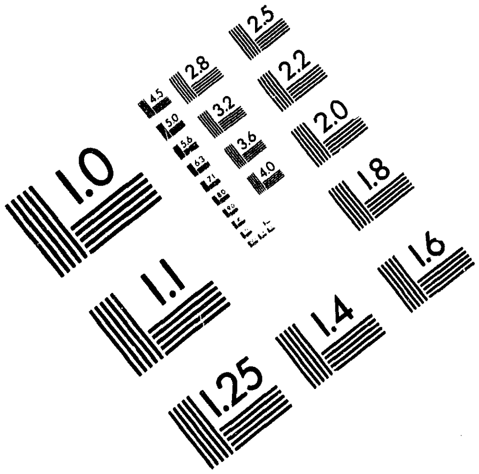

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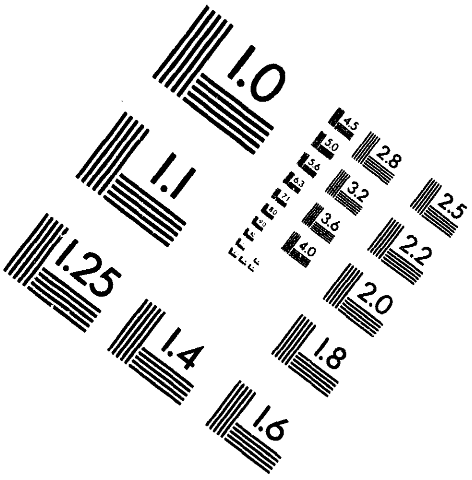

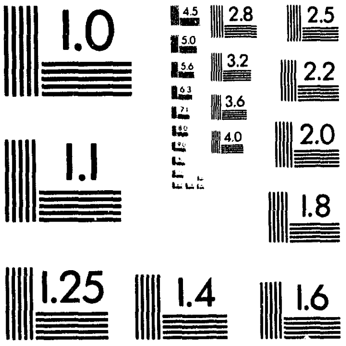

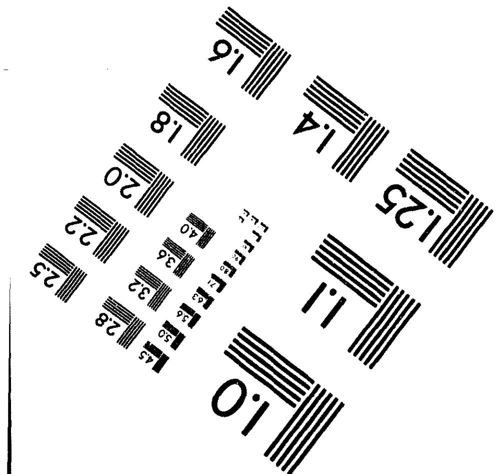

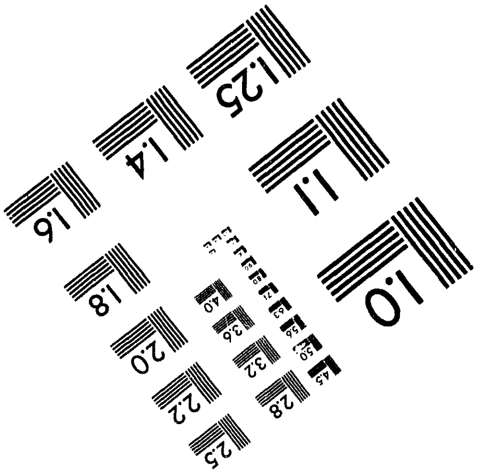

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Effects of Low-Temperature Catalytic Pretreatments on Coal Structure and Reactivity in Liquefaction

Technical Progress Report (Revised)
January - March 1994

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June 1994

Prepared for the U.S. Department of Energy
under Contract No.
DE-AC22-91PC91042

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ACKNOWLEDGEMENTS

This on-going project is supported by the U.S. Department of Energy, Pittsburgh Energy Technology Center, in Advanced Coal Research Program. Currently Dr. M.A. Nowak is DOE/PETC Project Manager; Dr. M. J. Baird was the project manager during the first three quarterly periods. Drs. H.H. Schobert, C. Song and P.G. Hatcher are the Co-Principal Investigators at Penn State. The authors wish to express their appreciation to Drs. M.A. Nowak, M. J. Baird, S. Lee, and E. B. Klunder of DOE/PETC for their support of this effort. The authors would also like to thank Dr. A. Davis and Mr. D. Glick for providing coal samples and data from DOE/Penn State Coal Sample Bank, and Mr. R.M. Copenhaver for the fabrication of tubing bomb reactors.

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ABSTRACT

Residues of two subbituminous coals from their liquefaction at 300-425°C were analyzed using cross-polarization magic-angle-spinning (CPMAS) and dipolar dephasing (DD) solid-state ^{13}C NMR techniques. The DDMAS and CPMAS NMR analysis of a Montana subbituminous coal (DECS-9) indicate that it has 63-64% aromatic carbons among total carbons; 34-35% of the aromatic carbons are protonated carbons, and 23-24% of the aromatic carbons are oxygen-bound carbons, with the remaining 31-33% bound primarily to other carbon atoms. CPMAS ^{13}C NMR spectrum of Wyodak subbituminous coal (DECS-8) is similar to that of Montana subbituminous coal (DECS-9).

CPMAS ^{13}C NMR of the residues from DECS-9 coal revealed that catechol-like structures and phenolic structures in the coal are thermally sensitive and diminish gradually with increasing temperature. The carbon aromaticity increased monotonically with increasing reaction temperature, whereas hydrogen aromaticity reached a maximum for residue from a 300°C run and then decline with further increase in temperature. The increase in carbon aromaticity is mainly driven by temperature, rather than by the adduction of aromatic solvents. DDMAS NMR analysis indicates that the degree of protonation of aromatic carbons decreased from 35% (for THF-extracted but unreacted DECS-9 coal) to 13% (for residue from a non-catalytic run) with increasing reaction temperature up to 375°C.

DDMAS ^{13}C NMR of the residues from DECS-8 Wyodak coal revealed that the degree of protonation of aromatic carbons (f_a^{aH}) is lower with the residues from catalytic liquefaction at 350°C. These results were surprising, as f_a^{aH} values usually decrease with increasing degree of condensation. However, if this is the case, this decrease should be accompanied by the increase in f_a values. It is possible that, relative to the residues from non-catalytic runs, the lower f_a^{aH} values for residues from catalytic runs were due to hydrogenation of the aromatic rings to form hydroaromatic rings.

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

CPMAS AND DDMAS ^{13}C NMR ANALYSIS OF COAL LIQUEFACTION RESIDUES

INTRODUCTION

We have shown in previous papers that spectroscopic analyses of liquefaction residues (by NMR, pyrolysis-GC-MS, and FT-IR) can provide important structural information which can be used for elucidating the chemical reactions of liquefaction (Song et al., 1992, 1993, 1994) as well as the effects of dispersed catalysts (Saini et al., 1992; Huang et al., 1993; Song et al., 1994). The work reported in this quarterly involves solid-state ^{13}C NMR studies of residues of two subbituminous coals from their liquefaction at 300-425°C, using cross-polarization (CP), dipolar dephasing (DD) and magic-angle-spinning (MAS) techniques. A preliminary survey of some CPMAS ^{13}C NMR results for one of the two coals was presented previously (Song et al., 1993). In a companion paper, we report on the analysis of oils from liquefaction of these coals by two-dimensional HPLC and GC-MS (Saini and Song, 1994).

EXPERIMENTAL

Sample Preparation

Three types of samples were examined in this study. The first set of samples are THF-insoluble residues from temperature-programmed liquefaction (TPL) of a Montana subbituminous coal (DECS-9) in tetralin solvent at a final temperature ranging from 300°C to 425°C for 30 min (Song et al., 1992). The second set of samples are THF-insoluble residues from liquefaction of a Wyodak subbituminous coal (DECS-8) at 350°C with and without a solvent in the absence and presence of a dispersed molybdenum sulfide catalyst (Song et al., 1994). The coals were predried in vacuum at about 100°C for 2 h prior to liquefaction. The third set of samples are the fresh raw coals (DECS-8, DECS-9) and THF-extracted but unreacted coals. Our experience shows that trace amounts of THF always remain in the THF-extracted residues even after vacuum drying at 100°C for over 6 h, which interferes with spectroscopic analysis. We have solved the problem by washing the residue first with acetone, then with pentane, followed by vacuum drying at 100°C for 6 h prior to spectroscopic analysis. The residue samples were also subjected to elemental analysis.

Solid-State ^{13}C NMR

NMR spectra were acquired on a Chemagnetics M-100 spectrometer. The measurements were carried out at a carbon frequency of 25.035 MHz. The spectrometer performance was checked with a standard sample of hexamethylbenzene to assure the Hartman-Hahn match. In a typical analysis, about 0.4-0.6 g of a sample was packed in a 0.4 mL bullet-type rotor made of polychlorotrifluoroethylene (Kel-F). Kel-F does not have a CPMAS ^{13}C signal. The MAS speed of the rotor was about 3.5 kHz.

The CPMAS ^{13}C NMR spectra were obtained by using the combined high power proton decoupling, cross-polarization, and magic angle spinning techniques. The experimental conditions for all the samples are as follows: a cross-polarization contact time of 1 msec, a pulse delay time of 1 sec, 50 kHz of proton decoupling, sweep width of 14 kHz, and 20-30 Hz line broadening. Carbon aromaticity was determined by integrating the peaks between 95 and 165 ppm (ppm relative to tetramethylsilane). Spinning sideband intensity was distributed for aromatic carbons. Other details concerning CPMAS maybe found elsewhere (Hatcher , 1987).

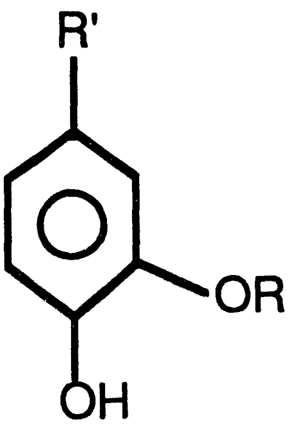
Dipolar-dephasing ^{13}C NMR spectra (DDMAS) were acquired by using the pulse sequence described by Alemany et al. (1983) and Wilson et al. (1984). After the protons are spin-locked and cross-polarization is induced, a variable dephasing time T_{dd} is inserted, during which the high-power decoupler is turned off. During this period, which lasts from 5 to 180 μsec, carbon magnetization becomes influenced and diminished (dephased) by the strong dipolar interactions between ^{13}C and ^{1}H spins. Carbons directly bonded to hydrogens (protonated carbons) dephase much more rapidly than those without attached hydrogens (non-protonated carbons). More details about the theory and procedures of dipolar dephasing may be found elsewhere (Hatcher, 1987, 1988; Pan and Maciel, 1993). In general, protonated carbons dephase within the first 60 μsec (T_{dd}), and the signals remain after 60 μsec are due to non-protonated carbons.

RESULTS AND DISCUSSION

Structural Characteristics of THF-extracted Coals

Figure 1 shows the CPMAS and DDMAS ^{13}C NMR spectra of THF-extracted but unreacted Montana subbituminous coal (DECS-9). In the CPMAS spectrum, there are two major bands, an aromatic bands from 95 to 165 ppm and an aliphatic band from 0 to 80 ppm. Among the aliphatic bands, methyl carbons appear at 0-25 ppm, methylene carbons resonate between 25-51 ppm, methoxyl groups around 51-67 ppm and ether groups between 67-93 ppm (Yoshida et al., 1987). The aromatic region includes two shoulders which may be attributed to catechol-like oxygen-bound carbons (centered around 142-144 ppm) and phenolic carbons (centered around 152-154 ppm). There are two other bands with lower intensities, including carboxyl groups between 170-190 ppm and ketonic carbonyl groups between 190-230 ppm.

DDMAS ^{13}C NMR was used to examine the degree of protonation of carbons. Protonated carbons decay at a rate that is dependent on T_{dd}^2 and is often referred to as the Gaussian component of signal decay; non-protonated carbons decay at a much slower rate that is exponential with respect to T_{dd} (Alemany et al., 1983). Compared to the CPMAS spectrum , signal decay in the 95-165 ppm region was due mainly to protonated aromatic carbons (95-130 ppm). The signal intensity remaining in the aromatic region in the DDMAS spectrum in Figure 1 can be attributed to bridgehead and substituted aromatic carbons (130-148 ppm) and oxygen-bound aromatic carbons (140-165). Apparently, the shoulders that we identified as catecholic (structure I) and phenolic (structure II) carbons remain in the DDMAS structure and are clearly non-protonated carbons.



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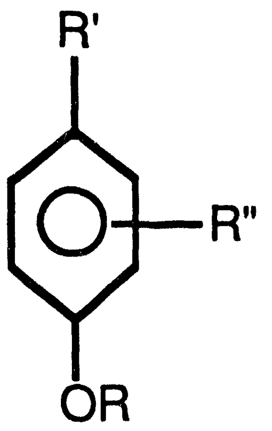

Str. II

Our assignment of the peak centred at 142-144 ppm in the DDMAS spectra is different from that of Pan and Maciel (1993). They assigned the 144 ppm peak for Beulah-Zap lignite (801) to an aniline-type aromatic carbon. We have assigned this peak to the catecholic oxygen-bound aromatic carbon (shown in structure I). This is based on the NMR spectra of lignin-related model compounds and lignin (Hatcher, 1987) and the combined CPMAS NMR and pyrolysis-GC-MS studies of low-rank coals, including DECS-9 (Song et al., 1993) and DECS-8 (Saini et al., 1992) coals used in this work, as well as a lignite (Wenzel et al., 1993).

Flash pyrolysis GC-MS of lignites (Hatcher et al., 1988; Wenzel et al, 1993), DECS-9 Montana coal (Song et al., 1993), and DECS-8 Wyodak coal (Saini et al., 1992) revealed that catechol and phenol as well as their homologs are important components in the pyrolyzates of low-rank coals. Another important evidence is that as catechol observed in the pyrolysis-GC-MS diminishes, so does the catecholic peak in the CPMAS ^{13}C NMR spectra (Hatcher et al., 1988; Song et al., 1993; Wenzel et al., 1993).

Quantitative CPMAS NMR analysis of Montana coal was performed by means of curve-fitting, as described in our recent paper (Song et al., 1993). This coal has 63-64% aromatic carbons among total carbons. Combination of DDMAS and CPMAS NMR data reveals that about 34-35% of the aromatic carbons are protonated carbons; 23-24% of aromatic carbons are chemically bound to oxygen atoms; the remaining 31-33% aromatic carbons are bound primarily to other carbon atoms and secondarily to nitrogen and sulfur. The above spectroscopic results suggest that the Montana coal contains approximately two or three protonated carbons, one or two oxygen-bound carbons, and two substituted or bridgehead carbons per aromatic ring.

Compared to the Montana coal, THF-extracted Wyodak subbituminous coal (DECS-8) has a lower aromaticity (57%). However, it also has all the characteristic peaks (aliphatic, aromatic, carboxyl, carbonyl) and shoulders (phenolic, catecholic) that DECS-9 Montana coal possess (Figure 1). The DDMAS ^{13}C NMR data indicate that about 29% of the aromatic carbons in the THF-extracted Wyodak coal (DECS-8) are protonated carbons. The curve-fitted CPMAS ^{13}C NMR data are not available for this sample at the present time.

Characterization of Residues from Non-Catalytic Liquefaction

Table 1 shows the carbon aromaticities of unreacted coal and residues from DECS-9 Montana coal determined by CPMAS ^{13}C NMR, and the degree of protonation of aromatic carbons determined by DDMAS ^{13}C NMR. Figure 2 presents the CPMAS and DDMAS ^{13}C NMR spectra of THF-insoluble residue from non-catalytic TPL of a Montana subbituminous coal (DECS-9) in the presence of tetralin solvent at a final temperature of 350°C for 30 min. Details of TPL procedures and results may be found elsewhere (Song and Schobert, 1992). Comparative examination of DDMAS data indicates at least three trends. First, relative to the THF-extracted unreacted coal, non-protonated carbons contribute more to the aromatic band in the residue from 350°C run. Second, the catecholic peak almost disappeared after 30 min at 350°C. Third, phenolic peak does not diminish as much as the catecholic peak upon reaction at 350°C, as can be seen by comparing the two DDMAS spectra (Figures 1 and 2).

Figure 3 shows the CPMAS and DDMAS ^{13}C NMR spectra of THF-insoluble residue from non-catalytic reaction of a vacuum-dried Wyodak subbituminous coal (DECS-8) in the absence of any solvent at 350°C for 30 min under 6.9 MPa H_2. Since no donor solvent or catalyst was used, the coal conversion is very low, only about 12.5 wt%. More liquefaction results of this coal are described elsewhere (Song et al., 1994). The characteristics of both CPMAS and DDMAS spectra of this sample resemble those of the corresponding spectra for residue from Montana coal (Figure 2), although the two samples were derived from different coals under different conditions.

The reaction temperature has the most significant impact on the spectral characteristics of the liquefaction residues. We have performed both DDMAS and CPMAS ^{13}C NMR analysis of the THF-insoluble residues from TPL reactions of Montana coal (DECS-9) at 300, 350°C, 375, 400 and 425°C for 30 min. Catechol-like structures were found to be thermally sensitive and diminish gradually with increasing temperature up to 350°C. The catecholic shoulder at 142-144 ppm disappears from the residue of 375°C run. Carboxyl (165-190 ppm) and carbonyl (190-230) peaks diminish significantly after 375°C and they disappear in the spectrum of residue from 400°C run. Phenolic structures diminish with increasing temperature up to 425°C. These results clearly indicate that there are thermally reactive oxygen functional groups in coal and their reactions can take place at temperatures as low as 300-375°C.

As shown in Figure 4, the carbon aromaticity of residues increased monotonically with increasing reaction temperature after 300°C. Comparison of the curve for H/C atomic ratio and that for carbon aromaticity indicates that THF extraction of unreacted coal and that reacted at 300°C, removed more aliphatic materials. However, the conversion level at 300°C in tetralin is below 10 wt% (dmmf). The H/C ratio of the residues decreased significantly with increasing temperature up to 425°C. The aromaticity of the residues increased with increasing coal conversion, being consistent with the observations by two other groups on residues from liquefaction (Fatemi-Badi et al., 1991; Franco et al., 1991). The increase in carbon aromaticity is driven primarily by temperature, and secondarily by the adduction of aromatic solvent molecules (Song et al., 1993, 1994). Another interesting observation is that, while the total aliphatic carbons decrease, the percentage methyl carbons relative to total aliphatic carbons increases with increasing temperature up to 425°C.

DDMAS analysis (Figure 5) shows that the degree of protonation of aromatic carbons in the residues decreased from 35% (for THF-extracted but unreacted Montana coal) to 13% for residue from the non-catalytic run at final reaction temperature of 375°C. General trends observed from DDMAS experiments for residues from DECS-9 are as follows. The degree of protonation of aromatic carbons in the residue decreases with increasing coal conversion. In other words, the higher the coal conversion into THF-soluble products, the more non-protonated aromatic carbons in the THF-insoluble residues. The higher content of non-protonated carbons among total aromatic carbons could originate from either higher degree of condensation or higher extent of substitution. Since the aromaticity increases and atomic H/C ratio decreases with increasing temperature, the decrease in the relative content of protonated aromatic carbon (or the increase of non-protonated aromatic carbons) is due mainly to the increased degree of condensation. This means that there are more bridgehead aromatic carbons or more condensed-ring aromatic structures in the residues from runs at higher temperatures.

As discussed above, there exists good correlation between carbon distribution and reaction temperature above 300°C. We have attempted mathematical correlation of the NMR data for the residue with reaction temperature (Song et al., 1993). Figure 6 shows that the changes in the aromatic, aliphatic, and oxygen-bound carbons of the residues can be related to the liquefaction temperature by a linear correlation. A general expression is given below:

$$C_i = \alpha f_i + \beta T \qquad \text{for specific carbon type } i \qquad (1)$$

where T is reaction temperature (°C), f_i and C_i represent the content of specific carbons (%) in the original coal and residue, respectively, and α and β are constants. The specific correlations for aromatic C (C_{ar}), aliphatic C (C_{ali}), and oxygen-bound carbons (C_{O-C}) are given in Figure 6. We have quantitatively analyzed the NMR spectra of 26 residues from liquefaction of DECS-9 coal under various conditions with and without solvents (Song et al., 1993). The results show that equation 1 holds for all the cases with good linear correlation.

Characterization of Residues from Catalytic Liquefaction at 350°C

We also performed CPMAS and DDMAS ^{13}C NMR analysis of THF-insoluble residues derived from non-catalytic and catalytic liquefaction of Wyodak subbituminous coal at 350°C for 30 min under 6.9 MPa (cold) H_2 pressure. Table 2 shows the results of carbon aromaticities determined by CPMAS ^{13}C NMR, and the degree of protonation of aromatic carbons determined by DDMAS ^{13}C NMR. Reactions at 350°C can be viewed as pretreatments or low-severity liquefaction. For the sake of convenience, we will call all the reactions as liquefaction.

The coal conversion data have been reported in a recent paper (Song et al., 1994). Briefly, in the absence of catalyst, coal conversion at 350°C into THF-solubles plus gas was 12.5 wt% (dmmf) without solvent, 18.3 wt% with 1-methylnaphthalene solvent, and 25.9 wt% with tetralin. The use of ATTM increased coal conversion to 29.8 wt% (dmmf) without solvent, 31.1 wt% with 1-methylnaphthalene solvent, and 36.4 wt% with tetralin. The data in Table 2 shows that using dispersed catalyst (in situ generated from impregnated ammonium tetrathiomolybdate, ATTM) not only improved coal conversion, but also resulted in small but consistent decrease in carbon aromaticity of the residues. This suggests the occurence of hydrogenation on some aromatic rings in the residues in the presence of dispersed molybdenum sulfide catalyst. These results are consistent with our recent work on the CPMAS NMR analysis of residues from DECS-1 Texas Big Brown subbituminous coal (Huang et al., 1993).

Compared to the THF-extracted but unreacted coal, the degree of protonation of aromatic carbons (f_a^{aH}) is higher with the residues from non-catalytic liquefaction. It should be mentioned that the amount of THF-soluble materials in the raw coal was about 8.5 wt% (dmmf), and the coal conversion into THF-solubles plus gas in the solvent-free non-catalytic run at 350°C was 12.5 wt% (dmmf). Therefore, on the basis of dmmf coal, the THF-extracted coal sample has about 4 wt% more organic material compared to the residue from solvent-free non-catalytic run. Since the latter has higher aromaticity (0.63) than the former (0.57), the higher f_a^{aH} value (0.40) could be due to the higher proportion of aromatics in the latter. Some of the aromatics were probably formed from dehydrogenation of hydroaromatic ring via hydrogen abstraction by thermally-derived radicals, which account for the simultanesous increase of f_a and f_a^{aH} values. If this is true, then the use of hydrogen-donor solvent should suppress the increase of f_a^{aH} value, because the reactive radicals would be stablilized by the hydrogen donation of solvent molecules. In fact, this is the case. The f_a^{aH} value decreased from 0.40 to 0.33 when a hydrogen-donor solvent, tetralin, was used, as shown in Table 2. When a hydrogen-donor solvent was replaced by a non-donor vehicle, 1-methylnaphthalene solvent, f_a^{aH} value increased from 0.33 to 0.37.

Interestingly, DDMAS ^{13}C NMR of the residues revealed that the degree of protonation of aromatic carbons (f_a^{aH}) is lower with the residues from catalytic liquefaction than that from non-catalytic reaction, as can be seen from Table 2. These results were surprising to us initially, as f_a^{aH} values usually decrease with increasing degree of condensation. However, if this is the case, this decrease should be accompanied by the increase in f_a values. It is possible that, relative to the residues from non-catalytic runs, the lower f_a^{aH} values for residues from catalytic runs were due to hydrogenation of the aromatic rings to form hydroaromatic rings.

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Plan for Future Work

It has been two and half years since the start of this project. Since the project is scheduled to terminate on September 17, 1994, our effort in the last two quarterly periods will be devoted to wrapping up the experimental work, summarizing and evaluating the experimental results, and preparing the final report. In the next quarterly report, a selective review of our project work on the three low-rank coals will be presented. We will also report on the strong synergistic effects between a dispersed molybdenum sulfide catalyst and added water for low-severity liquefaction of Wyodak subbituminous coal at 350°C.

Table 1. NMR-Derived Carbon Aromaticity (f_a) and Degree of Protonation of Aromatic Carbons (f_a^{aH}) of THF-insoluble Residues from Temperature-Programmed Liquefaction (TPL) of DECS-9 Montana Coal at Final Temperature of 300-425°C for 30 min under 6.9 MPa (cold) H_2 Pressure

Sample	Temp, °C	Solvent	CPMAS NMR f_a	DDMAS NMR f_a^{aH}
Raw coal			0.63	0.33
THF-extracted but unreacted coal			0.64	0.35
Residue	200°C-15 min 300°C-30 min	Tetralin	0.65	0.34
Residue	200°C-15 min 350°C-30 min	Tetralin	0.70	0.24
Residue	200°C-15 min 375°C-30 min	Tetralin	0.73	0.13
Residue	200°C-15 min 400°C-30 min	Tetralin	0.76	0.11
Residue	200°C-15 min 425°C-30 min	Tetralin	0.78	

Table 2. NMR-Derived Carbon Aromaticity (f_a) and Degree of Protonation of Aromatic Carbons (f_a^{aH}) of THF-insoluble Residues from Liquefaction of DECS-8 Wyodak Coal at 350°C for 30 min under 6.9 MPa (cold) H_2 Pressure

Sample	Temp, °C	Solvent	Catalyst	CPMAS NMR[a] f_a	DDMAS NMR f_a^{aH}
THF-extracted but unreacted coal				0.57	0.29
Residue	350°C	No	No	0.63	0.40
Residue	350°C	No	ATTM[b]	0.62	0.31
Residue	350°C	Tetralin	No	0.62	0.33
Residue	350°C	Tetralin	ATTM[b]	0.61	0.30
Residue	350°C	1-MN	No	0.68	0.37
Residue	350°C	1-MN	ATTM[b]	0.60	0.30

a) Integration of signal intensity between 95 and 165 ppm.
b) Ammonium tetrathiomolybdate, 1 wt% Mo on dmmf coal.

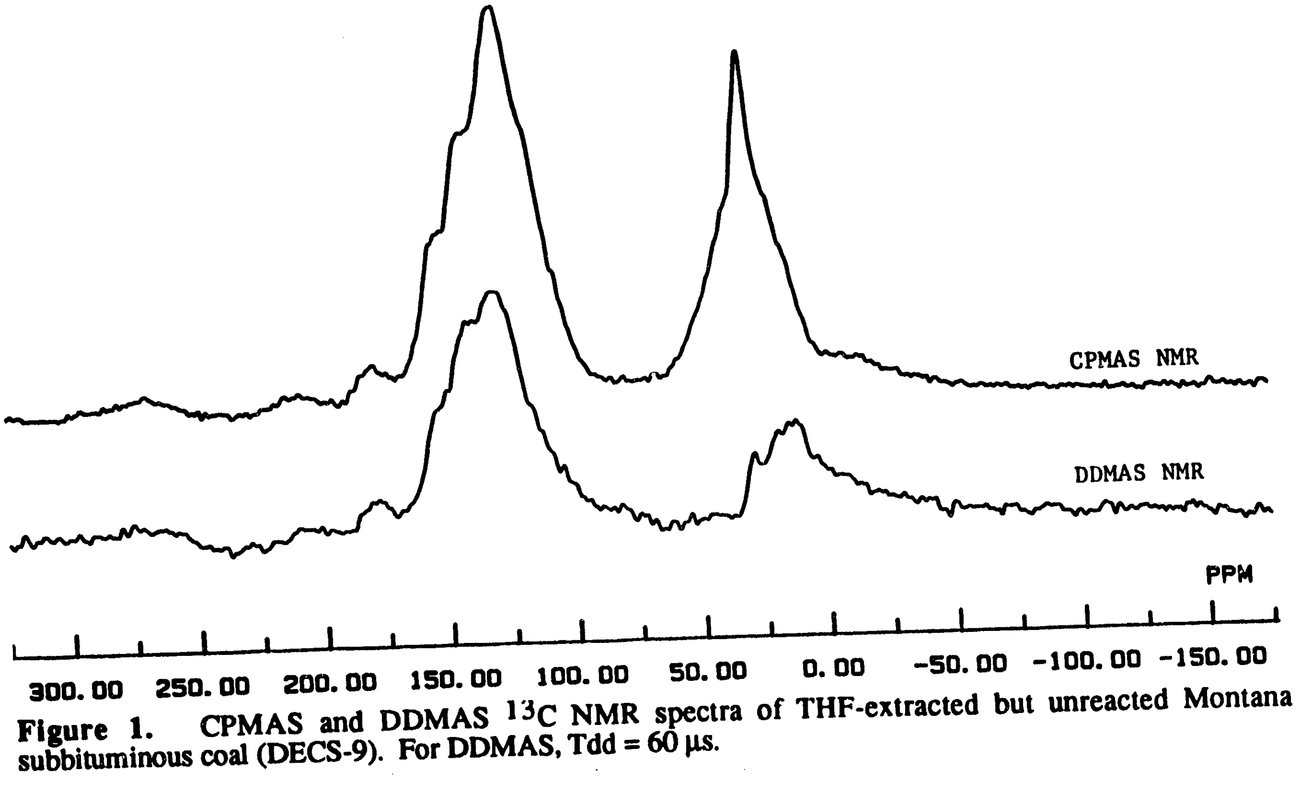

Figure 1. CPMAS and DDMAS ^{13}C NMR spectra of THF-extracted but unreacted Montana subbituminous coal (DECS-9). For DDMAS, Tdd = 60 μs.

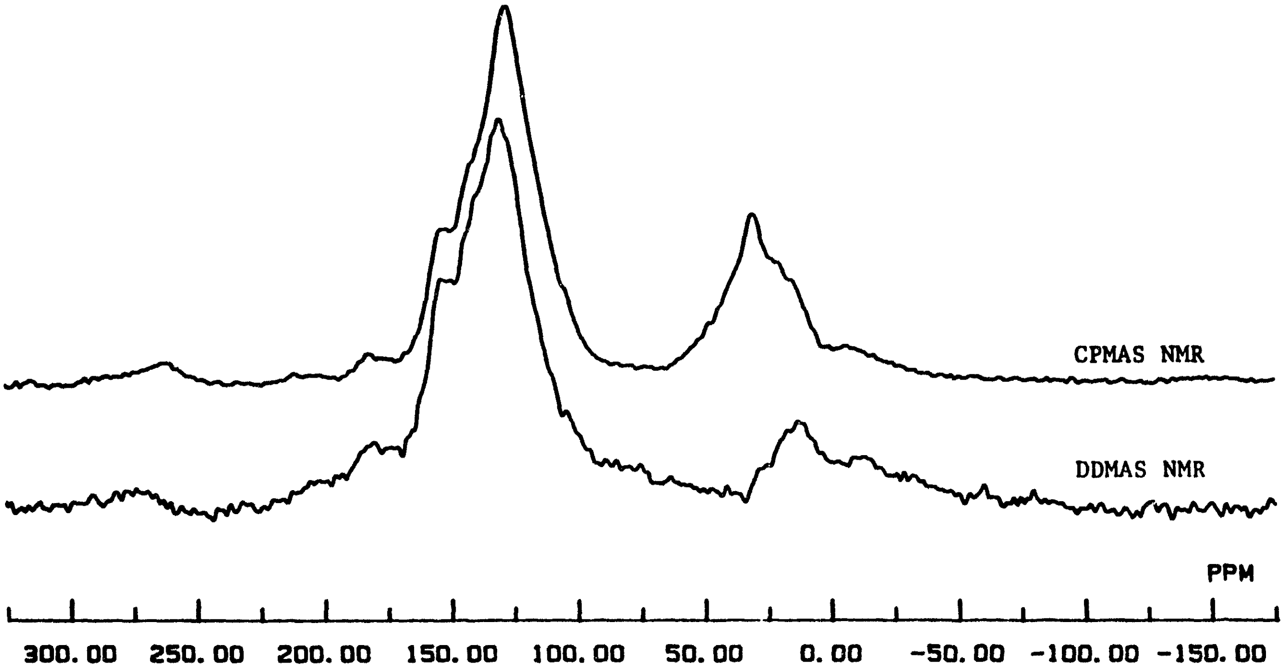

Figure 2. CPMAS and DDMAS ^{13}C NMR spectra of residue from TPL of Montana coal in the presence of tetralin at a final temperature of 350°C for 30 min. For DDMAS, Tdd = 60 μs.

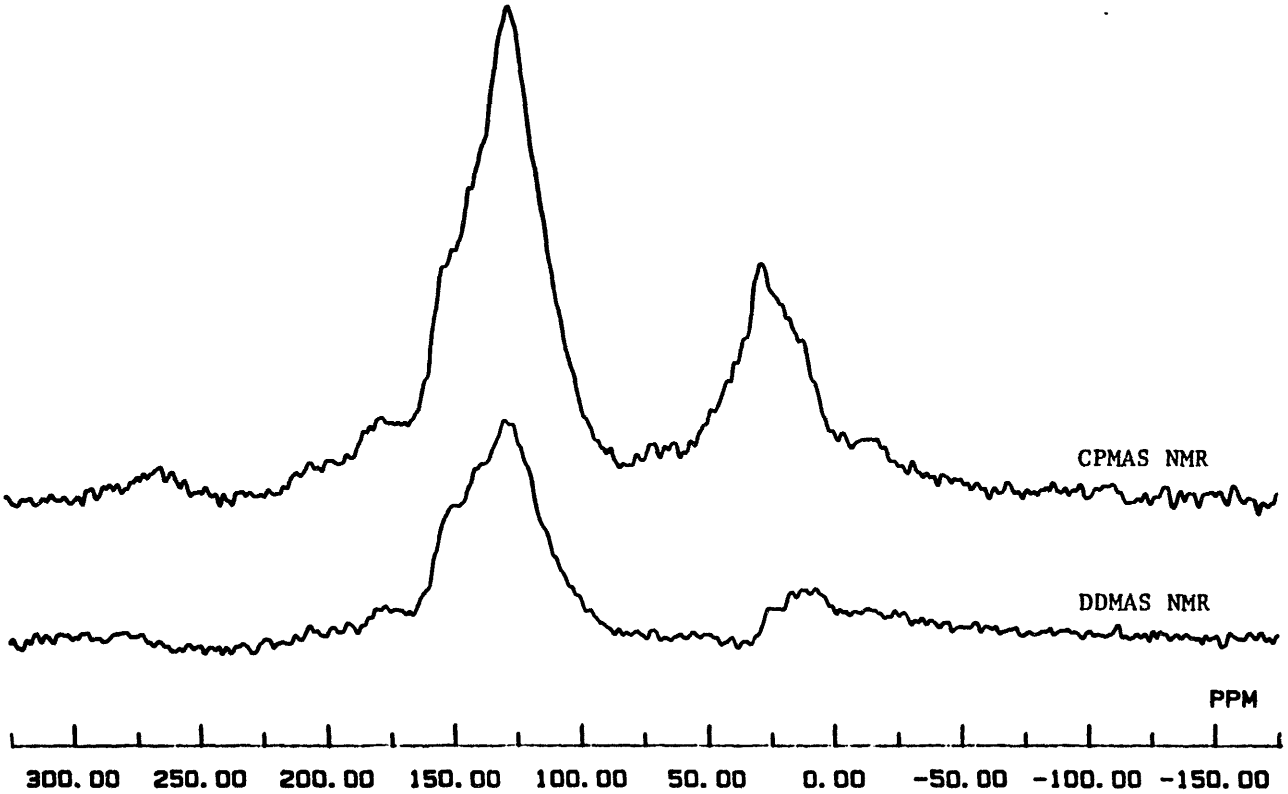

Figure 3. CPMAS and DDMAS ^{13}C NMR spectra of residue from liquefaction of Wyodak coal (DECS-8. vacuum-dried) without any solvent at 350°C for 30 min. For DDMAS. Tdd = 60 us.

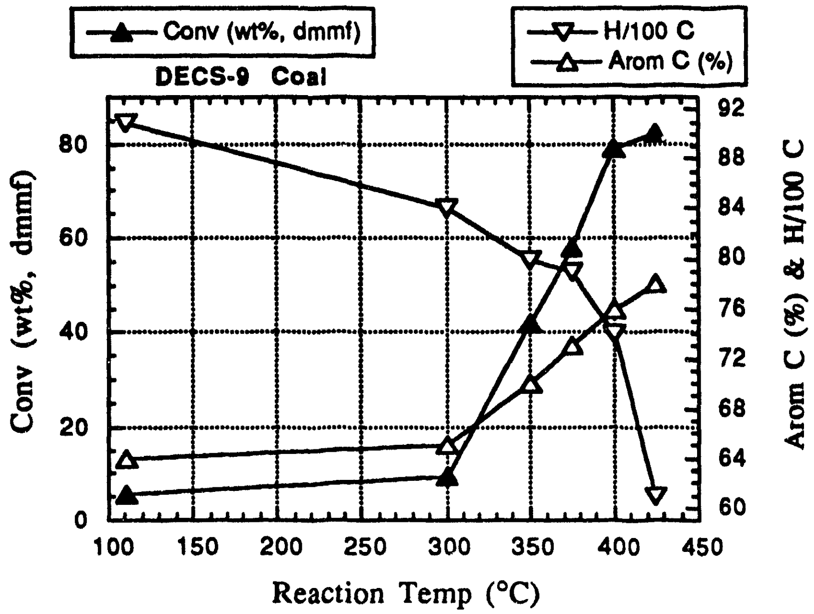

Figure 4. Conversion of Montana coal and changes in aromaticity (Arom C, %) and No. of H atoms/100 C in the residues versus final temperature of liquefaction (TPL) in tetralin.

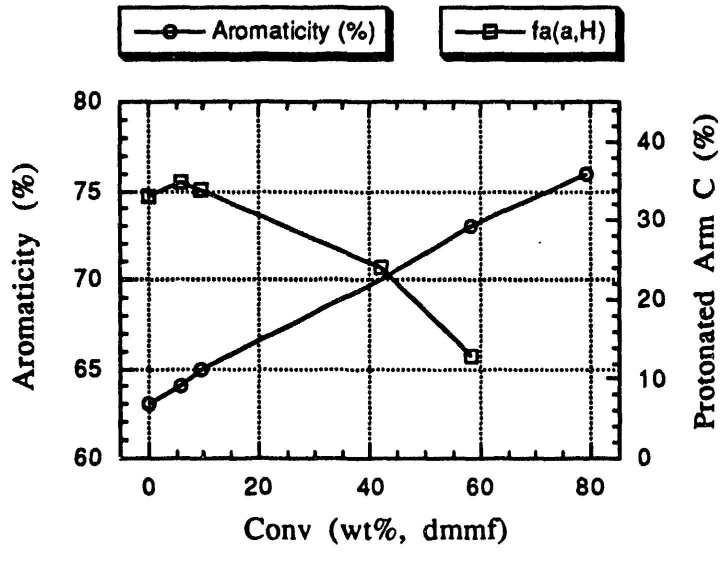

Figure 5. Change of aromaticity and percentage degree of protonation of aromatic carbons [fa(a,H)] in the residues versus conversion of DECS-9 Montana coal in TPL with tetralin.

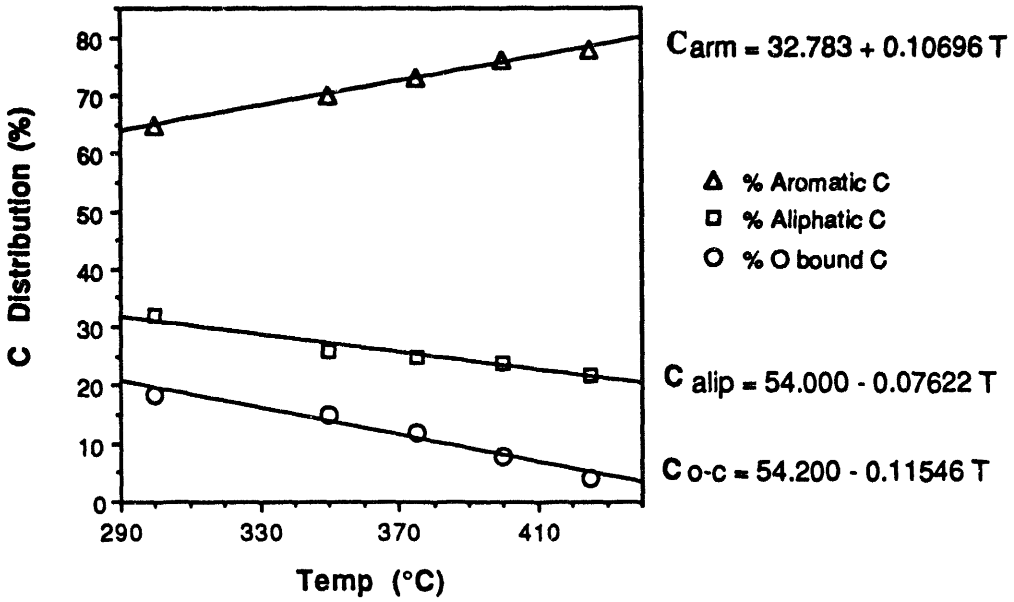

Figure 6. Linear correlation of contents of aromatic, aliphatic, and total oxygen-bound carbons in residues from DECS-9 Montana coal with final temperature of TPL in tetralin.

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