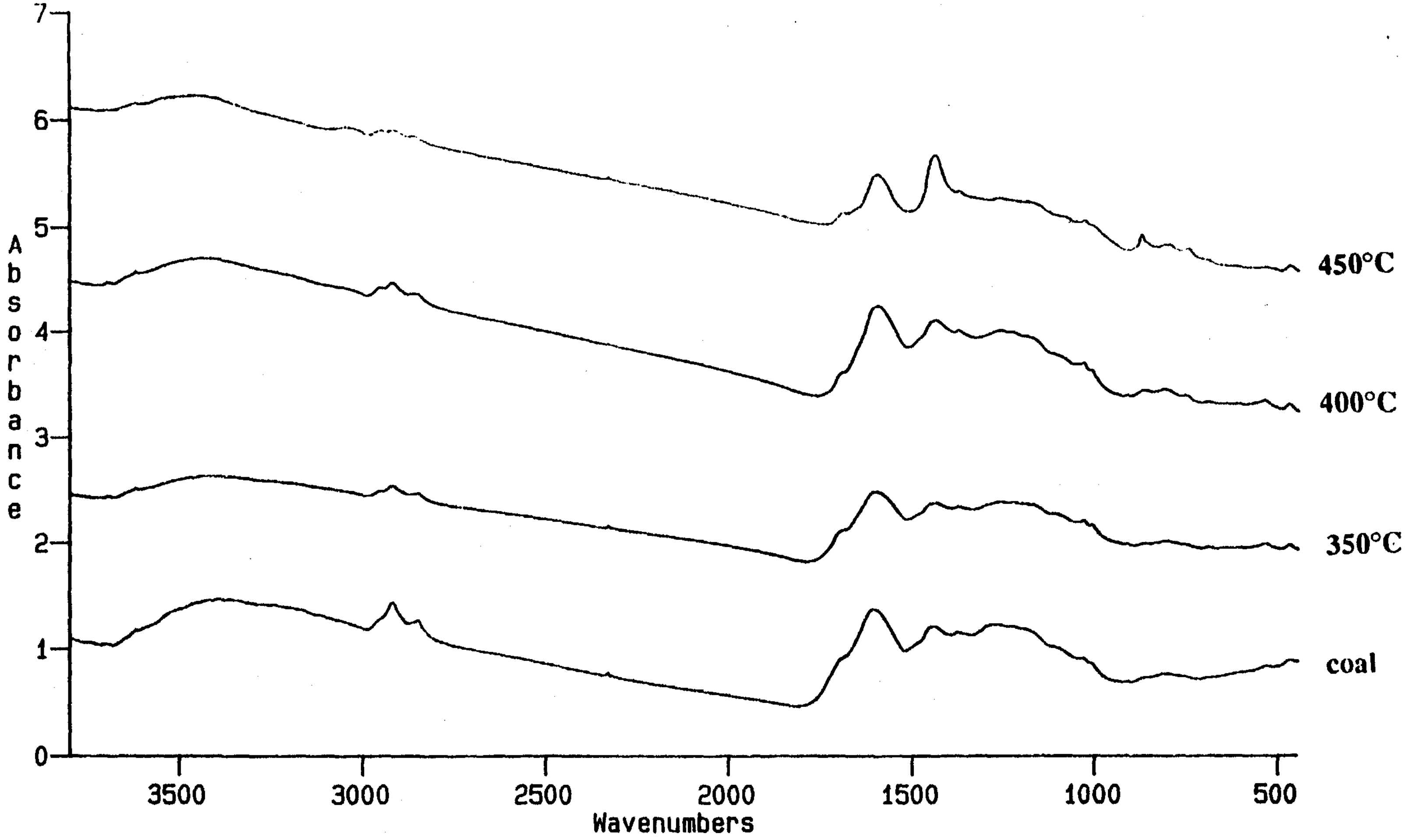
but no catalyst



FTIR spectra of preasphaltene, asphaltene and residue produced in liquefaction of the DECS-1 coal at 350°C with ATTM but no solvent

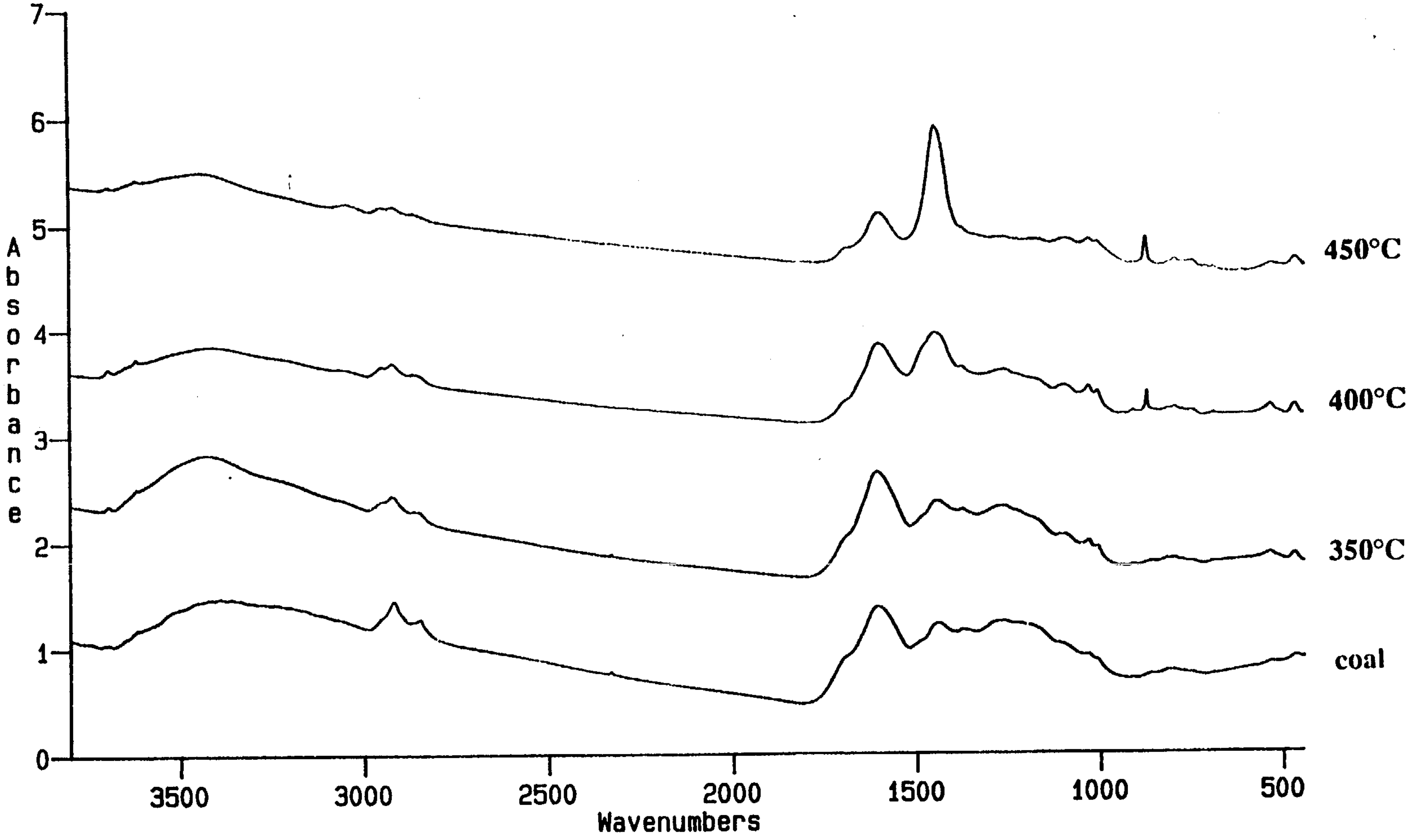


FTIR spectra of asphaltenes produced in liquefaction of the DECS-1 coal with ATTM but no solvent



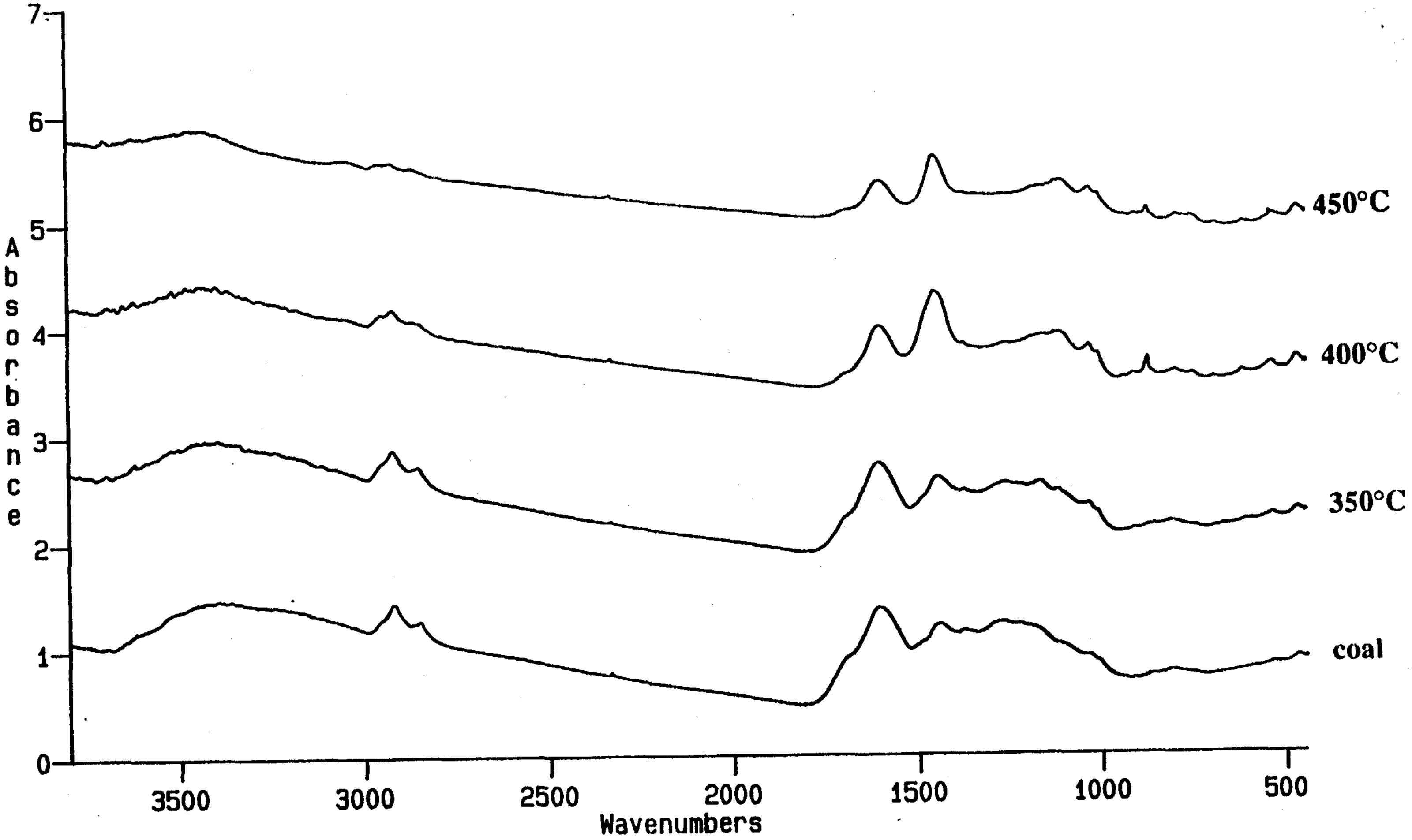
FTIR spectra of the DECS-9 coal and its residues from reactions

with no catalyst or solvent



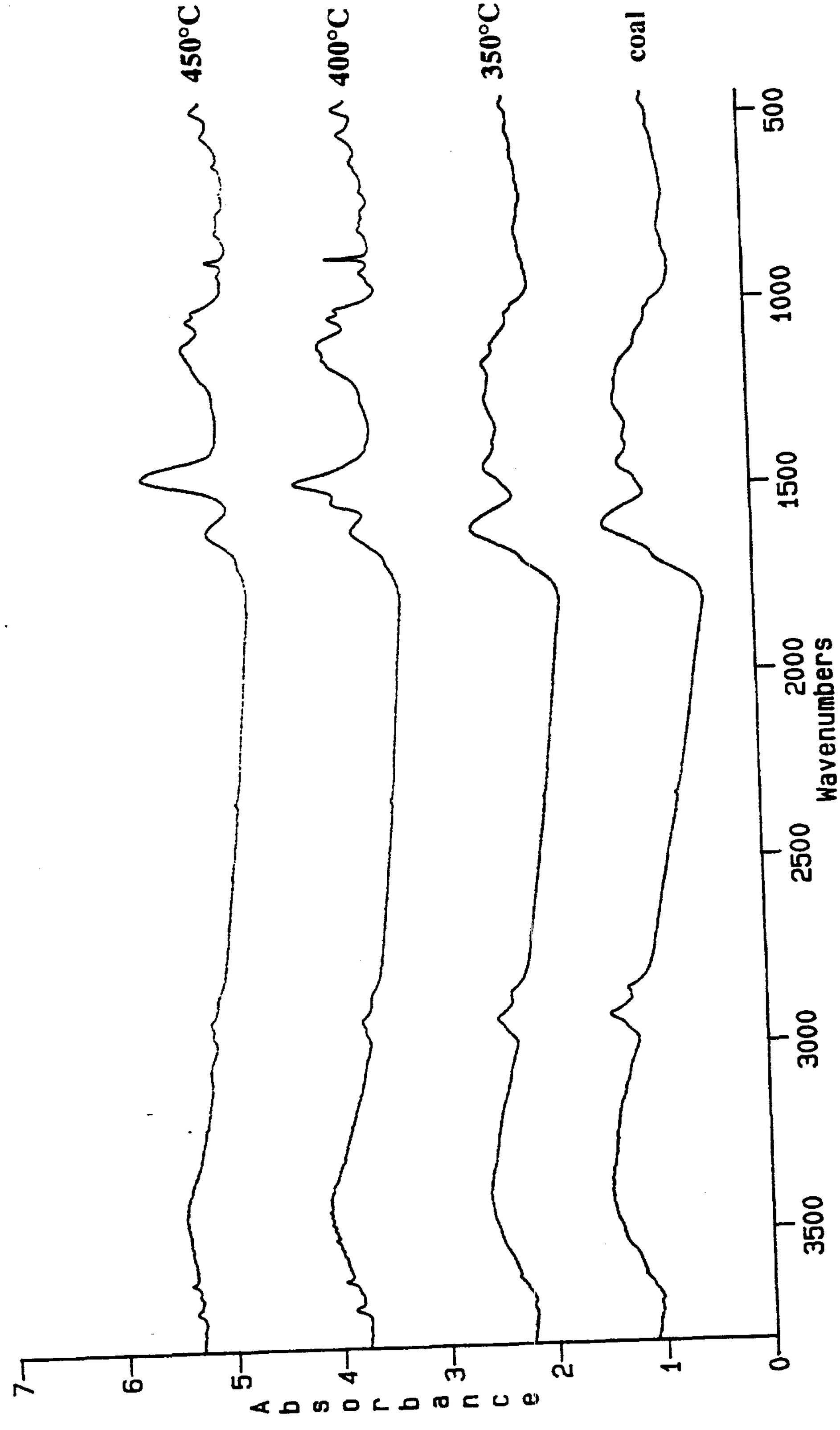
FTIR spectra of the DECS-9 coal and its residues from reactions

with tetralin but no catalyst



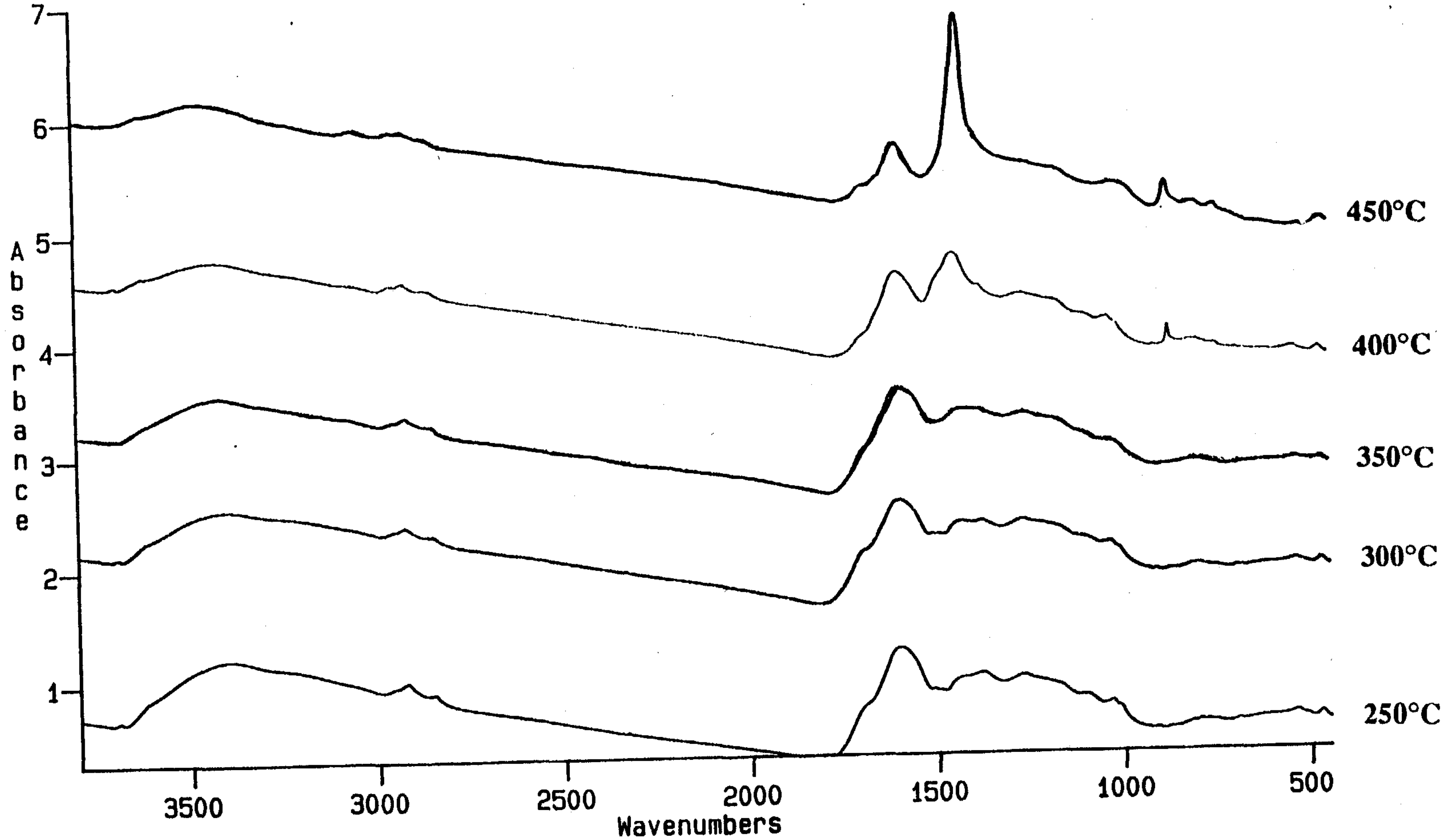
FTIR spectra of the DECS-9 coal and its residues from reactions

with catalyst but no solvent

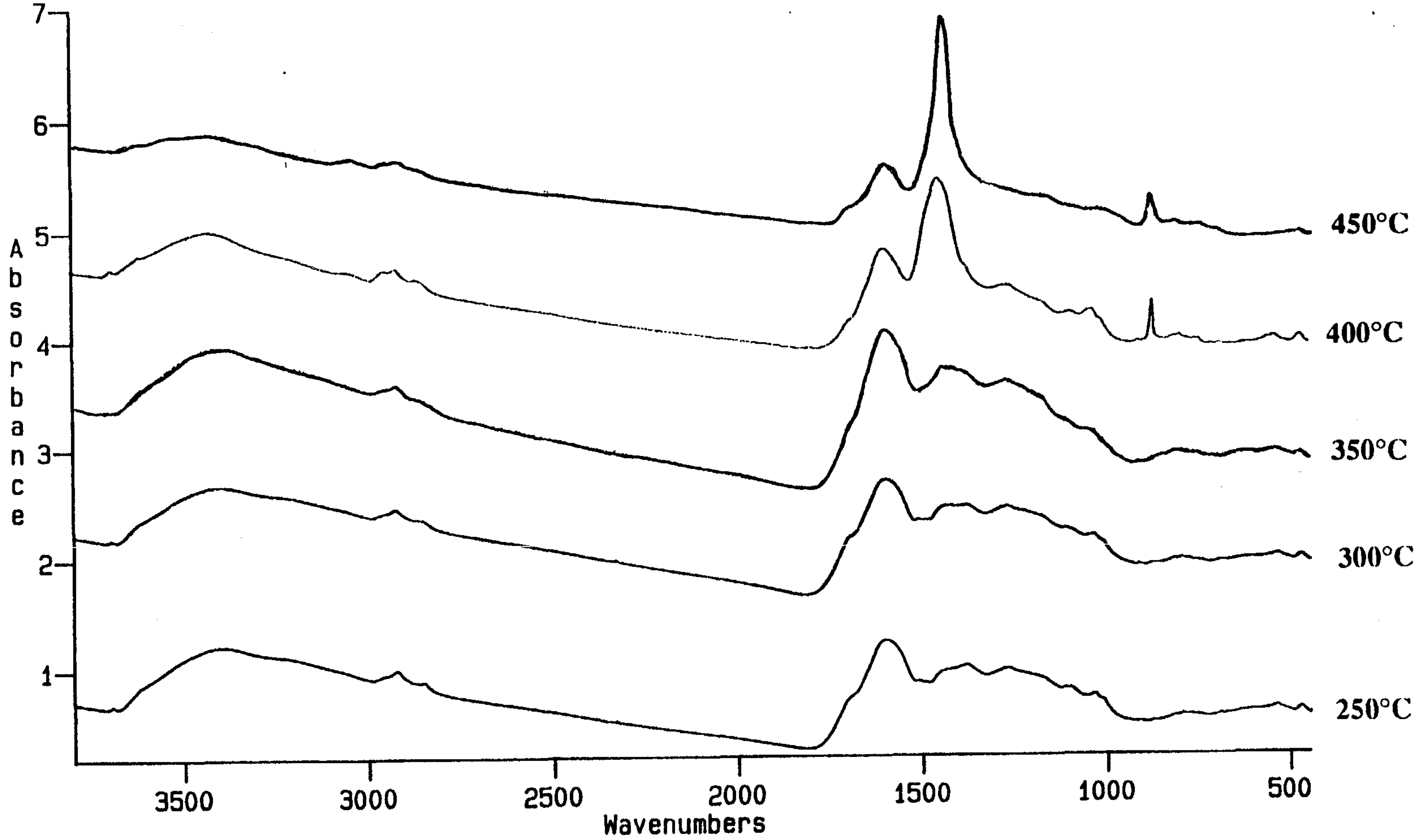


FTIR spectra of the DECS-9 coal and its residues from reactions

with ATTM and tetralin

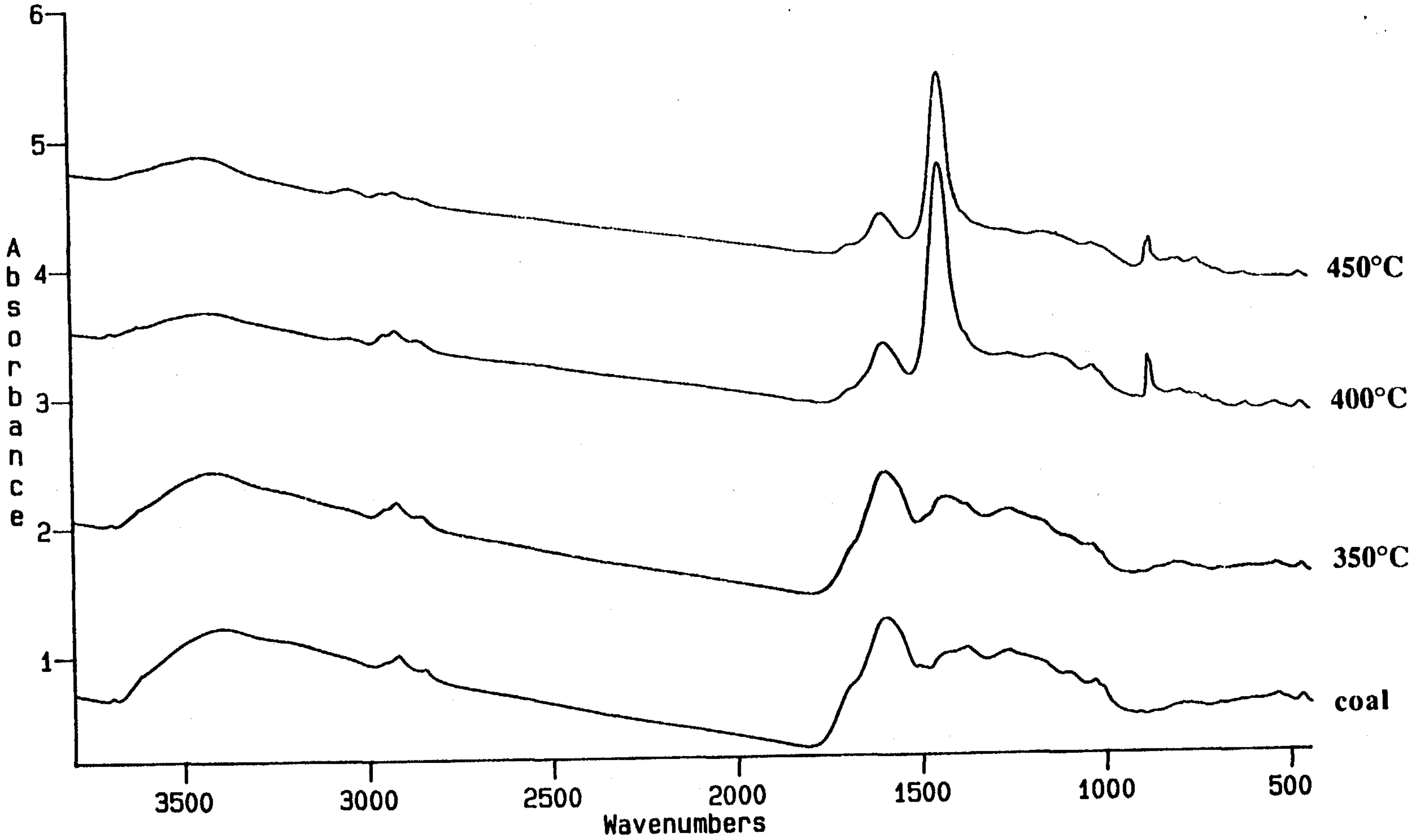


FTIR spectra of the DECS-11 coal and its residues from reactions with no catalyst or solvent

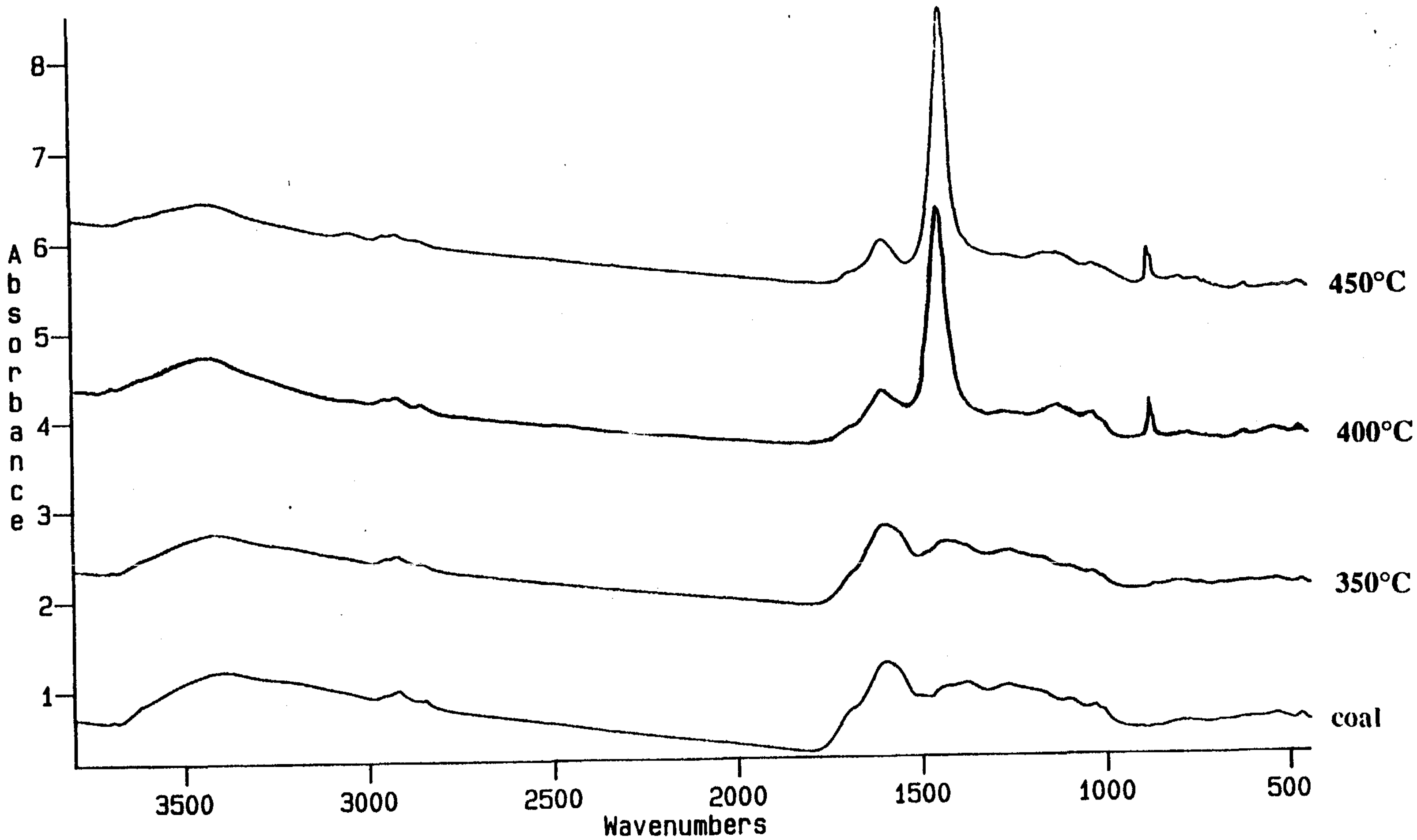


FTIR spectra of the DECS-11 coal and its residues from reactions

with tetralin but no catalyst

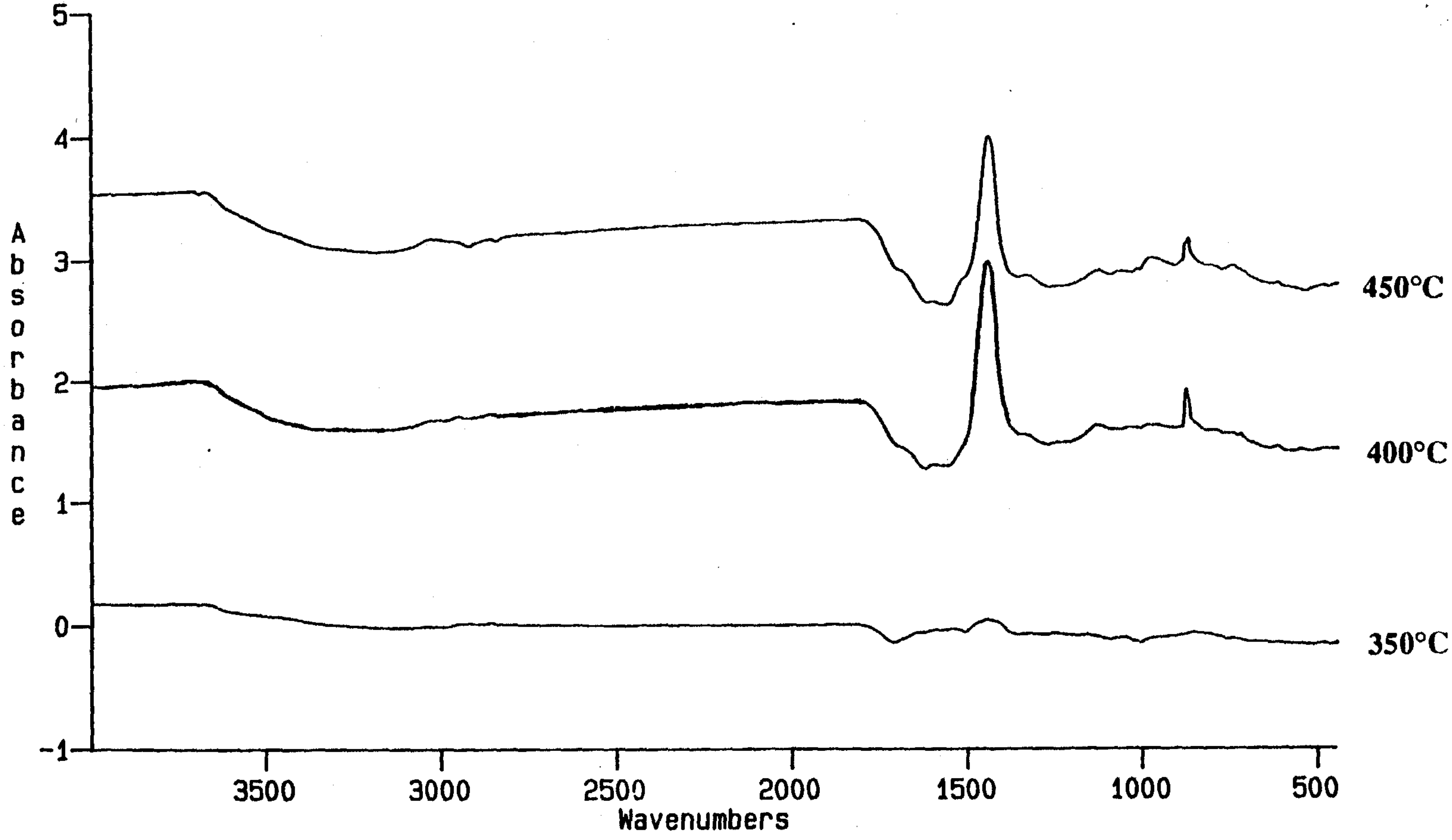


FTIR spectra of the DECS-11 coal and its residues from reactions with ATTM but no solvent



FTIR spectra of the DECS-11 coal and its residues from reactions

with ATTM and tetralin



Difference spectra of the residues from reactions with ATTM but no solvent

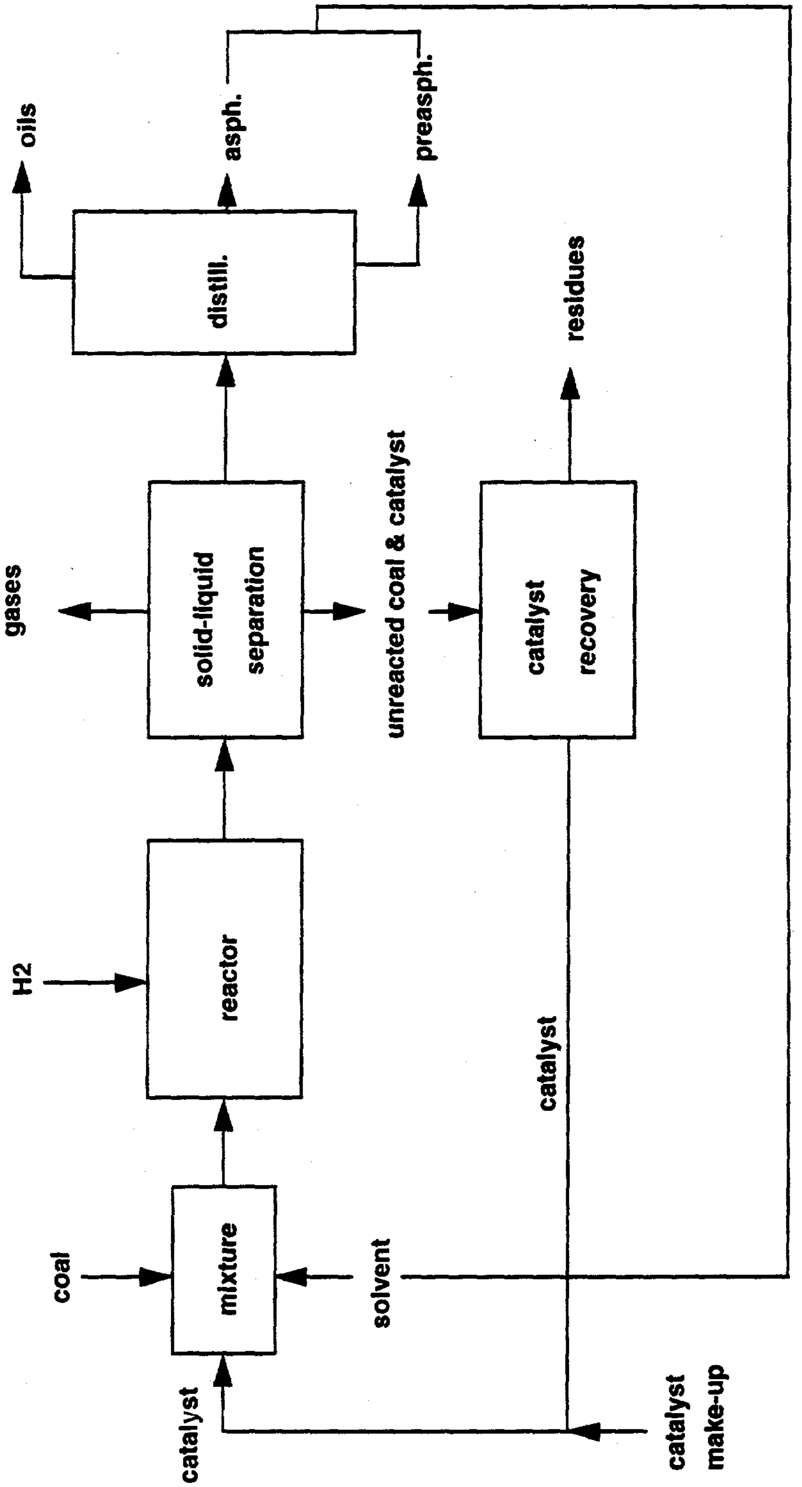
APPENDIX D

SUMMARY OF ABBREVIATIONS OFTEN USED IN THE TEXT

Al	Aliphatic
Ar	Aromatic
ar	As Received
Asph.	Asphaltene
ATTM	Ammonium Tetrathiomolybdate
C	Catalytic, or with a catalyst
CMN	Catalytic with 1-MN
CNS	Catalytic with no solvent
Conv.	Conversion
CTE	Catalytic with tetralin
DE or Deca.	Decalin
IW	Incipient Wetness
MN	1-Methylnaphthalene
NC	Non-Catalytic
NCMN	Non-Catalytic, with 1-MN
NCNS	Non-Catalytic, with no solvent
NCTE	Non-Catalytic, with tetralin
No Sol, or NS	with no Solvent
Preasph.	Preasphaltene
SL	Slurrying
SSL	Single-Staged Liquefaction
SW	Swelling
TE or Tetr.	Tetralin
TPL	Temperature-Programmed Liquefaction
TSL	Temperature-Staged Liquefaction
WIMD	Wilsonville Middle Distillate

APPENDIX E

A FLOW DIAGRAM OF LIQUEFACTION AND A SAMPLE CALCULATION OF OIL PRODUCTION


coal
catalyst
mixture
solvent
catalyst make-up
H2
reactor
solid-liquid separation
gases
unreacted coal & catalyst
catalyst recovery
catalyst
residues
distill.
oils
asph.
preasph.

The following is the calculation of the oil produced from the DECS-1 coal at 400°C, assuming that 1 ton of the coal is fed in the reactor.

The study in this thesis project showed that the catalytic effect is stronger than those of the solvent and temperature-condition at 400°C. The oil yield is 59% under this reaction condition (pp218).

Weight of the oil = 1 ton x 59% = 0.59 ton

assuming that the density of the oil is 0.8 g/cm^3 (or 0.8 kg/liter):

Volume of oil = 0.59 ton x 1000 kg/ton x 1 liter/0.8 kg

x 1 gallon/4.546 liter x 1 barrel/42 gallon

= 4 barrel

APPENDIX F

UNCERTAINTY AND REPRODUCIBILITY

A Sample of the Calculation of Total Uncertainty

(Expt. # 328)

Sample	Weight (g)	Absolute Error	Relative Error
Coal	4.023	0.001	2.49E-04
Thimble	22.342	0.001	4.48E-05
Thimble + Residue	23.284	0.001	4.28E-05

Residue = (thimble + residue) - thimble = 0.942

Absolute uncertainty of residue = 0.001 + 0.001 = 0.002

Total THF-solubles = coal - residue = 3.081

Absolute uncertainty of total THF-solubles = 0.002 + 0.001 = 0.003

Relative uncertainty of total THF-solubles $= \frac{0.003}{3.081} = 9.74 \times E^{-4}$

$$\text{Conversion} = \frac{\text{Total THF-solubles}}{\text{dry and mineral matter-free coal}} = 0.955$$

<u>Relative uncertainty of conversion</u> = Relative uncertainty of total THF-solubles +

Relative uncertainty of coal

$= 9.74 \times E^{-4} + 2.49 \times E^{-4}$

$= 1.22 \times E^{-4}$

A Sample Calculation of Reproducibility

(Pooled Standard Derivation)

Example #	Expt. #	Conversion (%)	Mean	S *	$\Sigma(Xi-X)^2$
1	328	95.5			
	347	92.0	93.8	2.5	6.13
2	313	49.6			
	314	52.9	51.3	2.3	5.44
3	315	57.5			
	316	54.7	56.1	2.0	3.92
4	105	90.5			
	110	91.3	90.9	0.6	0.32
5	106	85.9			
	111	82.9	84.4	2.1	4.50
6	101	54.3			
	113	52.2	53.3	1.5	2.20
7	222	94.2			
	225	97.2	95.7	2.1	4.50
8	223	83.2			
	226	84.0	83.6	0.6	0.32
9	224	91.8			
	225	90.0	90.9	1.3	1.62
10	230	75.2			
	233	76.3	75.8	0.8	0.60
				Total:	29.56

$$\text{Pooled S} = \left(\frac{29.56}{20-10}\right)^{2} = 1.7$$

* S: standard derivation