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Effects of Low-Temperature Catalytic Pretreatments on Coal Structure and Reactivity in Liquefaction

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DISCLAIMER

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ABSTRACT

In this quarter, progress has been made in the following two aspects: 1) spectroscopic and chemical reaction studies on the effects of drying and mild oxidation of a Wyodak subbituminous coal on its structure and pretreatment/liquefaction at 350°C; and 2) effects of dispersed catalyst and solvent on conversion and structural changes of a North Dakota lignite.

Drying and oxidation of Wyodak subbituminous coal at 100-150°C have been shown to have significant effects on its structure and on its catalytic and non-catalytic low-severity liquefaction at 350 °C for 30 min under 6.9 MPa H_2. Spectroscopic analyses using solid-state ^{13}C NMR, Pyrolysis-GC-MS, and FT-IR revealed that oxidative drying at 100-150°C causes the transformation of phenolics and catechol into other related structures (presumably via condensation) and high-severity air drying at 150°C for 20 h leads to disappearance of catechol-like structure. Increasing air drying time or temperature increases oxidation to form more oxygen functional groups at the expense of aliphatic carbons. For non-catalytic liquefaction at 350°C, raw coal gave higher conversion and oil yield than the dried coals, regardless of the solvent. Compared to the vacuum-dried coal, the coal dried in air at 100 °C gave a better conversion in the presence of either a hydrogen-donor tetralin or a non-donor 1-methylnaphthalene (1-MN) solvent. Catalytic runs were performed using impregnated ammonium tetrathiomolybdate (ATTM) precursor. In the presence of either tetralin or 1-MN, however, the runs using ATTM impregnated on air-dried coal (dried at 100°C for 2h) afford better conversions and oil yields than using vacuum-dried coal. Upon drying in air at 150 °C for 20 h, the conversion of air-dried coal decreased to a value significantly lower than that of the vacuum-dried coal both in the thermal and catalytic runs at 350°C. Such a clearly negative impact of severe oxidation is considered to arise from significantly increased oxygen functionality which enhances the cross-link formation in the early stage of coal liquefaction. Physical, chemical, and surface physicochemical aspects of drying and oxidation and the role of water are also discussed.

A North Dakota lignite (DECS-1) coal was studied in this quarter for its behaviors in non-catalytic and catalytic liquefaction. Reactions were carried out at temperatures between 250°C and 450°C. Regardless the reaction solvents and the catalyst being used, the optimum

temperature was found to be 400°C. The donor solvent has a significant effect over the conversion especially at temperatures higher than 350°C. The ATTM-derived catalyst can increase the conversions remarkably. When tetralin was applied as the reaction solvent, the catalyst enhances the conversion slightly indicating that the maximum value has been reached. At high temperatures, i.e. 450°C, the conversions of catalytic reactions dropped because of the dehydrogenation effect of this catalyst. Therefore the optimum temperature for the catalyst is 400°C. In the future research, the products, such as the oil, asphaltene and preasphaltene, and the reaction residues will be studied to identify effects of the temperature, solvent and the catalyst in terms of product distribution and their structures.

PROJECT OBJECTIVES

This work is a fundamental study of catalytic pretreatments as a potential preconversion step to low-severity liquefaction. The ultimate goal of this work is to provide the basis for the design of an improved liquefaction process and to facilitate our understanding of those processes that occur when coals are initially dissolved. The main objectives of this project are to study the effects of low-temperature pretreatments on coal structure and their impacts on the subsequent liquefaction. The effects of pretreatment temperatures, catalyst type, coal rank 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 by using spectroscopic, thermochemical and chemical techniques; and to determine the reactivity of the catalytically and thermally treated coals for coal liquefaction. Combining the two lines of information will allow us to identify the pretreatment-induced desirable or undesirable basic changes in coal structure; to clarify the impacts of pretreatments on coal liquefaction; to identify the structures responsible for retrograde reactions; to evaluate the structural differences resulting from different catalytic actions in relation to the overall catalytic effects in liquefaction; and ultimately, to develop a structure-reactivity relationship for liquefaction associated with catalyst type, coal rank and solvent. Furthermore, this research will contribute greatly to the development of effective pretreatment procedures which will allow coals to be liquefied more efficiently than the current practice. Finally, much of the knowledge to be generated from this research is not only critical for developing advanced hydroliquefaction processes, but also very useful to development of coal/petroleum resid co-processing, pyrolysis and hydropyrolysis processes.

TECHNICAL PROGRESS

TASKS 4 AND 5: EFFECTS OF PRETREATMENT ON COAL STRUCTURE AND LIQUEFACTION

1. SPECTROSCOPIC AND CHEMICAL REACTION STUDIES ON THE EFFECTS OF DRYING AND OXIDATION OF WYODAK SUBBITUMINOUS COAL ON ITS THERMAL AND CATALYTIC LIQUEFACTION.

Introduction

Low-rank coals, including subbituminous coals and lignites, are characterized by low aromaticities, high oxygen functionalities, and high moisture contents.[1] Because many low-rank coals contain as high as 20-35 wt % of moisture, an extensive amount of fundamental research has been done to develop an understanding of the occurrence of moisture in low-rank coals and their drying behavior.[2-16] Moisture in the coal has been classified[16] into four major forms: 1) superficial free water, 2) capillary condensed water, 3) sorbed water associated with polar groups and cations, and 4) water released only by chemical decomposition of organic or inorganic matter. Wroblewski and Verkade[16] have shown that the differentiation of surface water from pore water is possible by using some reagents in combination with ^{31}P NMR technique. Several methods, including thermal drying under vacuum and in air, microwave drying, chemical drying, or drying under a stream of dry inert gases, have been used and their impacts on coal structure have been studied.[13-21] It has been well established that low-rank coal has a colloidal gel-like structure that can shrink and swell in response to moisture loss and gain.[2,18,19] Suuberg et al.[18] pointed out that water is retained tightly in coal in several forms; coal behaves like a swellable colloid in the presence of water. A drying process, with minimal effect on the reactivity of a coal, is the ultimate goal of several coal conversion studies.[14,19-22] The changes caused by drying could be physical, chemical, or both, depending upon the drying method applied. Vorres et al. studied[13,14] the drying kinetics of Beulah-Zap lignite in detail. They have found that the lignite dehydration follows a unimolecular rate law which is first order in the water in the sample; there are two segments in the dehydration kinetics: the first includes about 80-85% of the water loss and the second covers most of the remaining water. Recently, Vorres[15] also reported that the behavior of a Wyodak subbituminous coal on drying is very similar to that of the Beulah-Zap lignite; there is a transition after about 80 % of moisture loss to a slower unimolecular process.

For thermal liquefaction (i.e., reaction without added catalyst), several groups have examined the effects of drying or oxidation on coal conversion.[14,17,19-22] Some experiences have shown that drying of coal has negative impact on its conversion reactivity,[19-22] while there is also evidence to the contrary in non-catalytic liquefaction.[14] It has been indicated that drying can cause an irreversible change in the pore structure such as collapse of pores,[13] which could limit accessibility of the reacting components during liquefaction and thus limit the rate of reaction. Oxidative drying of coal has been reported to have very detrimental effect on the coal conversion.[19-22] Atherton[20] pointed out that commercial coal-drying techniques (i.e., thermal) make low-rank coals prone to self-heating and cause a decline in reactivity for subsequent conversion. Neavel[21] reported a significant reduction in the conversion (at 400°C) of a hvC bituminous coal into benzene-soluble products as a result of oxidation. Cronauer et al.[22] found that partial drying of subbituminous coal in a mixture of nitrogen and oxygen or even in nitrogen alone reduced the conversion (at 450°C for 4-30 min) as compared to that of the raw coal. Serio et al.[17] observed that drying has a negative impact on the liquefaction (at 400°C for 30 min) of a lignite and a subbituminous coal but has little impact on the run of a bituminous coal. On the other hand, Vorres et al.[14] recently reported that the oil yield in liquefaction (at 400°C for 4 h) of a lignite sample was highest for the dried sample, lowest for the partially dried and intermediate for the starting material.

For liquefaction of coal with dispersed catalysts, there is little published information about the effects of predrying and mild oxidation. We recognize that, when one considers the overall economics of a coal conversion complex, there may be reasons, other than conversion achieved in liquefaction reactors, to consider drying the coal. Examples of such reasons might be the reduction of coal transportation costs, improvement of process thermal efficiency, lowering of the pressure in the reactors by eliminating the contribution from the partial pressure of water vapor, or reducing the amount of waste water generated. In addition to deliberate drying of the coal carried out as part of a process, some inadvertent drying may occur during storage or transportation. For example, drying and oxidation may occur simultaneously during natural weathering and during transportation. Therefore, it is important to study the effects of predrying and oxidation on catalytic liquefaction process. Fundamental understanding from such studies would provide answer to the question as to how should coals be handled or prepared for a given catalytic liquefaction process.

In the present study we examined the effects of drying of Wyodak subbituminous coal in vacuum (non-oxidative drying) and in air (mild oxidation) on its structure, and thermal (non-catalytic) and catalytic liquefaction. In order to follow the changes in chemical structure and moisture removal caused by drying and oxidation, we used several modern instrumental techniques to characterize the dried coals as well as the raw coal. To monitor the reactivity changes, we used low-severity liquefaction conditions such as 350 °C for 30 min. To detect the difference in physical changes (affecting diffusion) induced by drying under different conditions, we performed the reactions both in the absence of any solvent and in the presence of either a hydrogen donor tetralin or a non-donor 1-methylnaphthalene (1-MN) solvent.

This report will describe the effects of drying and oxidation of Wyodak coal on 1) its chemical structural features, 2) products distribution in non-catalytic liquefaction, 3) catalytic liquefaction using in-situ generated dispersed molybdenum sulfide, and 4) structural characteristics of the liquefaction residues. Also presented in this report are the physical, chemical, and surface physicochemical considerations of drying and oxidation effects and the role of original moisture.

Experimental

Materials. The coal used was Wyodak subbituminous coal, which is one of the U.S. Department of Energy Coal Samples (DECS-8) in the DOE/Penn State Coal Sample Bank and Data Base. It was collected in June 1990, ground to ≤ 60 mesh (sieve opening: ≤ 250 µm), and stored under argon atmosphere in heat-sealed, argon-filled laminated foil bags consisting of three layers. This coal contains 32.4 % volatile matter, 29.3% fixed carbon, 9.9 % ash and 28.4 % moisture, on as-received basis; 75.8% C, 5.2% H, 1.0% N, 0.5% S and 17.5% O, on dmmf basis. Tetralin and 1-methylnaphthalene (1-MN) were used as hydrogen donor and non-donor reaction solvents, respectively. The solvents were obtained from Aldrich Chemical Company with 98 %+ purity and were used without any further treatment.

Drying Treatment. Both air drying (AD) and vacuum drying (VD) were conducted, in order to distinguish drying from oxidation. The non-oxidative drying was performed by placing a flask containing about 20 g of the coal into an oven which was then evacuated at room temperature (to minimize any possible oxidation due to the presence of air) and gradually heated up within one hour to 100 °C followed an isothermal holding for 2 h and subsequent cooling down in the vacuum oven. The air drying was done by placing a beaker containing about 20 g of the coal into a preheated oven maintained at 100 °C for 2-100 h or at 150 °C for 20 h, with the door partially open to the atmosphere. The temperatures of coal particles during vacuum drying and air drying were measured and found to be similar to each other (within the experimental error range, ±3°C). Fresh as-received coal, with minimum possible exposure to air, was used as the raw coal.

Catalyst Loading. Reagent grade ammonium tetrathiomolybdate (ATTM, from Aldrich Chemical Company with 99.97 % purity) was used as the precursor for the dispersed molybdenum sulfide catalyst. ATTM [$(NH_4)_2MoS_4$] was dispersed onto the raw coal or dried coal samples by incipient wetness impregnation method from the aqueous solution. The same impregnation method was used in previous studies in this laboratory, but with different solvents.[23] The metal loading was kept at 1 wt % Mo on dmmf coal. Unless otherwise mentioned, the ATTM-impregnated coal was dried in a vacuum oven at 100 °C for 2 h before liquefaction.

Liquefaction and Product Work-up. The liquefaction experiments were carried out in 25 mL microautoclaves with 4 grams of coal at 350 °C for 30 minutes (plus 3 minutes for the reactor heat-up time to attain the reaction temperature). When a solvent was used, the ratio of solvent to coal was 1 to 1 by weight. The reactor was purged with H_2 at least three times, and finally pressurized with 6.9 MPa (cold) H_2. A fluidized sandbath was used as heater. After the reaction, the reactor was brought down to temperature below 200 °C by quickly immersing it in cold water and then letting it cool to room temperature in air. The total volume of the gaseous product was measured by the water displacement method and was collected for further analysis. The liquid and solid products were separated by sequential Soxhlet extraction with hexane to obtain oil; with toluene to obtain asphaltene; and with tetrahydrofuran (THF) to obtain preasphaltene.[24] Asphaltene and preasphaltene are solid at room temperature. They were dried at 100 °C for 6 h prior to weighing. Moisture content in the dried products is negligible. The THF-insoluble residues obtained after extraction were washed first with acetone and then with pentane in order to remove all the THF, followed by drying at 110 °C for 6 h under vacuum. The conversion of the coal into soluble products and gases was calculated on the basis of THF-insoluble residues. The water produced from liquefaction reactions would be included in the oil yield, which was determined by difference, as described elsewhere.[25] More experimental details may be found elsewhere.[24,25] All the liquefaction experiments were at least duplicated in order to obtain reliable data. The deviation in conversions and products yields are generally within ± 3 wt%.

The gas analysis was performed using a Perkin Elmer Auto-System gas chromatograph. The yields of CO and CO_2 were determined using a Carboxen-1000, 60/80 mesh column (1.7 mm x 4.5 m) with a thermal conductivity detector. C_1-C_4 hydrocarbon gases were determined using Chemipack C18 column (3.2 mm x 1.8 m) with flame ionization detector. Helium was used as a carrier gas for all the gas analysis. Hydrogen consumption from the gas-phase H_2 was calculated from the difference between the amount of hydrogen initially charged to the reactor and that found after reaction. The amount of H_2 gas left was determined by subtracting the volume of gaseous products [determined by GC using calibrated response factors (CO, CO_2, and hydrocarbon gases)] from the total volume. The dominant component of gases is CO_2, and the experimental errors for CO_2 yields are usually within ± 0.5 wt% on a dmmf basis. Tetralin and naphthalene present in the spent solvent (mixed with the hexane-soluble fraction) were analyzed using a Hewlett Packard gas chromatograph equipped with Rtx-50 capillary column (0.25 mm i.d. x 30m). The net hydrogen consumption (transfer) from tetralin was calculated from the naphthalene to tetralin ratio after reaction.[24] The experimental errors are usually within ± 0.2 wt% (on a dmmf basis) for net hydrogen consumption from tetralin, and within ± 0.3 wt% for gas-phase H_2 consumption. Most results reported here are average of two or three runs.

Spectroscopic and Thermal Analyses. Thermogravimetric analysis (TGA) of the raw and dried coals and residues was conducted on Mettler TG50MT Analyzer. In a typical run, about 10 mg dried coal was loaded into alumina pan cell, and the furnace temperature was raised at 5 °C/min to 105°C followed by holding at 105°C under N_2 flow (200 mL/min).

Pyrolysis-gas chromatograph-mass spectrometric (Py-GC-MS) analysis of the samples was carried out using Du Pont 490B GC-MS system with DB-17 capillary column coated with phenylmethylpolysiloxane stationary phase. The instrument was interfaced to a Chemical Data Systems Pyroprobe-1000 pyrolyzer. In a typical run, about 0.5-1.0 mg of a sample was loaded into a thin quartz tube, which was then inserted into the horizontal filament coil in the pyroprobe. The pyroprobe was then inserted into an injection port interfaced with the capillary column. The samples were flash (with a heating rate of 5000 °C/s) pyrolyzed at 610 °C for 10 s and the pyrolyzates were cryotrapped at the injection-port end of the column with liquid nitrogen. The GC oven temperature was programmed from 30 °C to 280 °C at a heating rate of 4 °C/min. The data acquisition and processing were controlled by a computer-aided system.

Solid-state ^{13}C NMR spectra were recorded on a Chemagnetics M-100 NMR spectrometer using the cross-polarization magic angle spining (CPMAS) technique. The measurements were carried out at a carbon frequency of 25.1 MHz. For all the samples, 20,000 to 30,000 scans were accumulated, with cross-polarization contact time 1 μs and a pulse delay time 1 s. More details about Py-GC-MS and CPMAS ^{13}C NMR may be found elsewhere.[26]

Fourier transform infrared (FT-IR) spectra of coal and liquefaction residues were recorded on a Digilab FTS-60 spectrometer by co-adding at least 200 scans at a resolution of 2 cm^{-1}. The samples were prepared as KBr pellets. The KBr was dried at 110 °C for over 10 h in a vacuum oven prior to sample preparation. An accurately weighed amount of the predried coal or residue sample (2±0.01 mg) was mixed with a pre-weighed amount of KBr (250-300±0.01 mg) in a Perkin-Elmer Wig-L-Bug Grinder-Mixer for 120 seconds. All the spectra were baseline corrected. The FT-IR difference spectra (I_d) were obtained by subtracting the reference spectra (I_r) from the sample spectra (Is) using equation 1. The subtraction factors (S_f) were determined using equation 2, assuming a constant pellet diameter.

$$I_d = I_s - S_f \times I_r \qquad 1)$$

$$S_f = \text{(dmmf organic matter of sample)/(dmmf organic matter of reference)} \qquad 2)$$

Results and Discussion

Characterization of Dried Samples. Figure 1 shows the TGA profiles for the air-dried and vacuum-dried coals, the ATTM-loaded and vacuum-dried coal as well as the raw DECS-8 coal. Because a slow heating rate (5 °C/min) and a nitrogen flow were used, most of the moisture loss (weight loss) occurred during heat up to 105°C in TGA cell, as can be seen from Figure 1. The amount of weight loss after 10 minutes holding at 105°C was taken as the moisture content. The moisture content value for the raw coal determined from TGA (29 wt%) is in good agreement with the value from the DECS sample bank (28.4 wt%). To get a reliable estimate of errors, we have performed duplicate TGA analyses, which give the following results in regard to moisture contents: 1-2 wt% for vacuum-dried samples; 2-3 wt% for air-dried samples; and 2-3 wt% for ATTM-impregnated and vacuum-dried samples. Relative to air drying, only slightly more water was removed by vacuum drying (Figure 1). Therefore, the moisture contents of all the dried samples are considered to be similar to each other.

Figure 2 presents the solid-state CPMAS ^{13}C NMR spectra of the coal samples predried under various conditions. In the spectrum of the raw coal, the region between 0 and 80 ppm consists of aliphatic carbons, which may include methoxy carbons, and the second region between 90 and 170 ppm is due to the aromatic carbons, including two shoulders due to catechol-like (at 142 ppm) and phenolic (at 152 ppm) carbons.[26] The carboxylic band appears between 170-190 ppm and carbonyl group between 190-230 ppm. Upon drying coal under vacuum, there is no apparent difference in the NMR spectrum as compared to that of the raw coal.

It appears that, as the coal is dried under oxidative conditions, there is a slight decrease in the intensity of the catechol shoulder, and after air drying at 150°C for 20 h, the catechol shoulder completely disappears from the NMR spectrum. The other changes include the broadening of the carboxyl and carbonyl bands. These changes become more apparent after air drying at 150 °C for 20 h, which are also accompanied by a significant decrease in relative intensity of the aliphatic band (Figure 2). On the other hand, any other structural changes that might occur under these conditions are too small to be detected by this NMR technique.

Figure 3 shows the FT-IR difference spectra of the dried coals obtained by subtracting the spectrum of vacuum-dried coal (100 °C for 2 h) from the spectra of the four air-dried coals. The difference spectra in Figure 3 are indicative of the structural changes caused by oxidation. Relative to the vacuum drying at 100°C for 2 h, the changes induced by air drying are the increased intensities in oxygen functional groups (bands in 1500-1800 and 3200-3600 cm^{-1}) and decrease in aliphatic groups (bands around 2920 and 2850 cm^{-1}). The positive band around 3200-3600 cm^{-1} may also includes -OH group in water. The bands around 1550, 1630 and 1700 cm^{-1} can be attributed to carboxylate ions ($Ar\text{-}COO^{-}M^{+}$), highly conjugated ketones (Ar-CO-Ar), and carboxylic acids (Ar-COOH) plus ketones, respectively.[27,28] The shoulder around 1770 cm^{-1} is due to esters. Figure 3 indicates that the extent of oxidation increased with increasing severity of air drying, as reflected by the progressive increase in carboxylic band (1700 cm^{-1}) and decrease in the aliphatic bands. As the air drying severity increased to 150°C for 20 h, the formation of etheric C-O becomes apparent, as shown by the small positive band in the 1100-1200 cm^{-1} region in Figure 3. It must be noted that this region is interfered by the peaks of minerals (1010, 1035, 1155 cm^{-1}).[29,30] Painter et al.[30] and Liotta et al.[31] also observed the formation of ethers from oxidation of bituminous coals from their FT-IR spectra.

Figure 4 presents the Py-GC-MS total ion chromatogram of the raw DECS-8 coal. In this chromatogram there are three major peaks due to phenolic compounds. Other peaks include those of alkylbenzenes, and paraffinic compounds ranging from C_4 to C_{30}, together with small amounts of two- to four-ring aromatic compounds. Also shown in Figure 2 are the area ratios of phenolics (phenol, C_1- to C_2-phenols, and catechols) to alkylbenzenes (C_1- to C_3-benzene) of the raw and predried coals, as determined from their Py-GC-MS analysis. This ratio decreased with increasing air drying time at 100°C, from 3.5 after 2 h to 2.3 after 100 h drying, and finally declined to 1.1 after air drying at 150 °C for 20 h. Interestingly, there is a marked catechol peak in the raw coal (Figure 4) and vacuum-dried coal, but this peak nearly disappears after air drying at 150°C, which is consistent with the CPMAS ^{13}C NMR data (Figure 2).

The information from the above instrumental analysis may be summarized as follows. Combination of FT-IR data (Figure 3) with NMR results (Figure 2) clearly indicates that the major changes in the coal structure due to oxidative drying are the increase in the carbonyl and carboxyl functionalities at the expense of the aliphatic groups in the coal. More of the increased oxygen functional groups would be expected to occur on the coal surface. Oxidation of aliphatic groups occurs preferrentially during air drying, presumably at the expense of alkyl side-chains attached to aromatic rings. Another interesting chemical effect revealed by NMR and Py-GC-MS is the disappearance of catechol after air drying at 150°C for 20 h. Furthermore, Py-GC-MS data in Figure 4 reveal that oxidative drying in air at 100-150°C tends to decrease the relative content of phenolic and catechol compounds in the pyrolyzates.

Effects of Drying and Oxidation on Non-catalytic Liquefaction. Table 1 presents the results for thermal liquefaction (i.e., without added catalyst). Predrying of Wyodak subbituminous DECS-8 coal, whether oxidative (air drying) or non-oxidative (vacuum drying), has a significant effect on the production of gases and liquid products at 350°C both in the absence and the presence of a solvent. Among the gaseous products, CO_2 and CO are the main constituents, and C_1 to C_4 hydrocarbon gases make up the remainder. The effect of drying on gas yields is manifested primarily by the changes in CO_2 yield and secondarily by CO yield. The yields of C_1-C_4 hydrocarbon gases in all the thermal runs were essentially constant; among the C_1-C_4 gases the yields of methane and ethane were always higher than the others.

Figure 5 shows the yields of CO and CO_2 from solvent-free liquefaction at 350°C versus predrying conditions. CO_2 yields increased remarkably when air drying severity increased from 100°C-20 h to 100°C-100 h or 150°C-20 h, which corresponds to the considerable increase in intensity of carboxylic band in FT-IR (Figure 3). It is considered that decarboxylation and decarbonylation produce CO_2 and CO, respectively. As can be seen from Table 1, both solvent-free and solvent-mediated runs of the vacuum-dried coal give lower gas yield compared to those of the raw coal and air-dried coal, due mainly to the lower CO_2 yield from the vacuum-dried coal. Figure 5 clearly indicates that increased oxidation of coal has a greater impact on CO_2 production, and a much lesser impact on CO formation. Probably decarboxylation can occur more readily at lower temperature compared to decarbonylation. The severity of drying at 100°C in air does not seem to have any marked effect on the yields of C_1-C_4 gases in thermal reactions at 350°C (Table 1).

With respect to the effects of drying on coal conversion, several trends are apparent from Table 1. First, using the fresh raw coal always affords the highest conversions and the highest oil yields, regardless of the solvents. Second, predrying the coal under either non-oxidative (vacuum drying) or oxidative (air drying) conditions decreased coal conversion and the yields of oil, asphaltene, and preasphaltene. Third, relative to vacuum drying, air drying at 100 °C for 2 h tends to afford higher coal conversions and oil yields, and this trend becomes more apparent when either a H-donor tetralin or a non-donor 1-MN solvent was used. However, the oil yield in thermal runs drops sharply when the time of predrying at 100 °C in air is increased from 20 to 100 h. Fourth, under the given drying conditions, the coal conversion generally increases in the order of solvent-free < 1-MN < tetralin. Relative to the non-donor 1-MN, the advantage of H-donor tetralin is more apparent for liquefying the coals that have been dried in air at 100 °C for 2-100 h. Finally, after drying in air under high-severity conditions such as 20 h at 150 °C, conversion of the dried coal decreased to less than 50% of that of the fresh raw coal on a dmmf basis. In this case, the advantage of using a H-donor solvent disappears, as there is no major difference in coal conversions and oil yields between runs with tetralin and 1-MN solvents. However, the runs of the highly oxidized coal using a solvent still gave better conversions (18.0-19.9 wt%) than the solvent-free run (10.9 wt%), as can be seen from Table 1.

Effects of Drying and Oxidation on Catalytic Liquefaction. Catalytic runs were conducted using in-situ generated molybdenum sulfide from ATTM impregnated onto raw coal or dried coal samples. ATTM is known to decompose at ≥ 275 °C to form MoS_3 which subsequently transforms to MoS_2; this transformation occurs readily under H_2 pressure.[31] Unlike the thermal reactions which also involve raw coal whose moisture (28.4 wt%) is present in the reaction system, the catalytic reactions discussed below involve only the ATTM-impregnated and dried samples (see curve C in Figure 1). The catalytic reaction at 350°C can be considered as low-severity liquefaction or catalytic pretreatment. Table 2 presents the data for catalytic runs at 350°C. For solvent-free catalytic runs, using fresh raw coal for impregnation of ATTM afforded significantly higher conversion and higher oil yield, which were also accompanied by higher H_2 consumption (see below), than using the vacuum-dried and air-dried coal. Loading ATTM onto the coals that were predried at 100 °C for 2 h under vacuum and in air gave similar results in the absence of a solvent. However, the coal conversion and oil yield decreased and CO_2 yield increased with further increase in the severity of air drying from 20 to 100 h at 100 °C and from 100 to 150 °C.

Figure 6 compares the yields of soluble products, excluding gases, between low-severity catalytic (top, with ATTM) and non-catalytic (bottom) liquefaction of dried coals at 350°C with tetralin solvent. For catalytic runs in the presence of either tetralin or 1-MN solvent, dispersing ATTM on air-dried coal leads to higher conversion and oil yield, especially in tetralin, than loading ATTM on vacuum-dried coal. These results indicate that, relative to the non-oxidative drying, predrying in air at 100°C has some beneficial effect when ATTM is used together with a solvent for runs at 350°C. This may be attributed to the mild oxidation-induced increase in surface functionality and hence increased hydrophilicity, which contributed to increasing catalyst dispersion in the impregnation process. In fact, with a given predrying time of 2 h at 100 °C, the use of air-dried coal in the catalytic runs with either tetralin or 1-MN solvent gave similar or slightly better conversion compared to the case of using the fresh raw coal (Table 2). This is in contrast with the trend observed in non-catalytic runs, where using dried coals always gives considerably lower conversion and oil yield at 350°C than using the raw coal (Figure 6, Table 1).

Similar to the thermal runs, the yields of gases in the catalytic runs also vary significantly due to predrying, which are mainly manifested by the changes of CO_2 yield (Table 2). CO_2 yield of catalytic runs increases with increasing severity of air drying. In the runs using ATTM loaded on the raw coal, water was not present during the reaction, but still a higher CO_2 yield was obtained compared to that with ATTM loaded on the vacuum-dried coal (Table 2). The presence of a solvent appears to slightly increase CO_2 yield in many cases in the catalytic runs, but has no marked effect on hydrocarbon gas make both in thermal and catalytic runs. In collateral work in this laboratory, it was shown that for a subbituminous coal sample, the gas yields are mainly a function of temperature but are independent of solvent.[32]

As can be seen by comparison of Table 1I with Table 1, there are some considerable differences in gas composition between thermal and catalytic runs. In general, the total gases yields in the thermal runs of the raw and the dried coal are always higher than those in the corresponding catalytic runs at 350°C. This is due mainly to the lower yields of CO_2 in all the catalytic runs than all the corresponding non-catalytic runs (Figure 5). This observation clearly indicates the occurrence of hydrogenation of the oxygen-functional groups in the presence of a dispersed Mo sulfide catalyst at 350 °C. On the other hand, the yields of hydrocarbon gases are always higher in the catalytic runs of the dried coal or the raw coal than in the thermal runs, suggesting that parts of the hydrocarbon gases from catalytic liquefaction resulted from catalytic hydrogenolysis of C-C bond or dealkylation of alkylaromatics. However, the extent of decrease in CO_2 yield due to the use of catalyst at 350 °C is higher than that of the increase in C_1-C_4 gas make.

Effects of Drying on Hydrogen Consumption. Figure 7 shows the effect of predrying of the coal on hydrogen consumption from gas-phase H_2 and on net hydrogen transfer from tetralin at 350°C. In the absence of an added catalyst, the runs of the raw coal gave somewhat higher consumptions of gas-phase H_2 than the runs of the coal that has been dried at 100 °C for 2-20 h under vacuum or in air, both in the absence and presence of a solvent (tetralin or 1-MN). This is consistent with the fact that the dried coals gave lower conversions and lower total yields of liquid products (Table 1).

Another general trend from the thermal runs is that H_2 consumption and the extent of hydrogen transfer from tetralin increased with increasing severity of oxidative drying from 100°C–20 h to 150°C–20 h. In fact, this parallels qualitatively with the increase in CO_2 formation (Table 1). The conversions and the yields of liquid products in the thermal runs of the highly oxidized coal (air dried at 150 °C for 20 h) are the lowest among all the thermal runs. Apparently, higher hydrogen consumptions being observed for runs of the highly oxidized coal This indicates that only a part of the hydrogen consumed in the runs of the highly oxidized coal is related to the coal conversion or oil formation. The oxidation of coal increases the surface and bulk functionalities, which upon thermolysis can increase the number of free radicals. These considerations point to the conclusion that, relative to the vacuum-dried coal, a significantly higher number of bonds in the highly oxidized coal (air dried at 150 °C for 20 h) are broken during liquefaction at 350 °C, but increased population of such weak bonds contributes to enhanced retrogressive crosslinking, rather than the enhanced dissolution of coal.

The predrying also affects the hydrogen transfer from tetralin during non-catalytic liquefaction (Figure 7C). Comparatively, the hydrogen transfer from tetralin in thermal runs of the vacuum- and air-dried coals is slightly higher than that of the raw coal; for the air-dried coal it tends to increase slightly with the severity of air drying. It is very interesting to note from Figure 7C that in the thermal run of the raw coal, the consumption of gas-phase H_2 is higher than the amount of hydrogen transferred from tetralin. Generally, radical reactions are dominant at ≥ 350°C and the hydrogen transfer from H-donor tetralin is usually more efficient than that from gas-phase H_2 during non-catalytic conversion. However, if non-radical reaction pathways exist in the presence of moisture (28.4 wt% in raw coal), or water participates in the reaction, then the higher contribution of gas-phase H_2 consumption (relative to the hydrogen transfer from tetralin) in the non-catalytic run of the raw coal compared to those of dried coals at 350°C may not be an unusual phenomenon. Clarification of this issue requires further study.

In the catalytic runs, the consumption of gas-phase H_2 is significantly higher than that for the corresponding thermal runs (Figure 7), regardless of the solvent (Figures 7B and 7C). This clearly shows that, at 350 °C, the dispersed Mo sulfide catalyst facilitates the dissociation of molecular H_2 thus making hydrogen atoms readily available for the free radicals formed during liquefaction, resulting in higher conversion (Table 2). It seems possible that the hydrogen atoms from catalytic dissociation of molecular H_2 have also induced bond cleavage to certain extent. This consideration is supported by the facts that using ATTM enhanced C_1-C_4 hydrocarbon gas make as compared to the corresponding thermal runs, but using H-donor solvent had little impact on C_1-C_4 hydrocarbon gas make.

The maximum H_2 consumption (1.9 wt %, dmmf) is observed in the solvent-free runs with ATTM impregnated on raw coal. When the coal is predried before ATTM impregnation, the catalytic runs consume considerably less hydrogen (in the solvent-free runs). These facts suggest that the water originally present in the coal affects either the catalyst impregnation or the catalyst dispersion, even when aqueous solution is used for ATTM impregnation. As compared to the solvent-free catalytic run with raw coal, the gas-phase H_2 consumption is lower in the catalytic runs at 350°C using either 1-MN (1.2 wt %, dmmf) or tetralin solvent (1.2 wt %, dmmf). It is also clear from Figure 7C that, except the case with raw coal, using ATTM generally reduces the net hydrogen transfer from tetralin compared to thermal runs. This observation is in good agreement with the earlier findings.[24, 33-35] Both Song et al.[24,33,34] and Artok et al.[35] observed that when an active dispersed[24,33,35] or a supported catalyst[34] is present, the majority of the hydrogen consumed comes from the gas-phase H_2 and only a small part from the H-donor solvent. The mechanisms of hydrogen transfer in catalytic reactions have been discussed elsewhere.[24, 33-35]

Spectroscopic Characterization of Residues. Figure 8 presents the 1400-1800 cm^{-1} region of FT-IR difference spectra of residues from solvent-free non-catalytic liquefaction (obtained by subtracting spectrum of residue of the vacuum-dried coal from the spectra of residues of the air-dried coals). It is interesting to note that the effect of oxidation due to air drying is even reflected in the liquefaction residues. Increasing the severity of air drying leads to increased oxygen functionality of the residues from air-dried coals as compared to those of vacuum-dried coal (Figure 8). The difference spectra between the residues and the predried coals shown in Figure 9 indicate that higher degree of coal oxidation corresponds to higher extent of decarboxylation (the negative band around 1700 cm^{-1}) during the non-catalytic reaction at 350°C. These results are consistent with the observed CO_2 formation trends (Table 1, Figure 5).

Figure 10 shows the changes of the phenolics/alkylbenzenes ratio determined by Py-GC-MS for predried coals and their residues from solvent-free liquefaction at 350°C versus the drying conditions. Compared to the coals dried at 100°C, the ratios for their liquefaction residues are generally lower. However, the ratio for residues from catalytic runs tends to be higher than that of the corresponding thermal runs. In other words, the relative content of phenollic compounds in the pyrolyzates of residues increases upon the use of dispersed Mo catalyst. It seems that this ratio may have potential to serve as a qualitative measure of extent of crosslinking reactions of phenolics caused by oxidation.

Figure 11 shows Py-GC-MS profiles of the residues from non-catalytic liquefaction at 350°C with tetralin solvent. It should be noted that the residues have been extracted by THF for over 24 h, washed by acetone and finally dried at 110°C for over 6 h. Tetralin, dihydronaphthalene, naphthalene, 2- and 1-methylnaphthalene peaks, eluted in that order, are due mainly to the use of tetralin as the reaction solvent.[36] Methylnaphthalene peaks are due mainly to the chemically bound molecular fragments of solvent origin. Apparently, as the severity of oxidative drying increases, the relative intensities of the adducted compounds increases. The adduction of solvent molecules depends on the number of reactive sites (free radicals) created during liquefaction and the inaccessibility of the donatable hydrogen to cap these sites. The solvent molecules can also form free radicals upon hydrogen abstraction by reactive radicals generated from coal. It is clear from Figure 11 that the adduction of solvent molecules during liquefaction is enhanced by oxidative drying of the coal, especially air drying at 100°C for 100 h and at 150°C for 20 h. The oxidized coal is richer in oxygen-containing functional groups, which can induce crosslinking reactions upon their thermal decomposition at 350°C.

Physical and Chemical Considerations of Drying Effects. There are at least four physicochemical effects that drying and oxidation may have on coal. The first is the removal of water. The second is the physical changes such as those in pore structure and density that are believed to accompany drying.[14,18] One way by which pore structure can be changed is the shrinkage caused by deswelling due to the removal of water, which is a good swelling solvent for low-rank coal.[18] If this happens, drying before the reaction could also affect the reaction with respect to diffusion of solvents, reactants, and products. The third is the change in surface characteristics such as hydrophobicity induced by drying, as we further describe below. Finally, some chemical reactions may occur during drying such as air drying at 100°C. Obviously, oxidation causes chemical change in oxygen functionality. The effects of these four factors in thermal and catalytic liquefaction are not straightforward, and some of them can exert influence on coal conversion in opposite directions under the same or different conditions.

Apparently, the first effect, the removal of water, was neglected in most previous work on the influence of drying in liquefaction. This is presumably because water was thought to be inert in coal liquefaction. We also examined the effect of water addition.[25] Table 3 shows the effect of adding water in the thermal runs of vacuum-dried coal without solvent and with tetralin solvent. Adding a small amount of water equivalent to the original moisture content (28.4 wt%) back to the vacuum-dried coal increased coal conversion from 9.2 to 22.3 wt% in the solvent-free runs, and from 25.9 to 39.9 wt% in the runs with tetralin solvent. In fact, adding water back to the vacuum-dried coal restored over 90 % of the oil yield and conversion of those with the fresh raw coal in non-catalytic runs at 350 °C both with and without a solvent, as can be seen from Table 3.

The above facts suggest that the decrease in conversion in thermal runs at 350°C upon drying is due primarily to the removal of water, and the changes in coal conversion and products distribution caused by drying at 100 °C (except oxidation) seem to be largely reversible upon addition of water. Although the presence of water has significant physical effect (see below), it may also have some impact on the chemical reaction at 350 °C. It has been reported that hydrothermal pretreatment of coal in presence of water is beneficial for improved conversion and better product quality in pyrolysis, liquefaction and coprocessing.[17,37-41] As can be seen from Table 1, CO_2 yield is always higher in the runs of raw coal than those of vacuum-dried coal. An increase in the CO_2 yield upon addition of water to vacuum-dried coal has been observed.[25,42]

Enhanced CO_2 formation upon water addition was also observed by Lewan[43] in his studies on hydrous pyrolysis of kerogen materials.

The decrease in CO yield upon water addition indicates that water gas shift reaction (equation 3) did occur but this reaction only contributes to a small part of the increased CO_2 yield, as can be seen by comparing the CO and CO_2 yields in Table 3 on a molar basis. The majority of increased CO_2 yields upon water addition is probably due to the interaction of water with carbonyl functional groups (equation 4), as also suggested by Petit.[44] This rationalizes the enhanced coal conversion together with increased CO_2 formation upon water addition. Since low-rank coals have high propensity towards retrogressive reactions due to their high oxygen functionalities, the removal of oxygen functional groups in the presence of water at 350 °C can make the coal network less refractory for dissolution and hence higher conversion is achieved.[25] In addition, the effects of water addition to vacuum-dried coal observed in this work has led the way to more efficient low-severity catalytic liquefaction,[25] but further studies are needed to clarify the mechanisms of chemical effects of water.

$$CO + H_2O = CO_2 + H_2 \qquad 3)$$
$$R'COR'' + H_2O = R'H + CO_2 + R''H \qquad 4)$$

From their model compound studies, Tse et al.[41] suggested that water can suppress the retrogressive crosslinking reactions such as those of polyhydroxy groups. On the other hand, according to Siskin et al.,[45] the presence of water during the preconversion step may facilitate depolymerization of the macromolecular structure to give a higher conversion yield by cleavage of ether type crosslinkages. From our data in Tables 1 and 3, it seems that the added water or the original moisture also participated in the chemical reaction at 350°C and acted also as a hydrogen source through some chemical reactions such as that represented by equation 4.

The second effect, physical change such as pore collapse and shrinkage caused by drying, has been discussed quantitatively in a recent paper by Suuberg et al.[18] Their work has demonstrated that water is a good swelling agent for coals ranging from lignites up to high-volatile bituminous coal, and the coals shrink when dried from the as-mined state. They found that shrinkage upon vacuum drying is correlated by equation 5:

$$\text{Volumetric shrinkage (\%)} = 0.863 \times (\text{moisture content, wt\%}) - 0.162 \qquad 5)$$

Applying this relationship would give a 24 % volumetric shrinkage of Wyodak subbituminous coal upon vacuum drying. It is reasonable to consider that drying in vacuum and in air may have somewhat different impacts on the pore collapse, and surface area change, but no data is available for comparison at the present stage.

In regard to surface area change, Vorres et al.[15] have recently observed that the N_2 BET surface areas of low-rank coals decrease on heating above room temperature to 40°C; the areas are relaively constant on heating in vacuum between 40-100°C. Swann et al.[46] reported that vacuum drying of a fresh Yallourn brown coal at 22, 35, and 70°C gives CO_2 surface areas of 290, 262, and 254 m^2/g, respectively. Mahajan and Walker[47] found that for a lignite, CO_2 surface areas following outgassing at 90, 110, 130, and 150°C were 206, 212, 198, and 184 m^2/g, respectively. Following vacuum drying of Yallourn brown coal at 35°C (or 70°C) for 7 days, oxidation by pure molecular oxygen at 35°C (or 70°C) for 45 days further decreased the CO_2 surface areas from 262 to 187 m^2/g (for 70°C vacuum drying followed by oxidation, 254 to 156 m^2/g).[46] On the other hand, these CO_2 surface area values may not be representative of the internal areas accessible by tetralin or 1-MN solvent molecules, which have much larger molecular sizes than CO_2 and N_2.

One of our hypotheses in designing the experiments with different solvents was the following: if drying affects the rate of solvent diffusion into the coal pores or the rate of uptake of solvents by the coal, then the reaction with a H-donor solvent should be more sensitive to the drying conditions than the one with a non-donor solvent. As can be seen from Table 1 and Figure 6, for thermal runs in the presence of tetralin solvent, considerably higher conversion (35.1 wt%) and higher oil yield (11.7 wt%) were obtained with the air-dried coal (100 °C for 2 h) than with the vacuum-dried coal (25.9 wt% conversion, 4.1 wt% oil yield), and this trend was confirmed by duplicate tests. However, using 1-MN in the thermal runs gave only slightly higher conversion and oil yield for the air-dried coal (100 °C for 2 h) than for the vacuum-dried coal. Neither the oxidation induced by drying in air (Figure 3) nor the difference in moisture contents of dried coals (Figure 1) can account for these facts. We believe that, for thermal runs in the presence of a H-donor solvent at 350°C, the advantage with air-dried coal (dried at 100 °C for 2 h) than with vacuum-dried coal is due to the lower mass transport limitations of H-donor molecules (and products) with the former.

The third effect of drying concerns surface characteristics. If drying in different atmosphere or under different conditions affects the surface characteristics of coal, then the dispersion of the catalyst precursor molecules on coal surface may change with drying. It has been shown that removal of the original moisture by drying contributes to increasing the hydrophobicity of coal surface,[48,49] but mild oxidation can convert some hydrophobic sites on coal surface into hydrophilic sites.[50,51] Relative to vacuum-drying, the beneficial effect of predrying in air at 100°C for 2 h in catalytic runs (Table 2) may be attributed to the mild oxidation-induced increase in surface oxygen functionality and hence increased hydrophilicity, which could contribute to increasing ATTM dispersion in the impregnation process. As Weller[52] pointed out ten years ago, the degree of dispersion is very important when unsupported Mo catalysts are used for coal liquefaction.

The hydrophobicity is a function of coal rank and maceral composition,[53] but is decreased by prewetting of dried coals.[49] We also performed several tests to see whether prewetting affects the catalyst impregnation, and the results are given in Table 4. The vacuum-dried coal was prewetted with a small amount of water which is equivalent to the original moisture (28.4 wt%). The prewetted coal was then impregnated with aqueous ATTM solution either immediately after prewetting or after 24 h storage of the prewetted sample. The results in Table 4 show that prewetting the vacuum-dried coal before impregnating ATTM from its aqueous solution has increased coal conversion and enhanced oil formation. The advantage of prewetting the vacuum-dried coal becomes more apparent when tetralin solvent was used for catalytic liquefaction at 350°C, where coal conversion and oil yield increased from 36.4 to 44.6 wt%, and from 10.2 to 18.4 wt%, respectively. Prewetting coal with water decreases hydrophobicity of surface on the one hand, and causes volume expansion due to coal swelling on the other hand. Both these two effects are desirable for better dispersion of ATTM during incipient wetness impregnation. Gorbaty[19] has shown that drying a Wyodak subbituminous coal in vacuum can decrease the amount of a metal salt (nickel sulfate) adsorbed onto coal from its aqueous solution. He attributed the drying-induced changes primarily to pore collapse and secondarily to the replacement of water by gas, namely the volume once occupied by water becomes occupied by the gas present during and after drying. Combination of our results and with those of Gorbaty [19] and Wei et al.[49] suggest that non-oxidative predrying also increases the surface hydrophobicity and reduces the adsorption of metal salt onto the surface of low-rank coals, although water is used to dissolve the metal salt. Prewetting the coal prior to the contact with metal solution, however, decreases the surface hydrophobicity and swells the coal, leading to improved the adsorption and dispersion of metal salt from its aqueous solution (onto more hydrophilic surface).

In this context, relative to vacuum drying, the advantage of predrying coal in air (mild oxidation at 100 °C for 2 h) before ATTM impregnation for the solvent-mediated catalytic runs (Table 2) can be rationalized by taking into account the following two factors: 1) mild oxidation (Figure 3) converting some hydrophobic sites into hydrophilic sites, which contributes to improved dispersion of the ATTM precursor during its impregnation; and 2) less mass transport limitations of solvent and products are encountered during reactions of air-dried coals at 350°C. In addition, we also examined the effect of drying ATTM-impregnated coal in air, as this may be more practical than vacuum drying for large scale application. ATTM was loaded on the raw coal by incipient wetness impregnation, followed by either vacuum-drying or air drying at 100°C for 2 h. The results given in Table 5 reveal that these two methods afford similar coal conversions (44-46 wt%) and oil yields (16-18 wt%) for runs with tetralin solvent at 350°C.

The fourth effect associated with drying is oxidation. It should be noted that, relative to vacuum drying, the advantage of air drying completely diminishes upon increasing the severity to 150°C for 20 h, both in thermal (Table 1) and catalytic runs (Table 2). In other words, high-severity air drying or oxidation has unambiguously negative impact on catalytic as well as thermal liquefaction of the coal. Such a clearly deleterious effect of severe oxidation on coal liquefaction is considered to arise from significantly increased oxygen functionality, which enhances the cross-link formation in the early stage of coal liquefaction.

Summary and Conclusions

Drying of Wyodak subbituminous coal (DECS-8), either under vacuum or in air at 100-150°C, can alter its physicochemical properties, which significantly affect its conversion, oil yields, and CO_2 yields both in non-catalytic and catalytic liquefaction at 350 °C.

Spectroscopic characterization using CPMAS ^{13}C NMR, Py-GC-MS, and FT-IR revealed that oxidative drying in air causes oxidation reactions leading to the formation of oxygen functional groups at the expense of aliphatic carbons. Furthermore, Py-GC-MS and NMR data also uncovered that oxidation of coal at 100-150°C can cause the transformation of phenolics and catechol into other related structures (presumably through condensation, or crosslinking), and high-severity air drying at 150°C for 20 h leads to disappearance of catechol from Py-GC-MS and NMR spectra.

For thermal liquefaction runs at 350°C, fresh raw coal gave higher conversion and higher oil yield than the dried coals, regardless of the solvent. In the presence of either H-donor or non-donor solvent, the coal dried in air at 100 °C for 2 h gave a better conversion as compared to the vacuum-dried coal. Runs of raw coal always produces more CO_2 than those of the vacuum-dried coal, both with and without solvent.

For catalytic runs using ATTM impregnated on coal, predrying has negative impacts for solvent-free liquefaction at 350°C. Namely, the runs using ATTM loaded on the raw coal gave higher conversion and higher oil yield than loading ATTM on vacuum- or air-dried coals. In the presence of either tetralin or 1-MN, however, predrying coal in air prior to ATTM impregnation has slightly beneficial effect, at least no apparent negative impact, on coal conversion as compared to the case using raw coal. The runs using ATTM loaded on air-dried coal with either tetralin or 1-MN solvent afford better conversions and oil yields as compared to the runs using vacuum-dried coal. These observations can be rationalized by taking into account the spectroscopic characterization data and the four physicochemical factors associated with drying and oxidation effects mentioned above.

The effect of non-oxidative (vacuum) drying on coal conversion in thermal liquefaction at 350°C is due primarily to the removal of water and secondarily to the physicochemical changes of coal induced by drying. Adding water back to the vacuum-dried coal can restore over 90 % of the conversion of the fresh raw coal in the runs without solvent and with H-donor solvent. For catalytic runs using impregnated ATTM, the effect of predrying is mainly caused by the drying-induced physicochemical changes such as those in pore structure (mass transport) and surface characteristics. If the moisture loss has occurred (due to deliberate or inadvertent drying), prewetting the dried coal with water before impregnation of the metal salt from its aqueous solution can help to improve the performance of resulting catalyst.

Upon highly oxidative drying coal in air at 150 °C for 20 h, the conversion significantly decreased to a lower value than that of the vacuum-dried coal in the non-catalytic runs. The same trend was observed in the runs of the dried coals loaded with ATTM. Such a clearly negative impact of severe oxidation on coal liquefaction is considered to arise from significantly increased oxygen functionality which enhances the cross-link formation in the early stage of coal liquefaction.

Finally, although mildly oxidative drying at 100°C displayed beneficial effects relative to vacuum drying for liquefaction at 350°C, this advantage may not be valid for liquefaction at higher temperatures such as 400-425°C. The Py-GC-MS results of the dried coals (Figures 4) and the residues (Figures 10, 11) suggest that oxidation can induce more crosslinking at high temperatures, which can lead to lower conversion or poorer products distribution. Study on the effects of drying and oxidation on both thermal and catalytic liquefaction at 400-425°C is now in progress, and the results will be reported in due course.

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2. EFFECTS OF DISPERSED CATALYST AND SOLVENT ON CONVERSION AND STRUCTURAL CHANGES OF A NORTH DAKOTA LIGNITE.

INTRODUCTION

In our recent work reported in previous quarter, liquefaction of a Big Brown Texas subbituminous coal (DECS-1), was studied in the temperature range from 250°C to 450°C. Tetralin and 1-methylnaphthalene (1-MN) were used as reaction solvents to compare with the reactions without any solvent. It was found that there was an apparent conversion jump when the reaction temperature was increased from 350°C to 400°C, indicating that the coal structure has a major break down at temperatures around 400°C. In the non-catalytic liquefaction reactions, tetralin, the donor solvent, always provided the highest conversions than 1-MN, a non-donor solvent, or no solvent when temperature was 350°C and higher. However, with ammonia tetrathiomolybdate as a catalyst, the effect of the donor solvent was diminished. It appeared that at temperature of 400°C and lower, conversions were almost the same no matter what kind of solvent was used or if a solvent was used. While at 450°C, the donor solvent showed its advantage by keeping the conversion high while with 1-MN or without a solvent, the conversions dropped significantly.

In this work, DECS-11, a North Dakota lignite, was studied in the temperature range from 250°C to 450°C. As in the previous work, tetralin and 1-MN was used as solvents. In some experiments, no solvent was used. ATTM was also applied as a catalyst precursor in some experiments. In this quarterly report, the conversions and products yields will be shown and the effects of the reaction solvents and the catalyst will be illustrated.

EXPERIMENTAL

The coal sample was a North Dakota lignite (DECS-11) obtained from the Penn State Coal Sample Bank. Its compositional data are summarized as the following on a dry and mineral matter free basis: 74.2% carbon, 4.4% hydrogen, 1.0% nitrogen, 0.4% organic sulfur and 20.0% oxygen (by difference). The reaction solvents were tetralin (Aldrich, 99%), and 1-methylnaphthalene (1-MN, Aldrich, 98%). The catalyst precursor was ammonium tetrathiomolybdate (ATTM, Aldrich, 99.97%). All the chemicals were used without further purification.

The catalyst loading was 1 wt% of Mo based on the dmmf coal. A THF/H_2O (1:1) mixture was used to make the solution of the catalyst precursor, because this binary mixture was superior to H_2O in terms of providing higher conversion and oil yield in subsequent liquefaction [10]. The catalyst precursor was first added to water, of just enough volume to dissolve the desired amount of the precursor. An equal volume of THF was then added to the H_2O solution. After being stirred to achieve a homogeneous mixture, the THF/H_2O/ATTM mixture was added to the dried coal to make a slurry. After 20 minutes of stirring at room temperature under N_2 atmosphere, the excess water and THF was removed by rotary evaporator. The "wet" sample (still containing some residual H_2O and THF) was then dried in a vacuum oven at room temperature for 20 hours, at 45°C for 5 hours and at 95°C for 4 hours, sequentially.

Liquefaction experiments were conducted in 25 ml microautoclaves in a fluidized sandbath. For each reaction, 4 grams of the coal sample and 4 grams of a solvent, if a solvent was applied, were loaded into a microautoclave. The reactor was purged three times with hydrogen and the final H_2 pressure was 1000 psi (7 MPa) at room temperature. For every reaction, the sandbath was preheated to a desired temperature, 250°C, 300°C, 350°C, 400°C, or 450°C. The microautoclave was then plunged into the sandbath and agitated at a rate of 200 cycles per minute. The total time in which a microautoclave was kept in the sandbath was 33 minutes, with 3 minutes being the time for rapid heat up. Finally, after reaction, the microautoclave was taken out of the sandbath and rapidly quenched by dipping into cold water.

After the microautoclave was cooled to room temperature, the reactor was vented, the volume of the gas was measured by the water displacement method, and a sample was collected for further analysis. The liquids and the solids in the microautoclave were washed into a tared ceramic thimble using hexane. Then the products were separated under a nitrogen atmosphere by Soxhlet extraction using hexane, toluene and THF sequentially. The soluble products are classified as oil, asphaltene and preasphaltene, respectively.

RESULTS AND DISCUSSION

The conversion data of all non-catalytic and catalytic liquefaction experiments of the DECS-11 coal are summarized in Tables 6-8.

Effect of Temperature on Liquefaction Conversion and Product Distribution

The effects of temperature on liquefaction conversion and product distribution are plotted in Figures 12-14. A general trend is that the conversion increases with the increase of the temperature. At temperature below 350°C, the liquefaction reactions are insignificant, with conversions lower than 20%. The temperature at which liquefaction reactions take place extensively is around 400°C, same as that observed from the DECS-1 coal. As the temperature further increases to 450°C, the conversions continues to increase. They are 49% when no solvent was applied, 71% when the donor solvent (tetralin) was applied, and 48% when the non-donor solvent (1-MN) was applied. A study of the product distribution shows that gas and oil yields always increase with the temperature (from 250°C to 450°C), while the asphaltene and preasphaltene yields were relatively low throughout the temperature range studied. They increase with temperature in the low end of the range, than drop when the temperature is increased from 400°C to 450°C.

The study of temperature suggests that in order to obtain significant reaction conversion, a temperature higher than 350°C is required. As shown in Figures 12-14, without the present of the catalyst, the conversion continue to increase even when the temperature increases to 450°C, which is different from that of the DECS-1 coal. In latter study, higher temperatures will be applied to find the maximum conversion and the temperature to achieve it.

Effect of Reaction Solvent on Liquefaction

A comparison of conversions of reactions with different solvents is presented in Figure 15. At low temperatures (≤ 350°C), the solvent effect is trivial. The three kinds of conversions (with tetralin, 1-MN, or without any solvent) appear to be very close. At high temperatures, i. e. 400°C, the conversion increases from 31% (with no catalyst and no solvent) to 66% (with no catalyst but tetralin). This increase is contributed mainly by significant gains in oil, asphaltene and preasphaltene. As temperature increased to 450°C, the conversions with 1-MN or no solvent continued to increase while that with tetralin had a very small gain (from 66% to 71%), indicating that the maximum conversion might be approached. Comparing the conversions of reactions in the presence of 1-MN with those in the absence of a solvent throughout the temperature range, it appears that using the non-donor solvent has no significant advantages in terms of conversion and oil yield.

Effect of the ATTM-Derived Catalyst on Liquefaction

Conversions of catalytic liquefaction with tetralin, 1-MN or no solvent are plotted in Figures 16-18. Comparing with the non-catalytic reactions, the ATTM-derived catalyst has no remarkable effects on the conversions at 350°C and below in all three cases (with different solvents). However, at 400°C, the catalyst was much more active shown by the significant increases in conversions. For the reactions with tetralin, using the catalyst increased the conversion from 66% to 77%; for that with 1-MN, from 38% to 66%; and for that with no solvent, from 31% to 64%. It appears that the catalyst has stronger effects on the reactions without a donor solvent than that with a donor solvent. This is because that the donor solvent itself can increase the conversion to a great extent already, adding the catalyst will only enhance the conversion a little bit more so to reach the maximum. When the temperature was further raised to 450°C, there were noticeable drops of conversions in all the cases, Figure 19. Similar phenomenon has been observed before with the DECS-1 coal. It can be explained as that the catalyst is both a hydrogenation catalyst and a dehydrogenation catalyst. High temperatures favors the dehydrogenation, so at 450°C, the "net" hydrogenation is to a smaller extent than that at 400°C.

CONCLUSIONS

The North Dakota lignite (DECS-1) coal was studied in this quarter for its liquefaction behaviors. Reactions were carried out at temperatures between 250°C and 450°C. Regardless the reaction solvents and the catalyst being used, the optimum temperature was found to be 400°C. The donor solvent has a significant effect over the conversion especially at temperatures higher than 350°C. The ATTM-derived catalyst can increase the conversions remarkably. When tetralin was applied as the reaction solvent, the catalyst enhances the conversion slightly indicating that the maximum value has been reached. At high temperatures, i.e. 450°C, the conversions of catalytic reactions dropped because of the dehydrogenation effect of this catalyst. Therefore the optimum temperature for the catalyst is 400°C. In the future research, the products, such as the oil, asphaltene and preasphaltene, and the reaction residues will be studied to identify effects of the temperature, solvent and the catalyst in terms of product distribution and their structures.

In the future, products and reaction residues will be characterized by gas chromatograph, gas chromatorgraph/mass spectrometer, and CPMAS ^{13}C NMR technique.

Table 1. Results of Non-Catalytic Liquefactions of Raw and Dried Wyodak Coal at 350 °C for 30 min with 6.9 MPa H_2

Drying	Reaction	CO	CO_2	C_1-C_4	Oil	Asphal.	Preasp.	Total	Conversion
conditions	solvent	dmmf wt%						Liquids[a]	dmmf wt%
Fresh raw coal	none	0.4	8.9	0.2	5.4	2.8	9.1	17.3	25.0
Vacuum, 100°C, 2 h	none	0.2	4.5	0.2	2.1	2.6	4.5	9.2	12.5
Air, 100°C, 2 h	none	0.3	5.9	0.1	3.3	0.7	5.8	9.8	14.8
Air, 100°C, 20 h	none	0.4	6.7	0.2	6.0	0.6	3.2	9.8	15.5
Air, 100°C, 100 h	none	0.7	11.2	0.2	1.2	0.7	3.3	5.2	12.7
Air, 150 °C, 20 h	none	0.8	12.3	0.1	0.6	0.2	0.4	1.1	10.9
Fresh raw coal	Tetralin	0.1	7.4	0.2	15.8	9.3	12.4	37.5	43.3
Vacuum, 100°C, 2 h	Tetralin	0.2	4.1	0.2	4.1	7.6	10.0	21.7	25.9
Air, 100°C, 2 h	Tetralin	0.2	5.9	0.2	11.7	7.4	10.6	29.7	35.1
Air, 100°C, 20 h	Tetralin	0.3	7.5	0.3	11.1	6.5	8.9	26.5	32.4
Air, 100°C, 100 h	Tetralin	0.5	10.9	0.2	6.1	6.3	9.7	22.1	30.8
Air, 150 °C, 20 h	Tetralin	0.6	15.9	0.1	2.1	2.8	3.2	8.1	19.9
Fresh raw coal	1-MN	0.1	7.0	0.2	15.9	6.6	11.4	34.0	39.9
Vacuum, 100°C, 2 h	1-MN	0.2	4.3	0.2	1.1	5.8	7.4	14.3	18.3
Air, 100°C, 2 h	1-MN	0.3	6.2	0.2	4.2	4.0	9.4	17.6	22.7
Air, 100°C, 20 h	1-MN	0.3	7.0	0.2	8.0	5.6	4.7	18.3	24.5
Air, 100°C, 100 h	1-MN	0.5	11.9	0.2	1.7	4.1	6.3	12.1	21.1
Air, 150 °C, 20 h	1-MN	0.7	15.7	0.1	1.8	2.2	2.5	6.6	18.0

a) Sum of yields of oil, asphaltene, and preasphaltene.

Table 2. Results for the Low-Severity Catalytic Liquefaction at 350 °C Using ATTM Impregnated on Raw and Dried Coals

Drying conditions	Solvent	CO	CO_2	C_1-C_4	Oil	Asphal.	Preasp.	Total Liquids[a]	Conversion
		dmmf wt%							dmmf wt%
Fresh raw coal[b]	none	0.3	4.1	0.5	16.9	9.2	14.9	41.1	43.3
Vacuum, 100°C, 2 h	none	0.2	2.3	0.3	10.0	5.4	11.4	26.8	29.8
Air, 100°C, 2 h	none	0.4	5.2	0.6	12.6	3.2	10.1	25.9	29.2
Air, 100°C, 20 h	none	0.4	5.7	0.7	14.6	3.1	8.7	26.4	31.2
Air, 100°C, 100 h	none	0.7	8.0	0.6	13.3	2.4	5.1	20.8	28.4
Air, 150 °C, 20 h	none	0.9	9.8	0.5	5.1	0.5	1.7	7.3	18.5
Fresh raw coal[b]	Tetralin	0.1	4.5	0.4	16.0	11.5	11.9	39.4	42.2
Vacuum, 100°C, 2 h	Tetralin	0.1	2.6	0.3	10.2	12.9	10.6	33.4	36.4
Air, 100°C, 2 h	Tetralin	0.2	4.8	0.4	15.7	11.1	14.9	41.7	45.6
Air, 100°C, 20 h	Tetralin	0.2	6.9	0.4	18.6	8.6	10.7	37.9	43.5
Air, 100°C, 100 h	Tetralin	0.4	8.8	0.5	16.5	10.8	11.0	38.3	45.0
Air, 150 °C, 20 h	Tetralin	0.4	12.4	0.4	9.6	2.3	5.7	17.6	29.4
Fresh raw coal[b]	1-MN	0.1	4.5	0.3	10.4	10.4	11.9	32.7	35.9
Vacuum, 100°C, 2 h	1-MN	0.1	3.4	0.3	6.1	10.1	12.3	28.5	31.1
Air, 100°C, 2 h	1-MN	0.2	5.2	0.4	10.3	8.1	16.0	34.4	37.4
Air, 100°C, 20 h	1-MN	0.2	9.3	0.5	14.1	8.7	10.5	33.3	39.7
Air, 100°C, 100 h	1-MN	0.3	9.5	0.4	14.4	8.7	11.1	34.2	39.4
Air, 150 °C, 20 h	1-MN	0.3	12.4	0.3	5.3	2.8	4.3	12.4	24.5

a) Sum of yields of oil, asphaltene, and preasphaltene.

b) Raw (fresh as-received) coal was used for catalyst impregnation followed by vacuum drying at 100 °C for 2 h before liquefaction.

Table 3. Effect of Adding Water Back to the Vacuum-Dried Coal on Its Non-Catalytic Liquefaction at 350 °C

Coal drying	H_2O addition	Reaction	CO	CO_2	C_1-C_4	Oil	Asphal.	Preasp.	Conversion
conditions	after drying	solvent			dmmf wt%				dmmf wt%
Vacuum, 100°C, 2 h	no	none	0.2	4.5	0.2	2.1	2.6	4.5	12.5
Vacuum, 100°C, 2 h	yes	none	0.1	8.2	0.3	5.4	1.9	7.7	22.3
Fresh raw coal	Orig. Moist.	none	0.4	8.9	0.2	5.4	2.8	9.1	25.0
Vacuum, 100°C, 2 h	no	Tetralin	0.2	4.1	0.2	4.1	7.6	10.0	25.9
Vacuum, 100°C, 2 h	yes	Tetralin	0.1	6.9	0.2	14.5	9.2	10.2	39.9
Fresh raw coal	Orig. Moist.	Tetralin	0.1	7.4	0.2	15.8	9.3	12.4	43.3

Table 4. Effect of Prewetting of Vacuum-Dried Coal before ATTM Impregnation on Catalytic Liquefaction at 350 °C

Coal drying conditions	Prewetting with H_2O	Reaction solvent	CO	CO_2	C_1-C_4	Oil	Asphal.	Preasp.	Conversion
			dmmf wt%						dmmf wt%
Vacuum, 100°C, 2 h	no	none	0.2	2.3	0.3	10.0	5.4	11.4	29.8
Vacuum, 100°C, 2 h	yes[a]	none	0.4	5.6	0.5	16.7	4.2	9.0	34.1
Vacuum, 100°C, 2 h	yes[b]	none	0.3	4.7	0.4	14.0	7.9	8.7	35.0
Fresh raw coal	Orig. Moist.	none	0.3	4.1	0.5	16.9	9.2	14.9	43.3
Vacuum, 100°C, 2 h	no	Tetralin	0.1	2.6	0.4	10.2	12.9	10.6	36.4
Vacuum, 100°C, 2 h	yes[a]	Tetralin	0.1	4.3	0.3	18.4	11.5	11.5	44.6
Fresh raw coal	Orig. Moist.	Tetralin	0.1	4.5	0.4	16.0	11.5	11.9	42.2

a-b) ATTM was impregnated onto the prewetted coal immediately after prewetting (a) or after 24 h storage of the prewetted sample (b), followed by vacuum drying at 100 °C for 2 h before liquefaction.

Table 5. Effect of Drying Conditions before and after ATTM Impregnation on Catalytic Liquefaction with Tetralin at 350 °C

Coal drying conditions	Drying after IWI / ATTM	CO	CO_2	C_1-C_4	Oil	Asphal.	Preasp.	Conversion
		dmmf wt%						dmmf wt%
Fresh raw coal	Vacuum, 100°C, 2 h	0.1	4.5	0.4	16.0	11.5	11.9	42.2
Fresh raw coal	Air, 100°C, 2 h	0.2	7.4	0.3	18.3	8.8	11.2	43.6
Vacuum, 100°C, 2 h	Vacuum, 100°C, 2 h	0.1	2.6	0.4	10.2	12.9	10.6	36.4
Air, 100°C, 2 h	Vacuum, 100°C, 2 h	0.2	4.8	0.4	15.7	11.1	14.9	45.6

Table 6 Conversion and product yields of cataytic and non-catalytic reaction without a solvent

Exp. #	Conditions	Conversion	Gas	Oil	Asphaltene	Preasphaltene
#364	450C, C, NS	0.536	0.203	0.260	0.040	0.034
#367	400C, C, NS	0.635	0.166	0.200	0.164	0.105
#355	350C, C, NS	0.171	0.062	0.057	0.022	0.061
#370	450C, NC, NS	0.491	0.168	0.253	0.006	0.064
#401	400C, NC, NS	0.306	0.117	0.143	0.004	0.042
#341	350C, NC, NS	0.154	0.065	0.084	0.003	0.002
#344	250C, NC, NS	0.047	0.020	0.013	0.002	0.012

Table 7. Conversion and product yields of cataytic and non-catalytic reaction with tetralin

Exp. #	Condition	Conversion	Gas	Oil	Asphaltene	Preasphaltene
#365	450C, C, TE	0.711	0.242	0.317	0.079	0.073
#366	400C, C, TE	0.768	0.123	0.232	0.218	0.195
#356	350C, C, TE	0.298	0.057	0.119	0.055	0.067
#371	450C, NC, TE	0.709	0.184	0.364	0.085	0.076
#402	400C, NC, TE	0.659	0.125	0.253	0.123	0.157
#342	350C, NC, TE	0.281	0.066	0.199	0.050	0.032
#345	250C, NC, TE	0.046	0.017	0.000	0.012	0.017

Table 8. Conversion and product yields of cataytic and non-catalytic reaction with 1-MN

Exp. #	Condition	Conversion	Gas	Oil	Asphaltene	Preasphaltene
#366	450C, C, 1-MN	0.546	0.184	0.269	0.052	0.041
#369	400C, C, 1-MN	0.655	0.117	0.186	0.147	0.205
#357	350C, C, 1-MN	0.286	0.060	0.083	0.080	0.063
#372	450C, NC, 1-MN	0.467	0.168	0.235	0.034	0.031
#403	400C, NC, 1-MN	0.377	0.106	0.162	0.040	0.069
#343	350C, NC, 1-MN	0.233	0.068	0.113	0.039	0.013
#346	250C, NC, 1-MN	0.053	0.020	0.015	0.012	0.006

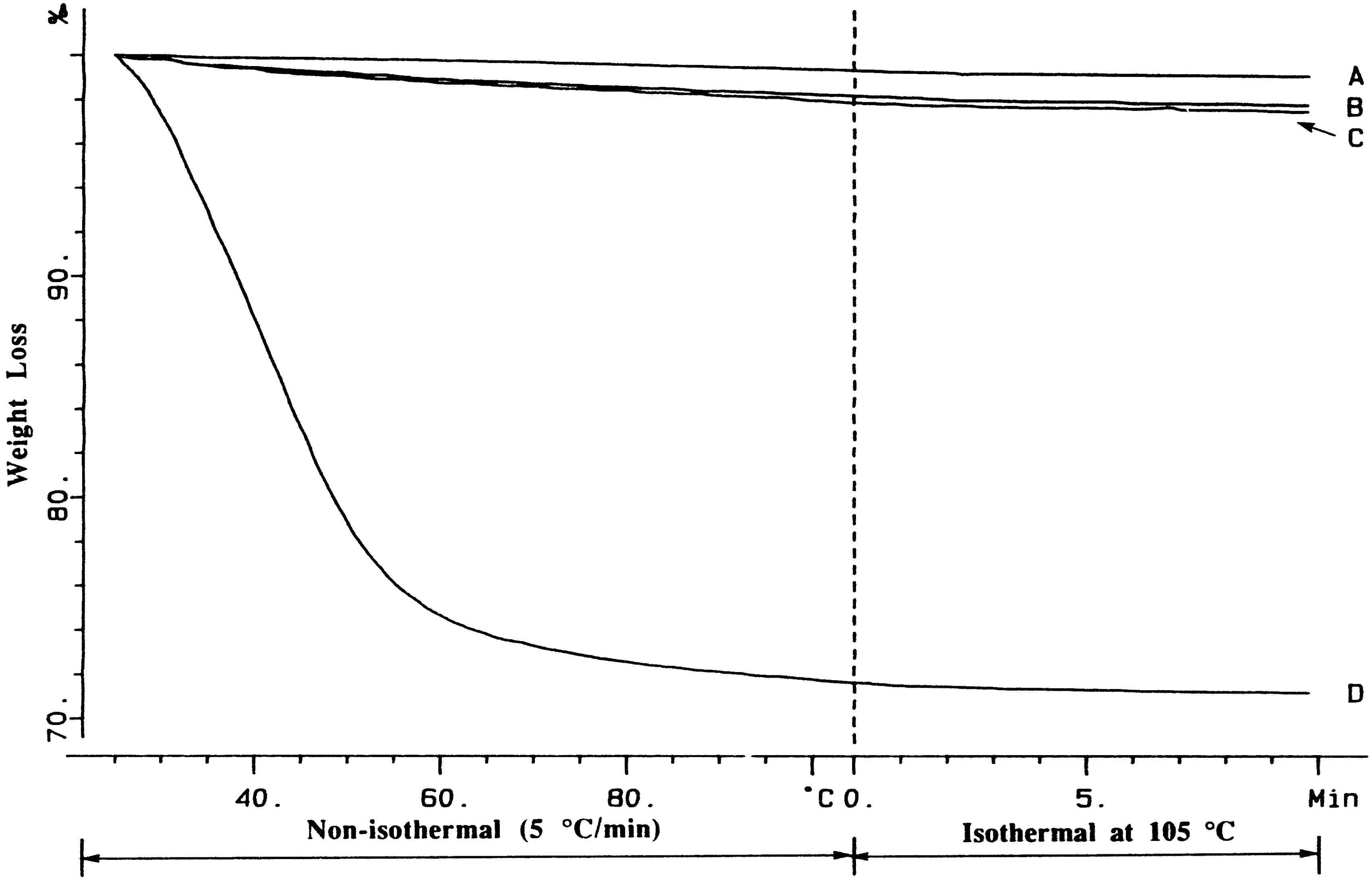


Figure 1. Weight loss of predried and raw Wyodak subbituminous coal (DECS-8) during TGA in N_2 flow. **A**: vacuum-dried at 100°C for 2 h; **B**: air-dried at 100°C for 2 h; **C**: raw coal impregnated with ATTM followed by vacuum drying at 100°C for 2 h; **D**: as-received raw coal.

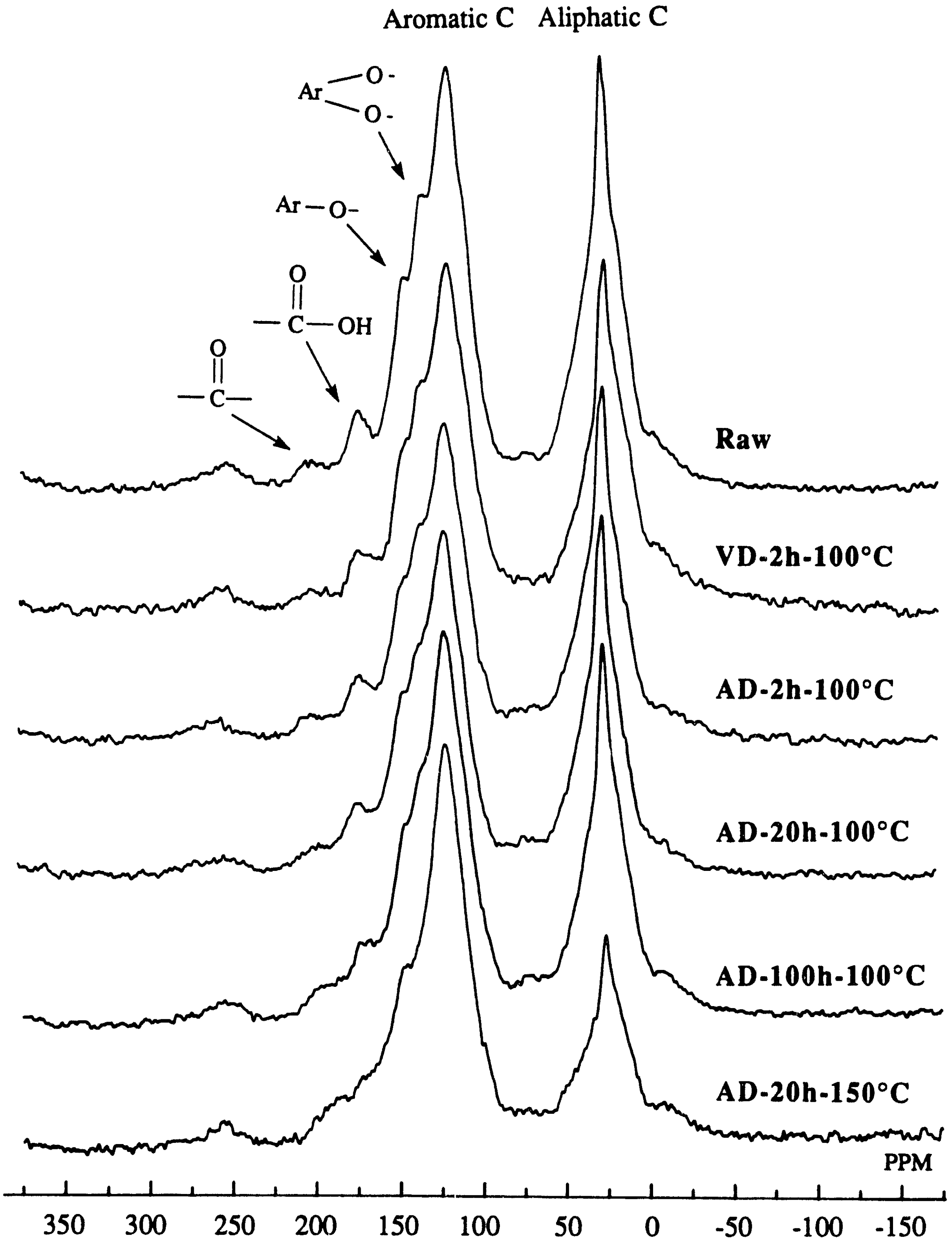


Figure 2. CPMAS solid-state ^{13}C NMR spectra of the DECS-8 coal samples predried under various conditions.

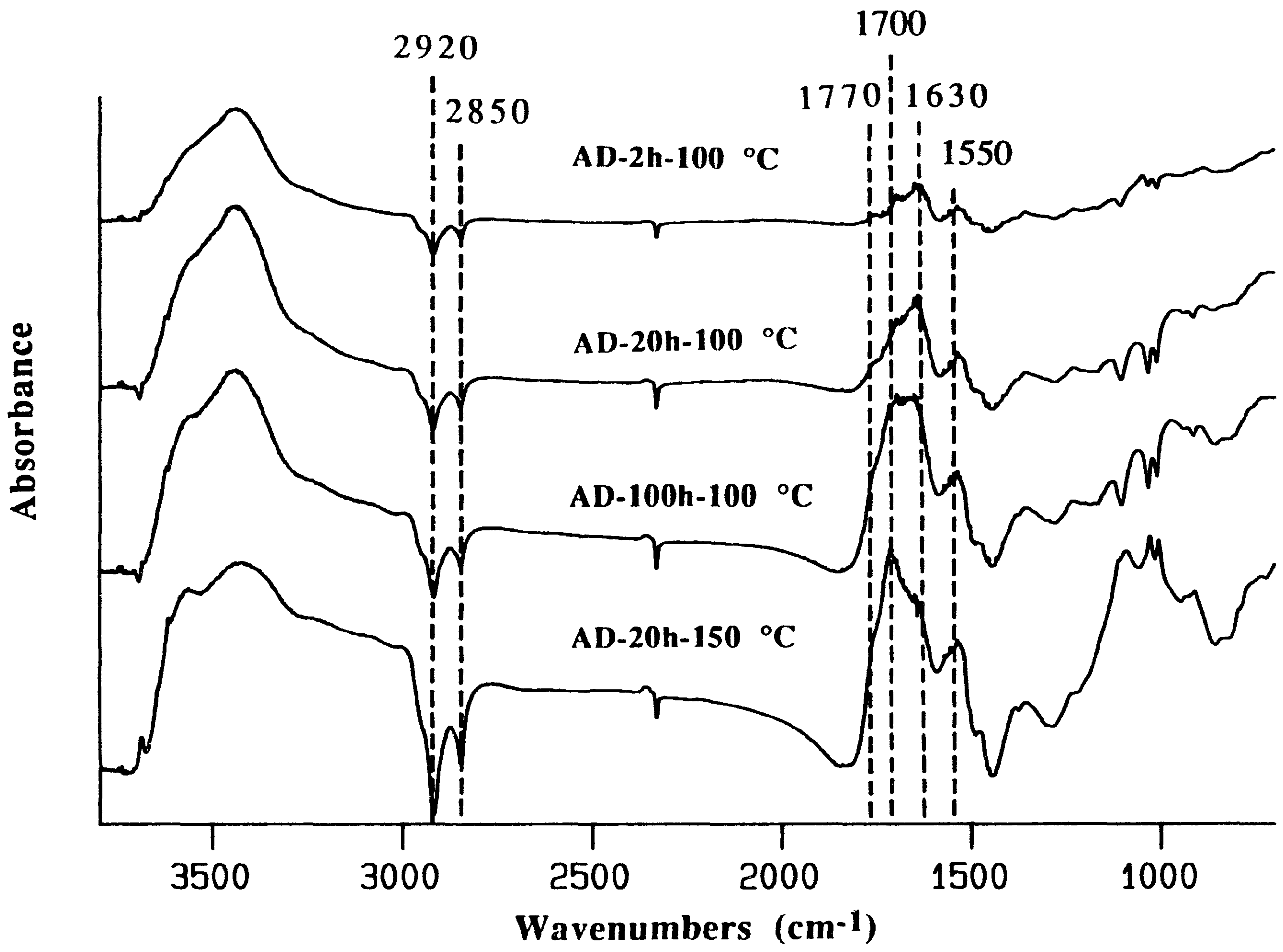
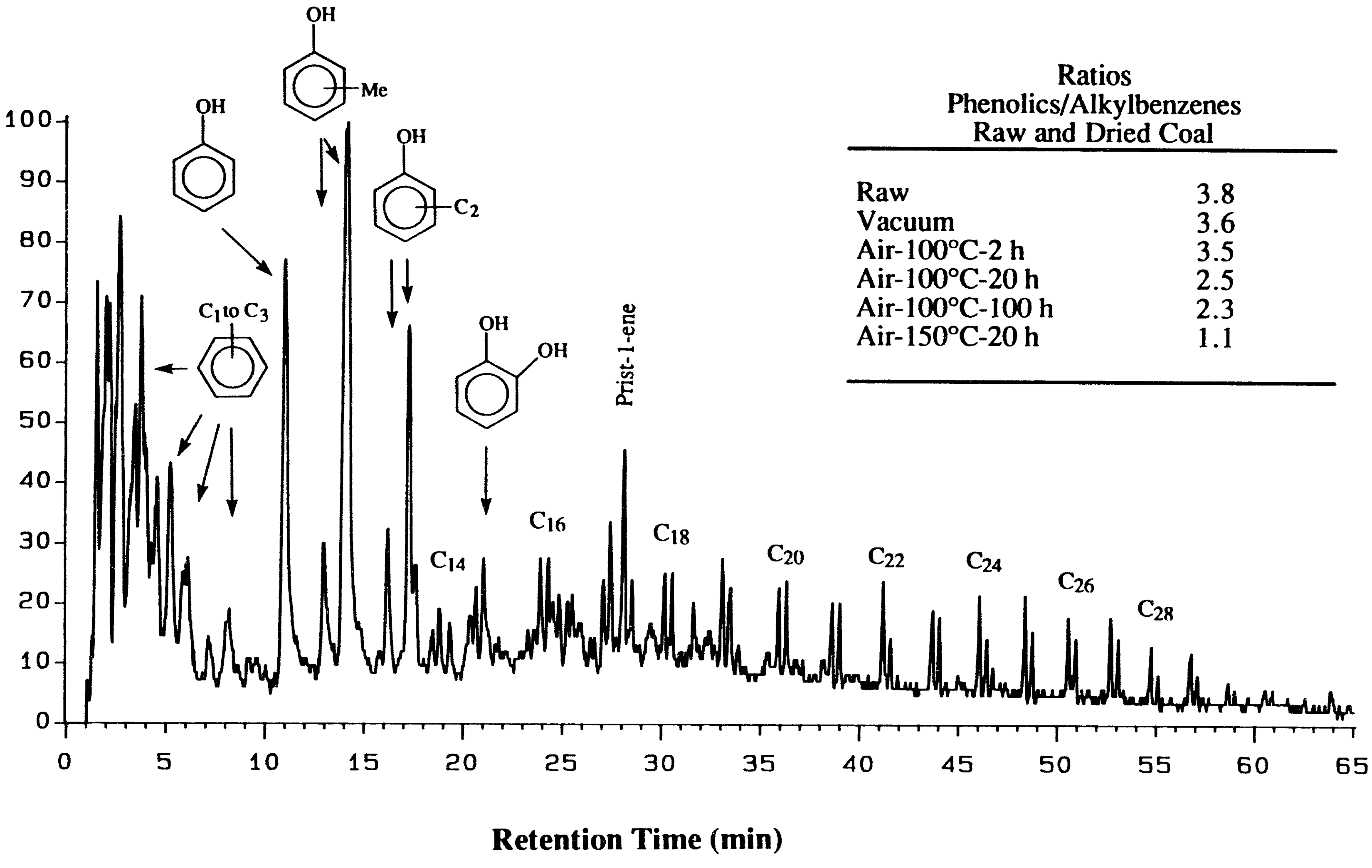


Figure 3. FT-IR difference spectra obtained by subtracting the spectrum of vacuum-dried DECS-8 coal (100 °C for 2 h) from the spectra of the four air-dried coals.



Ratios Phenolics/Alkylbenzenes Raw and Dried Coal	
Raw	3.8
Vacuum	3.6
Air-100°C-2 h	3.5
Air-100°C-20 h	2.5
Air-100°C-100 h	2.3
Air-150°C-20 h	1.1

Figure 4. Py-GC-MS total ion chromatogram of the raw DECS-8 coal, together with the area ratios of phenolic compounds to alkylbenzenes of the predried coals.

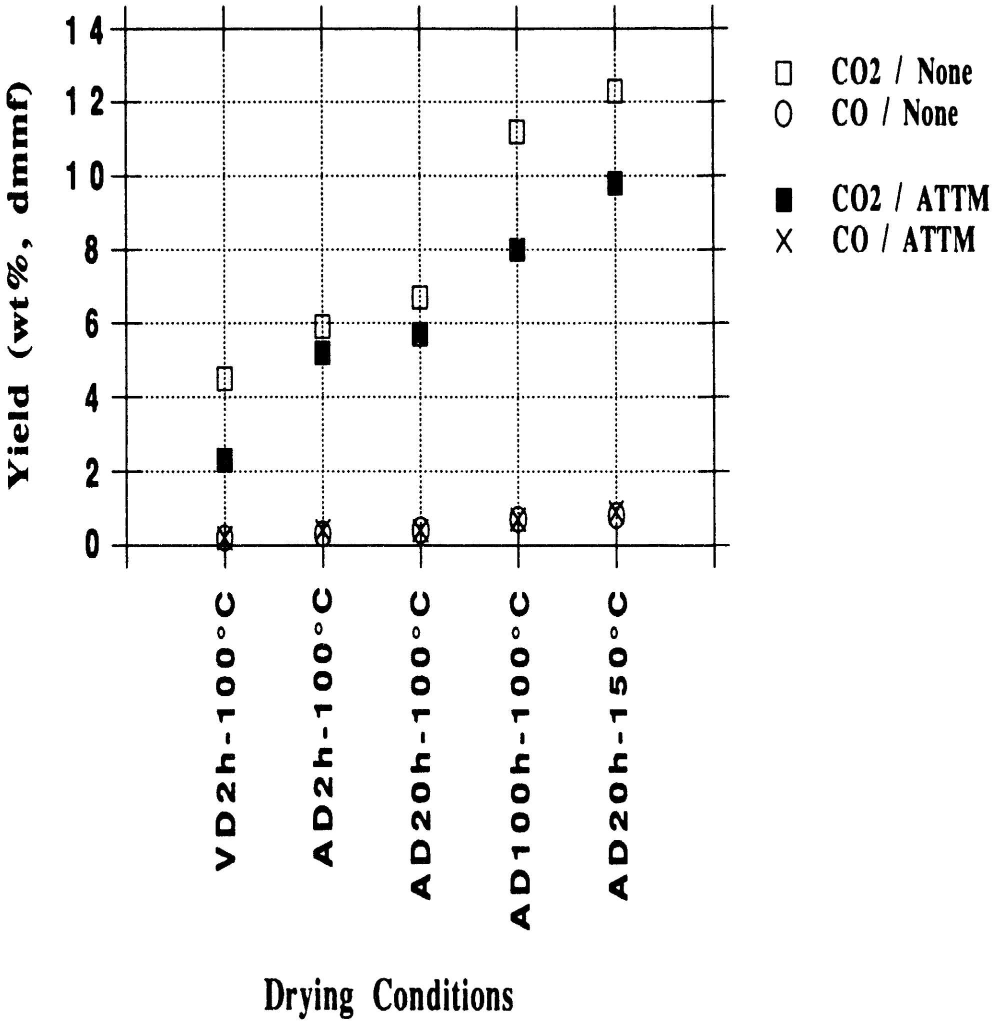


Figure 5. Yields of CO and CO_2 from solvent-free non-catalytic and catalytic (ATTM) liquefaction of DECS-8 coal at 350°C versus predrying conditions.

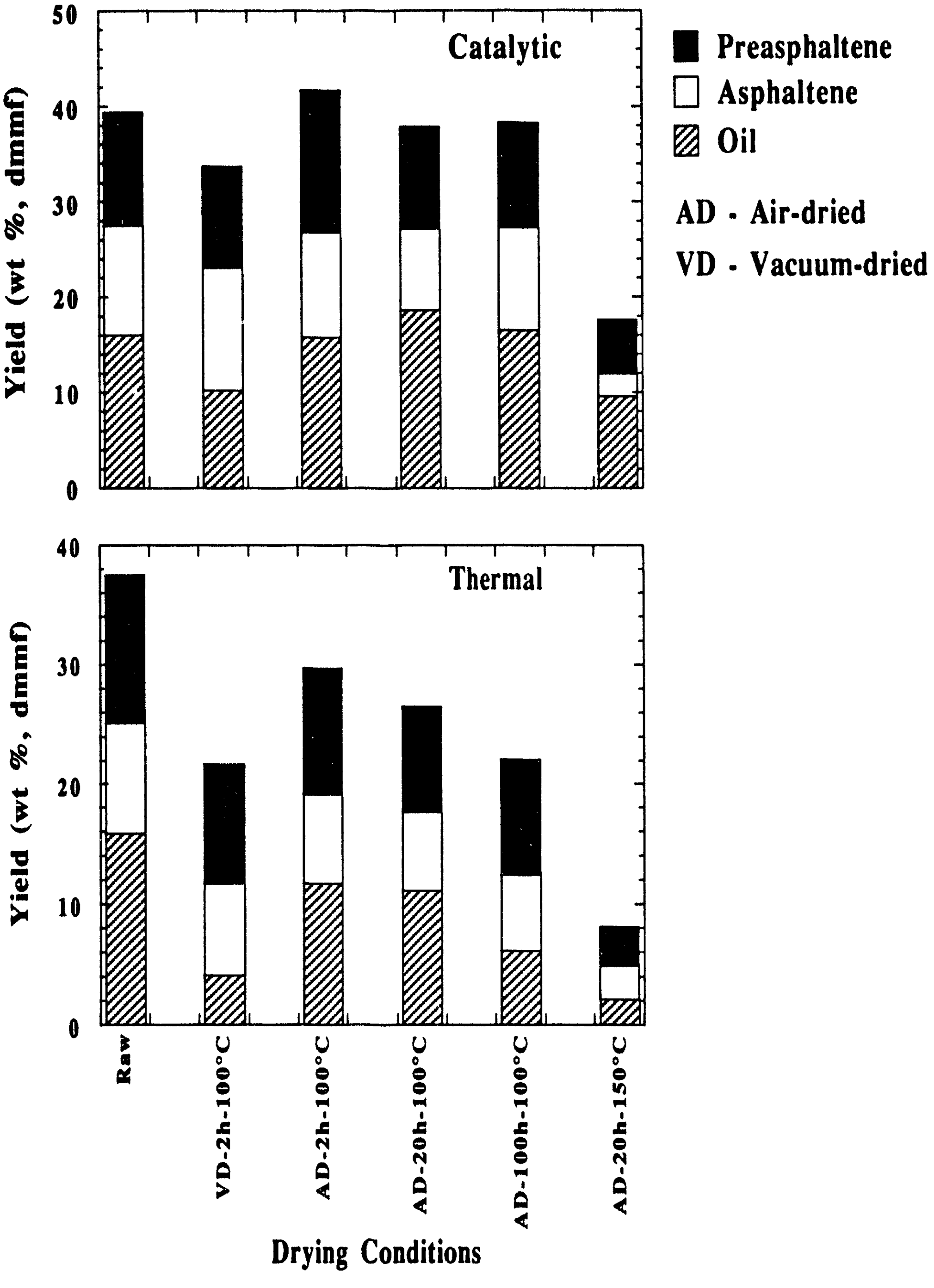


Figure 6. Yields of soluble products excluding gases for low-severity catalytic (top, with ATTM) and non-catalytic (bottom) liquefaction with tetralin solvent at 350°C.

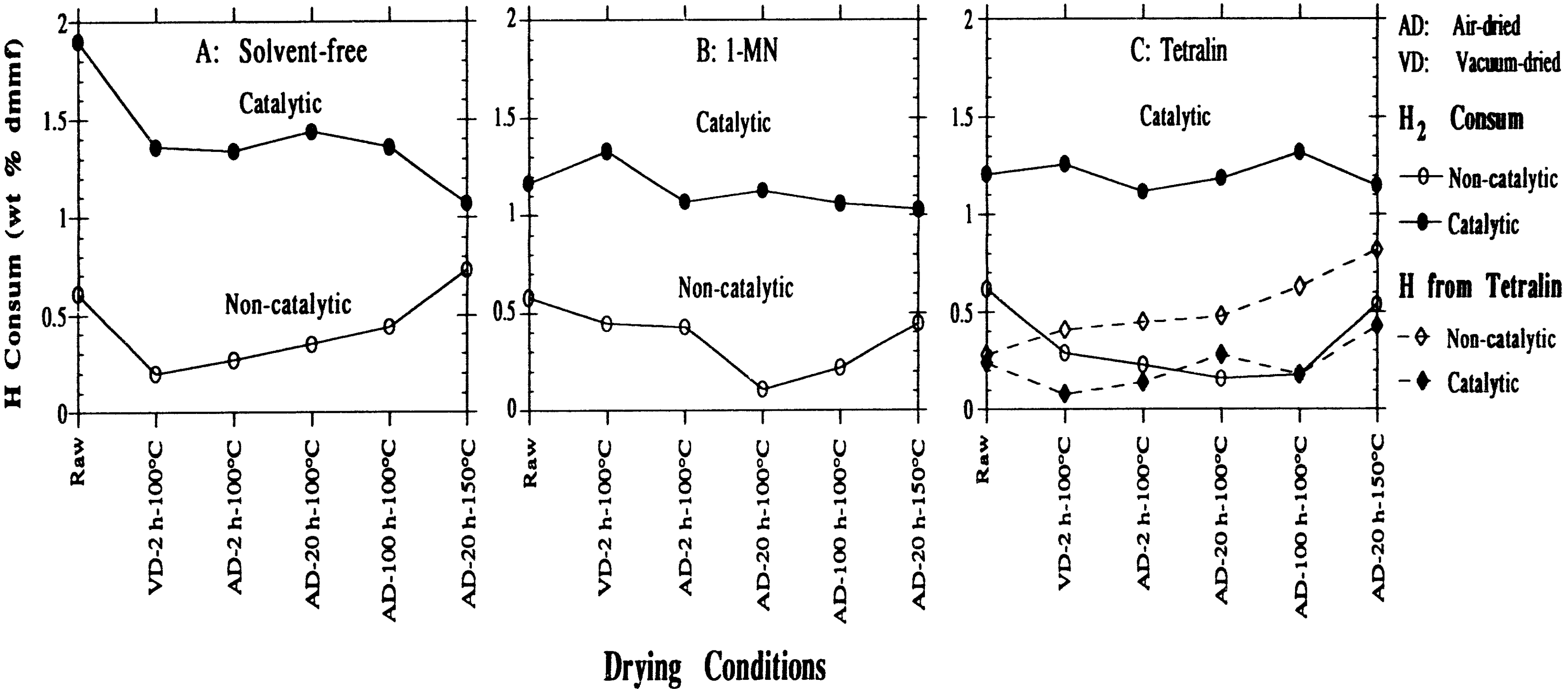


Figure 7. Effect of predrying Wyodak subbituminous coal on hydrogen consumption during its liquefaction at 350 °C with 6.9 MPa H_2 (cold).

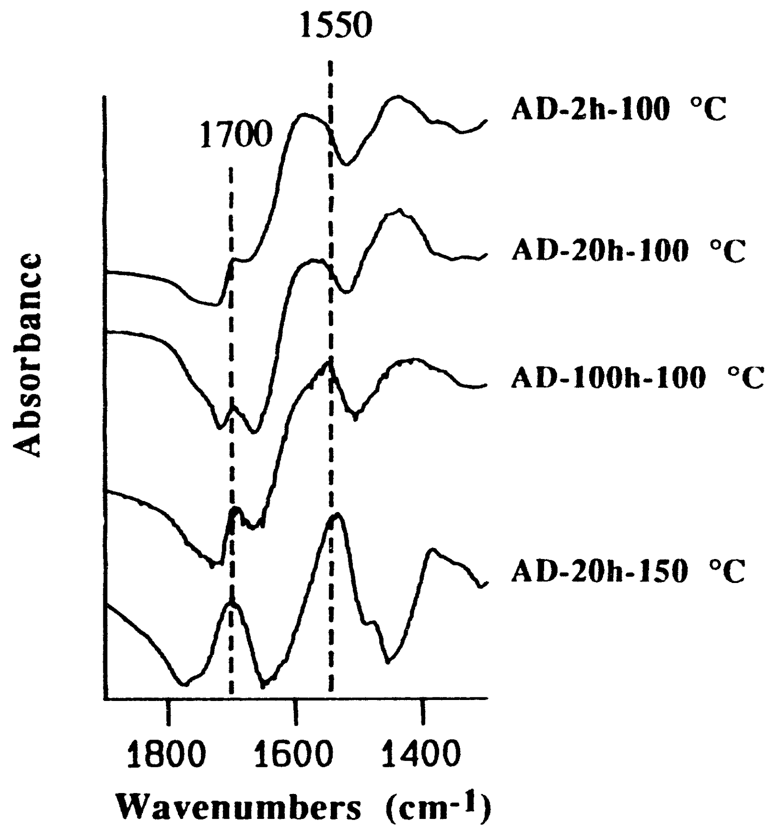


Figure 8 FT-IR difference spectra of liquefaction residues (1400-1800 cm^{-1} region: the spectra of residues of the air-dried coals — spectrum of residue of the vacuum-dried coal).

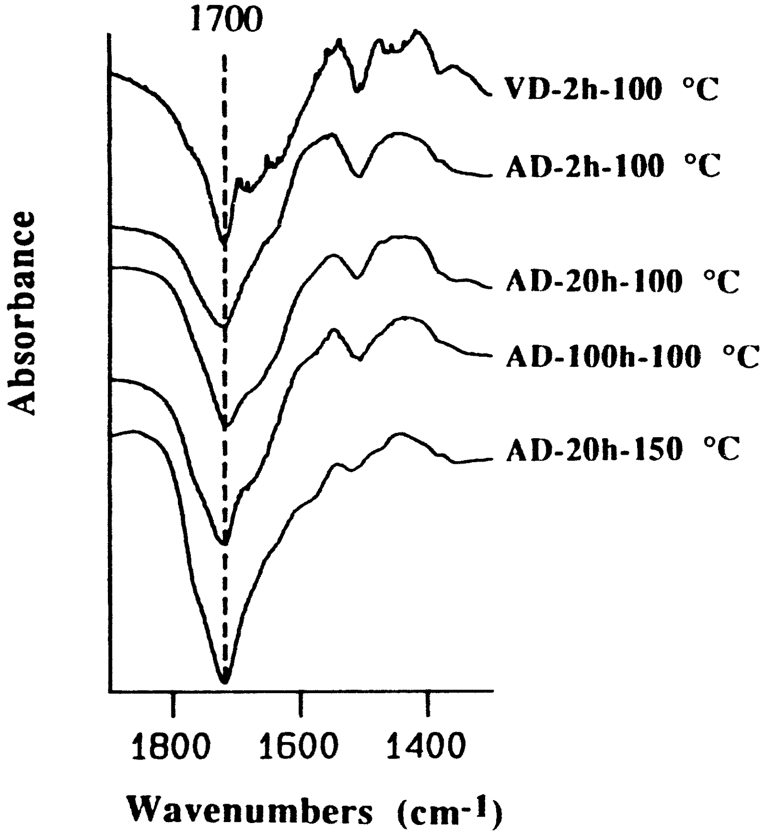


Figure 9 FT-IR difference spectra (1400-1800 cm^{-1} region) between liquefaction residues and coals (spectra of liquefaction residues — spectra of the corresponding predried coals).

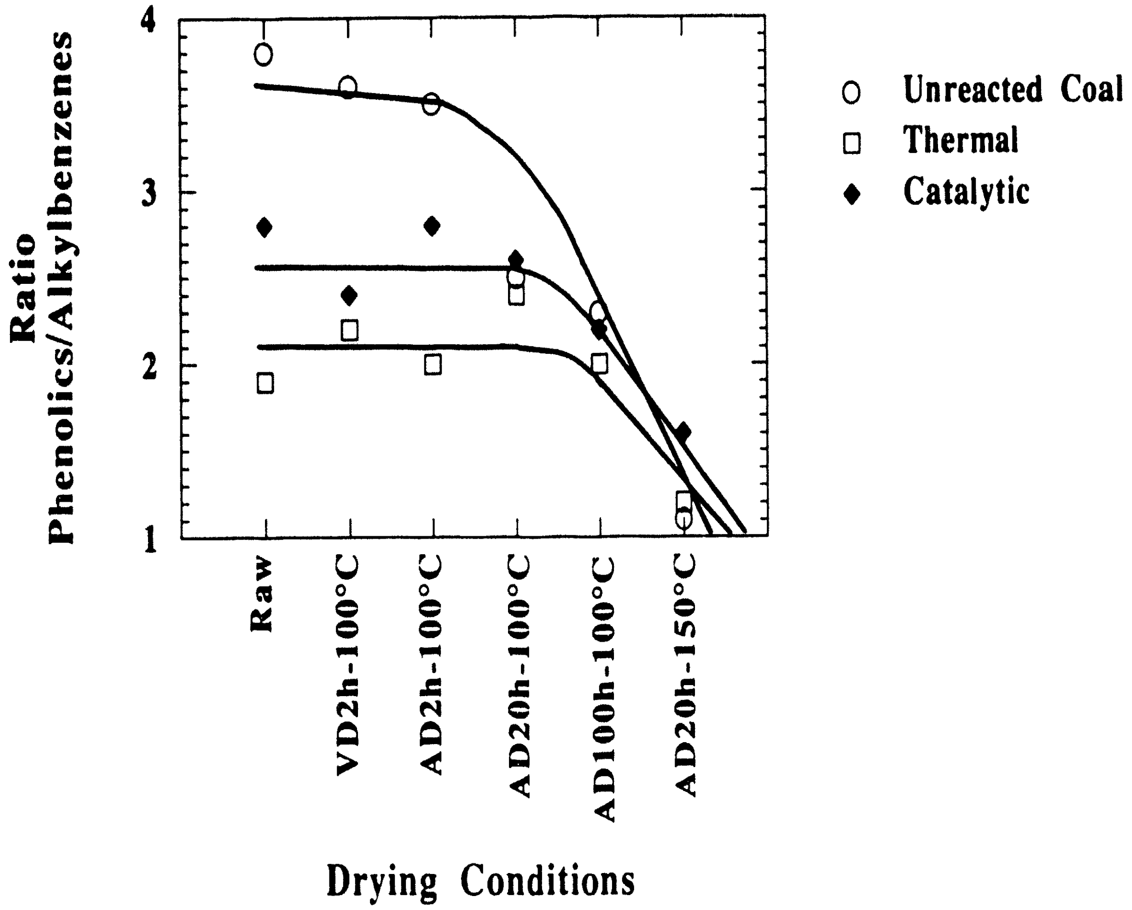


Figure 10 Changes in the ratio of phenolics/alkylbenzenes determined by Py-GC-MS for predried coals and their residues from solvent-free thermal and catalytic liquefaction at 350°C.

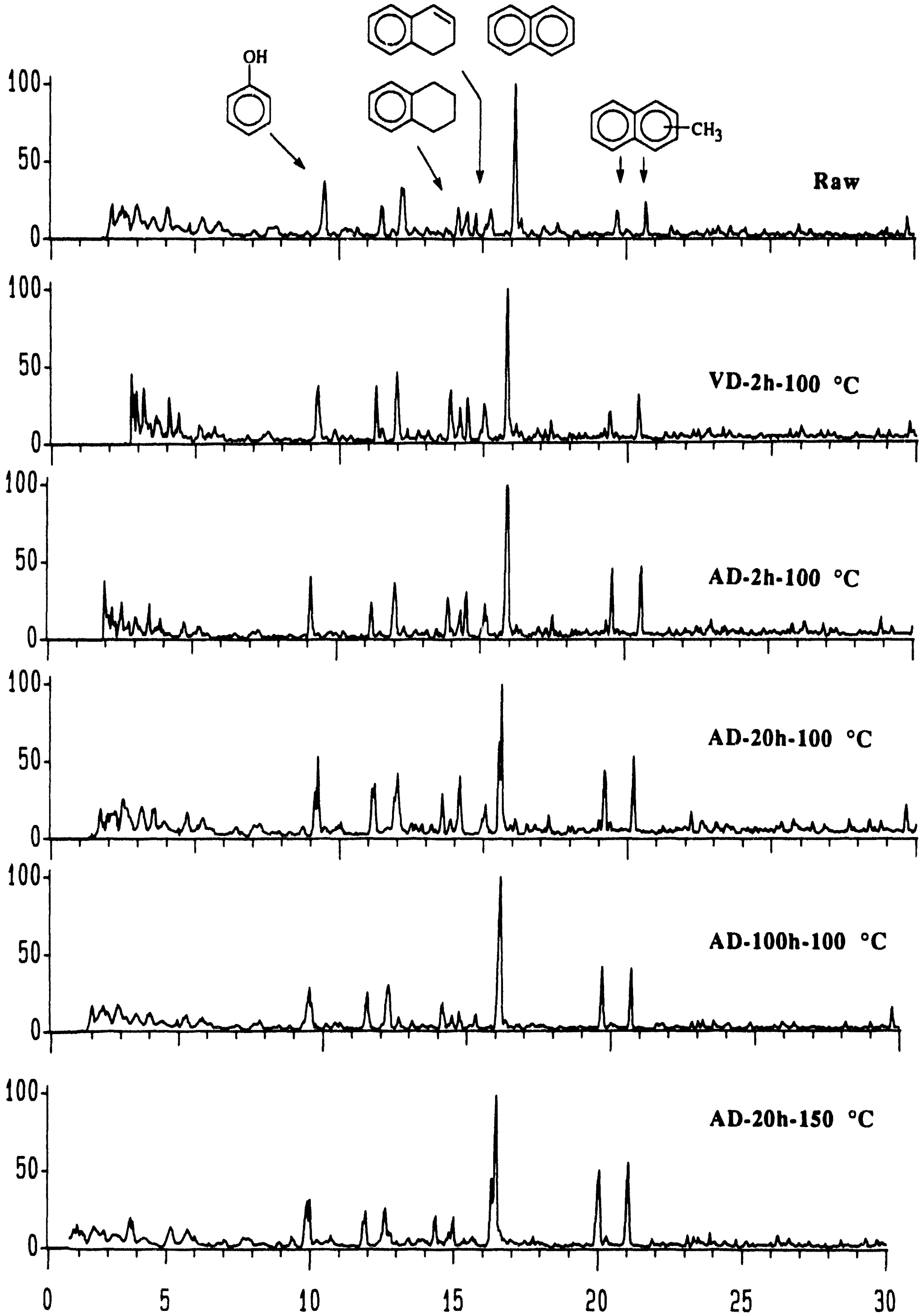


Figure 11 Py-GC-MS profiles for residues from non-catalytic liquefaction of raw and dried coals with tetralin solvent at 350°C.

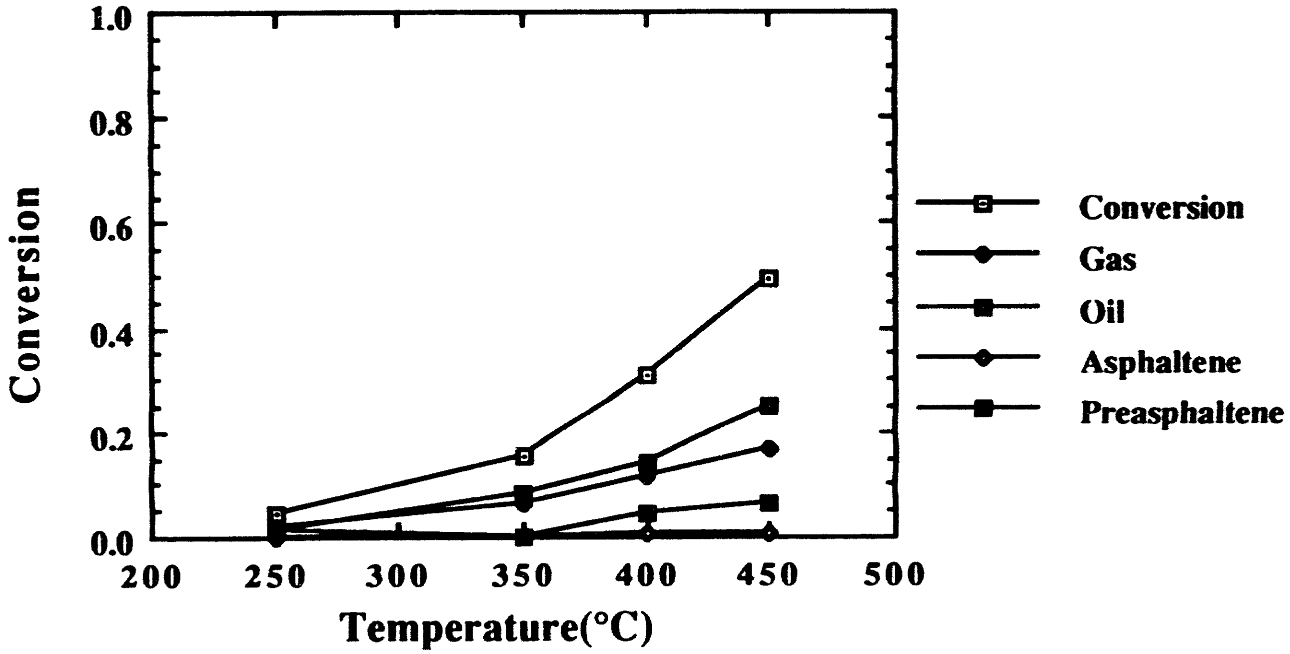


Figure 12.Conversion and yield of non-catalytic reaction with no solvent

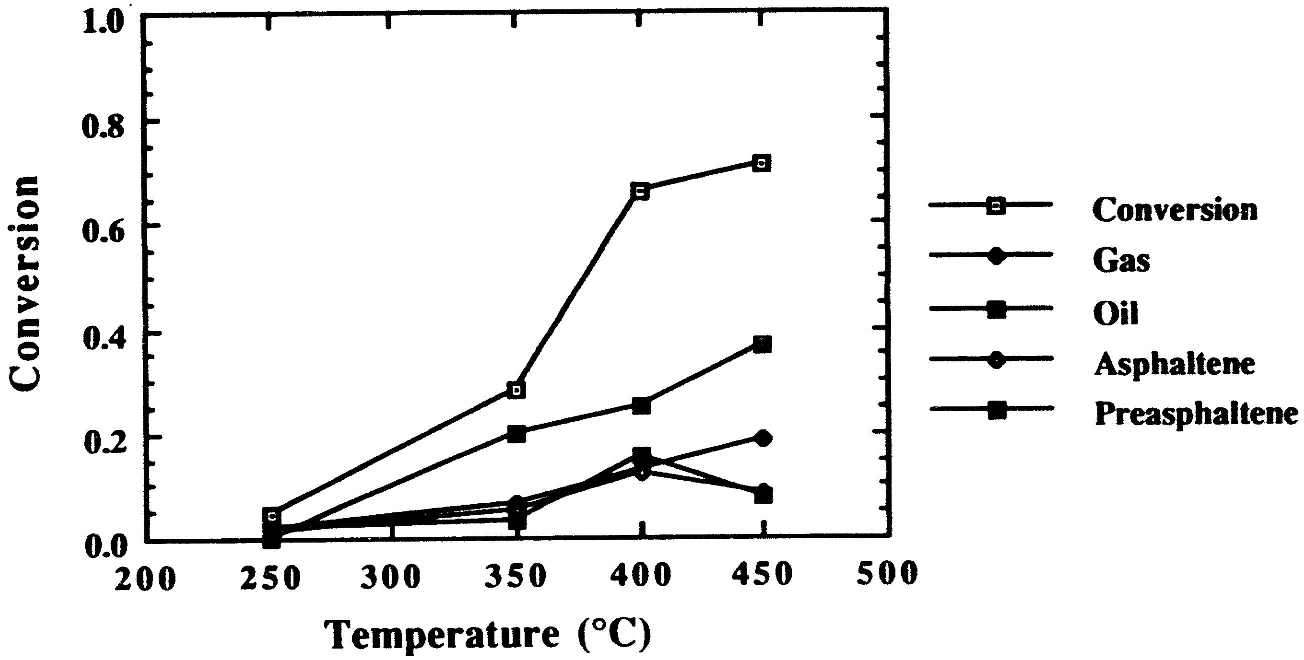


Figure 3 Conversion and yield of non-catalytic reaction with tetralin

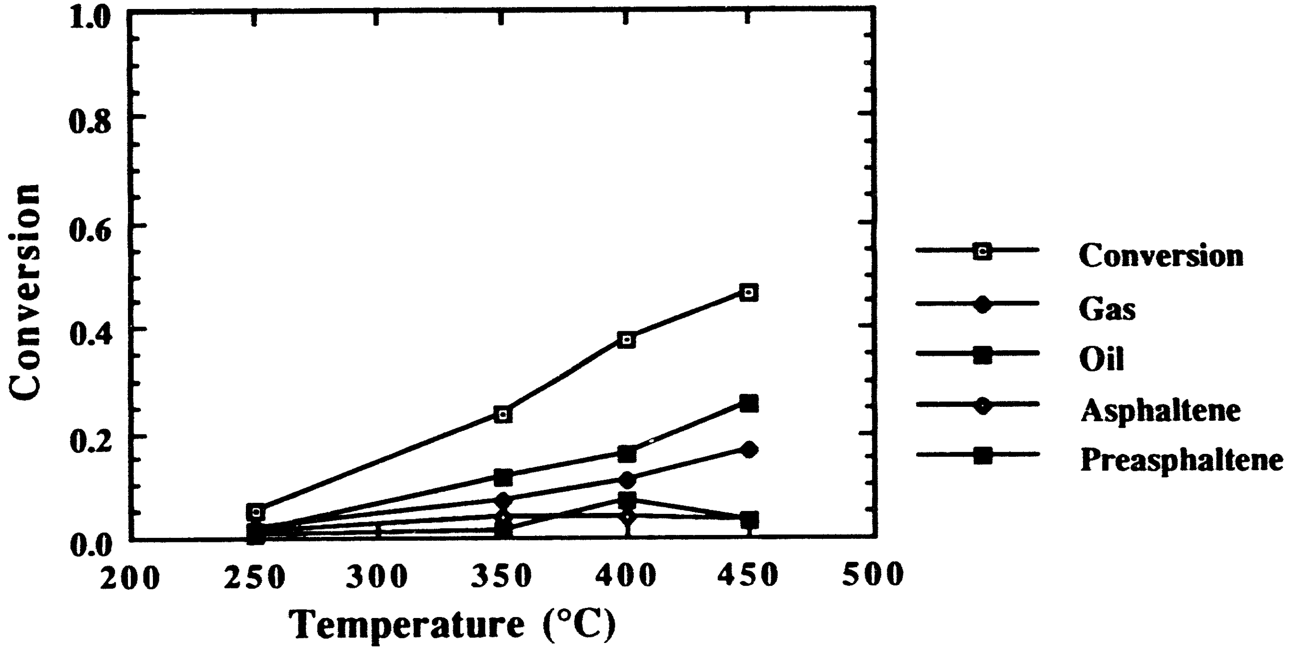


Figure 4. Conversion and yield of non-catalytic reaction with 1-MN

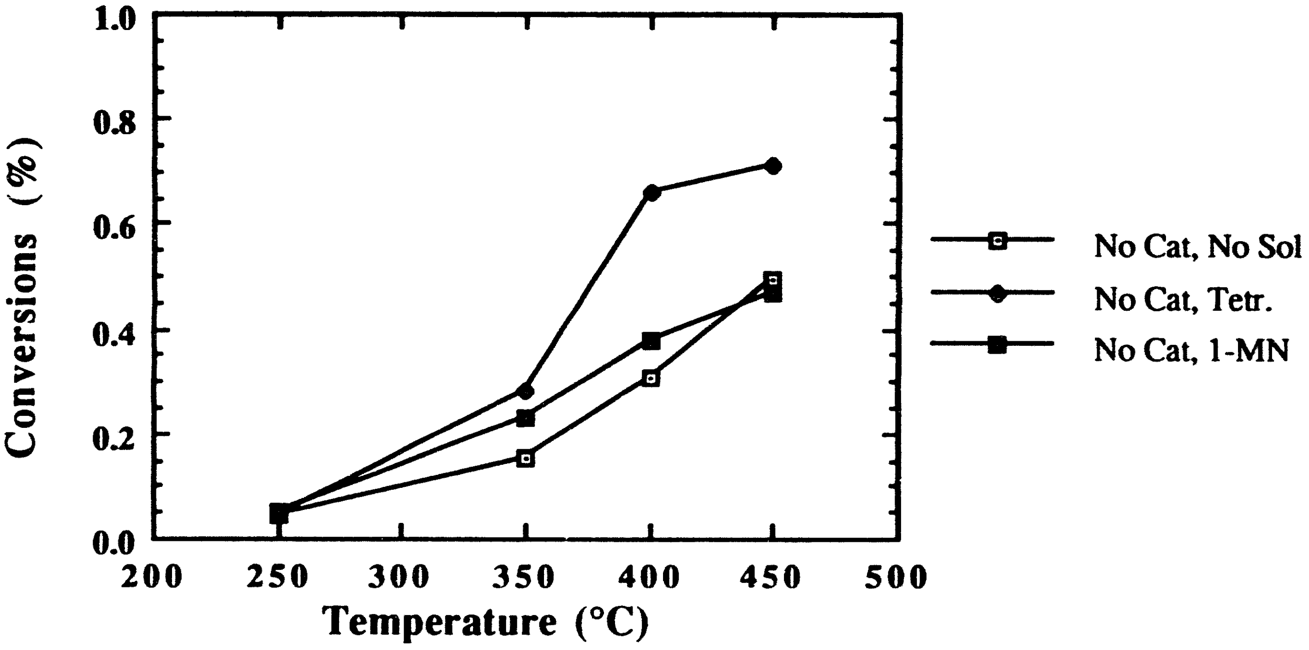


Figure 15 A comparison of non-catalytic reactions with different solvent

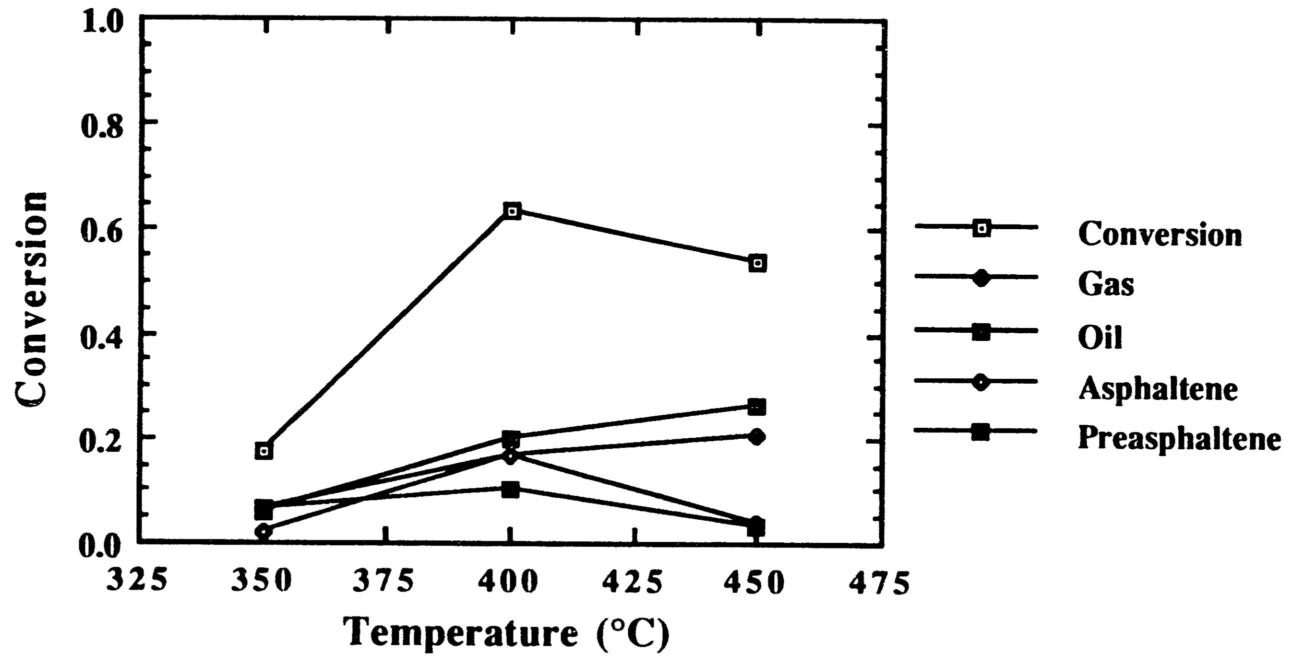


Figure 16. Conversion and yield of catalytic reactions with no solvent

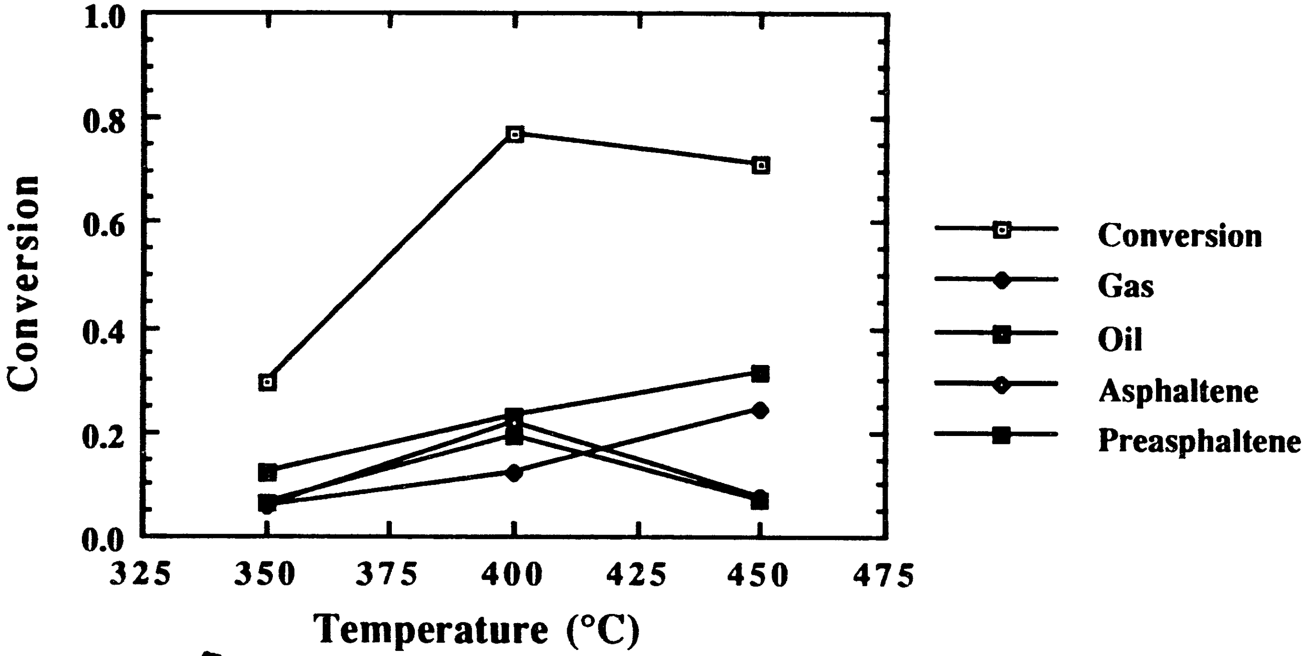


Figure 17. Conversion and yield of catalytic reactions with tetralin

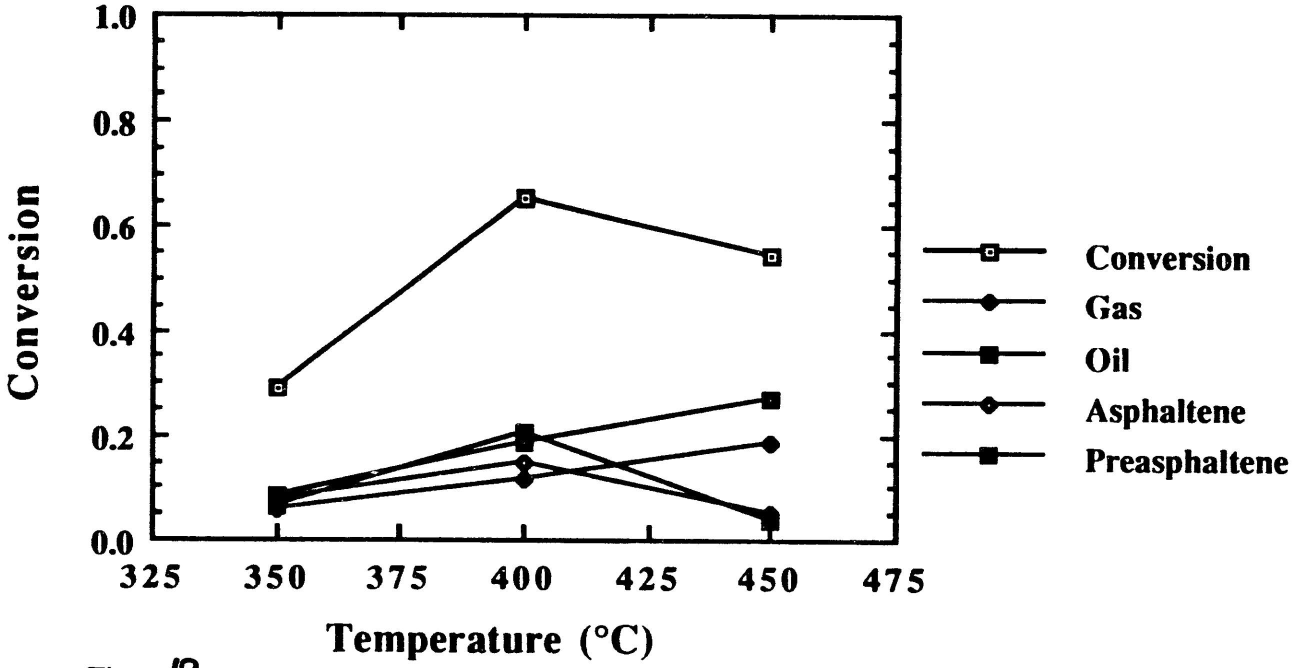


Figure 18 Conversion and yield of catalytic reactions with 1-MN

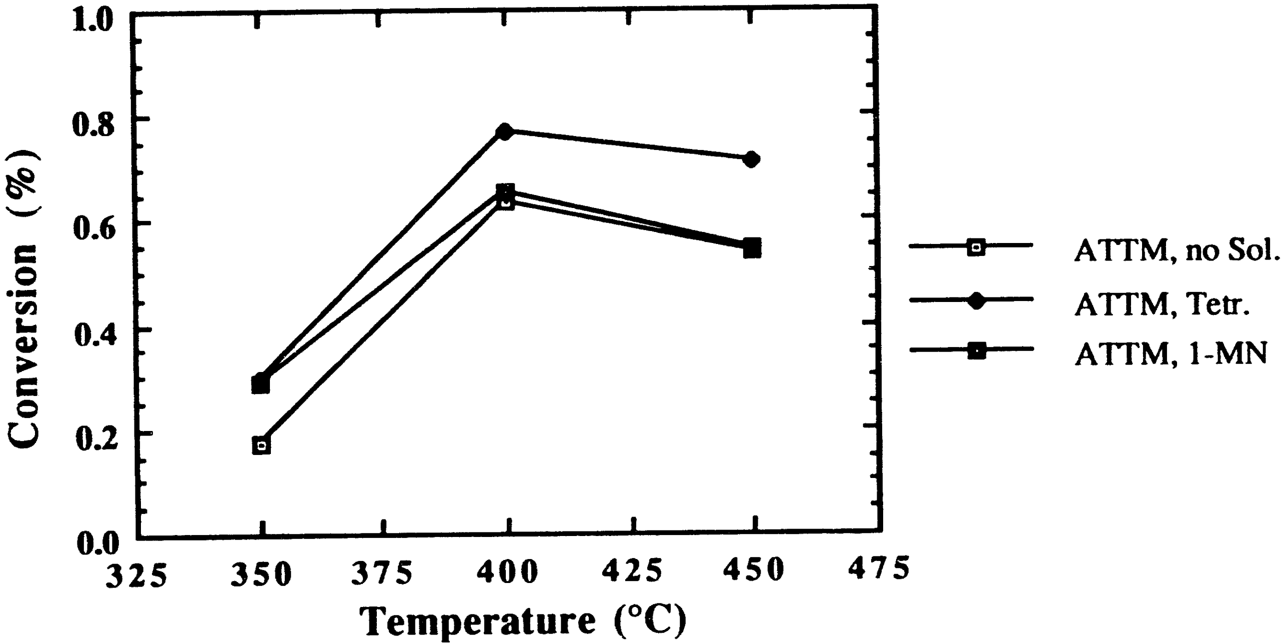


Figure 19. A comparison of catalytic reactions with different solvent

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