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FINAL REPORT

THE USE OF NMR TECHNIQUES FOR THE ANALYSIS OF WATER IN COAL AND THE EFFECT OF DIFFERENT COAL DRYING TECHNIQUES ON THE STRUCTURE AND REACTIVITY OF COAL

*Prepared for
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Pittsburgh Energy Technology Center*

February 1995

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**THE USE OF NMR TECHNIQUES FOR THE ANALYSIS OF WATER
IN COAL AND THE EFFECT OF DIFFERENT COAL DRYING
TECHNIQUES ON THE STRUCTURE AND REACTIVITY OF COAL**

Final Report

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EXECUTIVE SUMMARY

Western Research Institute (WRI), under the a contract from the U.S. Department of Energy (DOE), has conducted a study of different methods of coal drying as pretreatment steps before liquefaction. The objectives of this study were to develop a combined chemical dehydration/ nuclear magnetic resonance (NMR) method for measuring the moisture content of coal, to measure the changes in coal structure that occur during drying, and to determine the effects of different drying methods on liquefaction reactivity of coals. Different methods of drying were investigated to determine whether coal drying can be accomplished without reducing the reactivity of coals toward liquefaction. Drying methods included thermal, microwave, and chemical dehydration. Coals of rank lignite to high volatile bituminous were studied.

Coal liquefaction experiments were conducted using a magnetically coupled, continuously stirred, microautoclave reactor using a 2:1 weight ratio of tetralin to coal. A fluidized sandbath was used for rapid heating to liquefaction temperatures. Coal liquefaction experiments were carried out at 425°C for 60 minutes on coals having moisture levels ranging from zero to 100% of the equilibrium moisture.

Solid-state ^{13}C NMR techniques of cross polarization with magic-angle spinning were employed to measure any changes in coal structure caused by the different drying methods and on the residues from the liquefaction of dried and partially dried coals. Gas chromatographic analyses were made on the coal liquid products from the liquefaction process to obtain an assessment of product quality. Solvent swelling ratios were measured for the dried and premoisturized coals to determine the amount of cross linking that might occur because of drying by different methods.

In general, there were no major changes in the NMR spectra of coals dried thermally or with microwaves other than some partial decarboxylation. Chemically dried coals exhibited increased resolution in the aliphatic carbon region that was attributed, in part, to adsorbed methanol, a reaction product and solvent for the chemical dehydration method. An increase in the mobility of coal molecules due to less hydrogen bonding as a result of replacing water with methanol is also suggested for the increase in resolution.

Coals that were dried or partially dried thermally and with microwaves had lower liquefaction conversions than coals containing equilibrium moisture contents. However, chemically dried coals had conversions equal to or greater than the premoisturized coals. The conversion behavior is consistent with changes in the physical structure and cross linking reactions because of drying. Thermal and microwave drying appear to cause a collapse in the pore structure, thus preventing donor solvents such as tetralin from contacting reactive sites inside the coals. Chemical dehydration does not appear to collapse the pore structure.

These results are supported by the solvent swelling measurements in which the swelling ratios of thermally dried and microwave-dried coals were lower than those of premoisturized coals, indicating a greater degree of cross linking in the dried coals. The swelling ratios of the chemically dried coals were greater than those of the premoisturized coals because the pore structure remaining unchanged or increased when water was removed. These results are consistent with the NMR results, which did not show significant changes in coal chemical structure apart from some partial decarboxylation, which could lead to cross-linking in the dried coals.

From the study of the kinetics of the chemical dehydration of coals, it was possible to quantify the amount of water on the surface, the amount readily accessible in pores, and the amount more strongly bonded in the internal structure of the coals. The results indicate that high-rank coals have proportionally less surface and easily accessible water than the lower rank coals.

INTRODUCTION

While great strides have been made in developing the technology of coal liquefaction processes in recent years, many unsolved problems still remain before a viable and economical process can be achieved. The technological problems that still exist can be solved through a more fundamental understanding of the chemistry associated with each stage of the coal liquefaction process, starting with any pretreatment steps that may be carried out on the coal itself. Western Research Institute (WRI), under the a contract from the U.S. Department of Energy (DOE), has conducted a study of different methods of coal drying as pretreatment steps before liquefaction. The results of that study are the subject of this report.

In principle, the fundamental constraint for the conversion of coals to liquids is well known (Whitehurst 1980; Whitehurst et al. 1980; Neuworth and Gray 1985; Snape 1987; U.S. DOE 1989). Coals are hydrogen-deficient fossil fuels that have a highly aromatic carbon structure and do not readily produce liquids upon heating. In addition, coals have a macromolecular structure attendant with various cross-links that contain heteroatoms which can affect their conversion properties. In particular, cross-linking reactions in low-rank coals are thought to be responsible for the lower conversions of these coals to liquid products during pyrolysis and liquefaction (Suuberg et al. 1985; 1987; Deshpande et al, 1988; Ibarra et al. 1990). Therefore, to enhance the conversion of coal (coal liquefaction) to useful products, hydrogen must be added or carbon removed at elevated temperatures to disrupt the macromolecular network and to stabilize and reduce the molecular weights of the fragments.

Current knowledge suggests that the initial step in coal liquefaction is thermolysis caused by temperature, although this view has been challenged recently (McMillen et al. 1987). There is considerable experimental evidence to suggest that if there is insufficient hydrogen available to stabilize the thermally produced matrix fragments, retrograde and condensation reactions can occur that produce materials more refractory than the original coal. Further, these reactions can occur during preconversion before the main stage of coal liquefaction. As a result, the coal fed into the liquefaction reactor may be less reactive and, thus, require higher severity conditions (Rao et al. 1988).

The initial coal liquefaction processes to convert coal directly into distillable hydrocarbon fuel products employed single-stage reactors under high-severity operating conditions of pressure, temperature, and coal/solvent contact time to achieve the highest conversion and distillate yield possible. However, because of the many disadvantages, single-stage processes were downplayed in favor of current processes that use low-severity operations in separated stages to optimize the coal dissolution step and coal extract upgrading step. The integrated two-stage liquefaction process (ITSL) substantially reduces, and in some cases eliminates, the disadvantages associated with high-severity processing. With the ITSL process, the high hydrocarbon gas yield that causes high hydrogen consumption is substantially reduced; the yields and quality of the distillate products and recycle donor solvent are enhanced; the heteroatom content of the distillate product and recycle donor solvent are greatly reduced; the heteroatoms are more easily hydrogenated; the highly exothermic reaction of molecular hydrogen with aromatics is more easily controlled; and the regressive formation of high-boiling distillate and nondistillables that are refractory to hydrogenation and the major cause of catalyst deactivation is reduced.

Catalytic two-stage liquefaction (CTSL) processes are the best available today in the world, however, the liquids produced are still more costly than conventional crude oil. Significant improvements are required before the CTSL processes become competitive with crude oil. One of the more promising areas for improvement is the physicochemical pretreatment of coal (Rao et al. 1988; U.S. DOE 1989).

One pretreatment process that can improve the economics of coal liquefaction is coal drying, particularly for the lower rank coals. There are many theoretical advantages to drying coal prior to liquefaction, particularly in systems not dependent on the use of the water-gas shift reaction and in the two-stage liquefaction process recently practiced at the DOE Advanced Coal Liquefaction Research and Development Facility at Wilsonville, Alabama. Because direct liquefaction conversion and kinetics are heavily dependent upon the partial pressure of hydrogen in the liquefaction reactor, the removal of moisture in the coal allows the partial pressure of hydrogen to be increased without increasing the operating pressure. Eliminating the partial pressure of steam in the reactor increases the partial pressures of hydrogen and other gaseous components if the reactor operating pressure is held constant. In addition, removal of most of the water from the coal prior to liquefaction reduces the cost of both separating water from the coal and wastewater treatment. Water removed from the

coal at low temperature presently can be vented to the atmosphere as steam without treatment. Finally, moisture in the coal reduces the throughput of coal on a dry basis if the liquefaction reactor has a fixed capacity.

However, there is also considerable evidence to show that drying has a detrimental effect on the liquefaction behavior of coals (Silver and Frazee 1985; Silver et al. 1986; Serio et al. 1990). Coals have both a physical and chemical structure, so it is conceivable that drying affects one, the other, or both of these structures. The problem is that removing the moisture from subbituminous coals prior to liquefaction reduces the amount of coal that is converted to liquid during the liquefaction process (Silver and Frazee 1985). Silver and Frazee dried a Clovis Point subbituminous coal using a variety of methods. In all cases considered, the reactivity of the completely dried coal was lower than the reactivity of the original coal, based on unreacted coal and distillate yields.

The problem that needs to be solved is that of economically drying coal without adversely affecting its liquefaction reactivity. This is particularly true for subbituminous coals and lignites for which the U.S. reserves are huge. These coals contain significant amounts of water so that simply drying these materials before transportation to their final destination can represent a sizeable reduction in cost. Therefore, to derive economic benefits from coal drying, the causes of the lower reactivity of dried coals must be understood, or other methods of drying must be developed that circumvent this problem. Two coal drying methods innovative to coal chemistry and liquefaction studies are the use of a chemical dehydrating agent and microwave heating, as discussed in this report.

The moisture content of coals plays an important role in coal processing and use. Indeed, coals are bought and sold on the basis of their heating value, ash, and sulfur contents. The heating value is directly affected by the moisture content. In addition, to obtain the correct elemental composition of coal, the elemental values must be corrected for moisture and ash, or mineral matter. Therefore, there is also a need to develop more accurate methods to determine the moisture content of coal in addition to understanding the role of water in coal liquefaction. Only recently have there been any systematic studies of the methods of coal drying on coal structure and the role water plays in enhancing or lessening coal reactivity toward liquefaction (Song et al.

1994; Okuma et al. 1990). In part, this may be the result of the techniques that have recently become available, such as solid-state NMR.

With the solid-state nuclear magnetic resonance (NMR) technique of cross-polarization with magic-angle spinning (CP/MAS), studies of chemical structural changes that may occur in coals as a result of drying are feasible. Applications of solid-state NMR to the study of coals have been reviewed (Davidson 1986; Miknis 1988). Most of the solid-state NMR studies have used CP/MAS ^{13}C techniques to study the basic carbon structure of coal and how it changes with rank, the origin and evolution of coal, and the behavior of coal under various heating and processing conditions. Most of the applications of solid-state NMR to study coal liquefaction have dealt with changes in the carbon aromaticity between products and the original coal (Wilson et al. 1982; Foster et al. 1983; Bockrath et al. 1984; Finseth et al. 1985; Vassallo et al. 1987; Shin et al. 1989).

Thermal Drying

The most common method of coal drying is to heat the coal in air to some elevated temperature to drive off the moisture. Even a simple process such as this can cause changes in the physical and chemical structure of coals, particularly low-rank coals. For example, subbituminous coals contract and crack on drying. Further, only about 60% of the moisture that is removed can be replaced. This is attributed to collapse in the gel structure of the low-rank coals (Evans 1973). On the other hand, a dried Illinois bituminous coal can reabsorb about the same amount of water as it loses in drying. However, some coals dried at room temperature reabsorb more water than when they are dried at a higher temperature (Evans 1973). This suggests that drying does not significantly alter the physical structure of bituminous coals, but because water is an intimate part of the gel structure of low-rank coals, drying might alter the physical structure of these coals.

Thermal drying can also cause changes in the chemical structure of the coal, which in turn can affect the liquefaction properties. Low-rank coals show a strong tendency to form cross-links even at low temperature because of the high concentration of organic oxygen functionalities such as carboxyl, hydroxyl, and methoxyl. These functional groups are involved in condensation reactions and free-radical reactions stabilized by cross-links. Measurement of the volumetric swelling ratio using the

procedure of Green et al. (1984) can be used to determine the degree of cross-linking that forms during coal processing (Suuberg et al. 1985, 1987, 1993; Deshpande et al. 1988; Ibarra et al. 1990). Cross-linking also produces simple molecules such as CO_2 , H_2O , and CH_4 so that correlations have been developed to relate the degree of cross-linking to gas evolution (Suuberg et al. 1985; Deshpande et al. 1988). Drying in air can also produce CO_2 and H_2O as a result of low-temperature oxidation reactions, which can be very rapid at $<100^\circ\text{C}$. Moreover, these reactions are sensitive to water content (Gethner 1986). Thus, it appears that a variety of chemical reactions can occur in coals prior to any high-temperature liquefaction processing. The fate of a coal conversion process may well be predetermined by simple coal drying pretreatment methods.

Microwave Drying

Microwave drying (Chatterjee and Misra 1991 and literature cited therein) appears to be relatively novel with regard to coal drying as a pretreatment step for coal liquefaction. The study of Silver and Frazee (1985) is the only one that relates microwave-dried coals to their liquefaction behavior. In their study, solid-state NMR techniques were not available; consequently, any effects on coal structure caused by microwave drying could not be assessed. Because microwaves heat and dry coal by a different mechanism than thermal or chemical methods, make this form of drying an attractive pretreatment step for coal liquefaction.

The process of drying with microwaves is different from that of simply heating the coal. In order for a substance to absorb microwaves and become heated, it must have a dipole moment. Therefore, the functional groups that are the most efficient absorbers of microwaves are those that are highly polar, such as the $-\text{OH}$ group in water. In fact, the common use of microwaves for cooking foods is to heat the water molecules in the food.

When a substance containing water molecules is exposed to microwaves of the proper frequency, typically 2450 MHz, the water molecules attempt to align and realign themselves with the alternating electric field of the microwaves. This process causes friction on a molecular level, which is transformed into heat. Because the water in coals can be distributed on the surface in pores of various sizes or as part of the coal structure as in a gel depending on rank, microwaves may be used to provide

some selectivity for coal drying without appreciably affecting the overall structure and liquefaction behavior of the coal. This is suggested in Figures 1 and 2 (reproduced from the study by Silver and Frazee [1985]). Their results show that drying a Clovis Point subbituminous coal (~ 26 wt % moisture) down to a level of ~ 4 wt % moisture using microwaves actually leads to an increase in the coal reactivity, both in terms of pyridine solubles and distillate yields. Drying with microwaves below the level of 4 wt % moisture (~ 84% water removed) adversely affects the coal reactivity (see Figures 1 and 2). This result can be explained by examining the temperature at which coal drying occurs using microwaves (Figure 3, Silver and Frazee [1985]). The drying temperature stays relatively constant near the boiling point of water until about 75% of the moisture is removed (less than 20 wt % of the original moisture). The easily removed surface water and pore water probably accounts for most of this loss. However, above the level 75%, the moisture that is removed may be an integral part of the gel structure of the coal. These water molecules would have a more difficult time aligning and realigning with the radiation field and thus could cause heating and possible disruption of part of the coal matrix, enabling some retrograde reactions to take place that diminish the reactivity toward liquefaction (Figure 1). Silver and Frazee (1985) suggest that at the lower moisture content other polar groups are also being heated, which results in the decrease in coal reactivity.

There does not appear to have been a systematic study of changes in coal structure induced by microwave drying. Figures 1-3 suggest that using solid-state NMR techniques to study the coal residues as a function of water removed will be valuable. One would expect little or no structural changes during microwave drying down to a minimum moisture content (~ 4 wt % for the Clovis Point coal). Further drying with microwaves causes lower reactivities (as shown in Figures 1 and 2) and higher temperatures (as shown in Figure 3) in the coal. The change in reactivities should result from changes induced in the coal structure.

Chemical Drying

Chemical drying of coals is a relatively unexplored technique for removing water at low temperature. As discussed, thermal methods of drying alter the physical structure of coal as well as promote undesirable chemical reactions. Drying coal at room temperature, however, should preserve the structural integrity, reduce retrograde reactions, reduce thermal degradation, and provide information on

Figure 1. Unreacted Coal as a Function of Coal Moisture in Microwave Dried Coal (Silver and Frazee 1985)

Figure 2. Distillate Yield as a Function of Coal Moisture in Microwave Dried Coal (Silver and Frazee 1985)

nonbonded, chemisorbed, and physisorbed water. In principle, this method of dehydrating coal could provide a baseline for studying initial stages of retrograde/condensation reactions. That is, decarboxylation and low-temperature oxidation reactions (not pursued in this study) could then be studied in the presence and absence of water.

Figure 3. Coal Temperature as a Function of Moisture Removed by Microwave Drying (Silver and Frazee 1985)

Almost all solvents used to swell coals remove some water from the pores and surfaces of coal by solubilization. Water still remains an integral part of the system until heat and vacuum are applied to remove the solvent and water. The applied heat can promote initial chemical reactions such as decarboxylation. However, pore water and surface-adsorbed water of coal can be rapidly and effectively removed at room temperature using chemical dehydration agents, which react with water to form volatile reaction products.

A common chemical dehydrating agent is 2,2-dimethoxypropane. This agent has been used in inorganic chemistry to remove water of hydration in inorganic compounds (Donoghue and Drago 1962) and in biological sciences for drying tissues for microscopic examination (Adams 1974; Muller and Jacks 1975). The reaction of 2,2-dimethoxypropane with water is shown in scheme I (Critchfield and Bishop 1961).

Scheme I

This reaction is rapid and endothermic (i.e. the reaction mixture cools). The reaction products CH_3OH and acetone are easily removed by vacuum at ambient temperature. Removing water by chemical means rather than by physically forcing exchange by mass action preserves the ultrastructural integrity of the coal cellular components. It is also possible to measure the water content remaining in coals that have been partially dried (thermal or microwave methods) by reacting the water remaining in the coal with 2,2-dimethoxypropane and measuring the acetone content using ^1H NMR.

The use of the dehydration agent 2,2-dimethoxypropane in this study to dry coals is an innovative approach to understanding the role of water in coal chemistry (see Wroblewski and Verkade 1992 for another approach). The use of 2,2-dimethoxypropane has lead to a better method for moisture determination in coal. A computer search of the DOE Energy Data Base did not reveal any literature references

on the use of chemical drying agents for coal moisture determinations. Finseth (1987) discussed the need for accurate moisture determinations in coal. In that study, Finseth employed isotopic dilution to study the exchange of oxygen in moisture equilibration experiments. His results showed higher moisture levels obtained by isotopic dilution than by the standard ASTM method for the Argonne Premium coal samples as well as for two coals that were not as well prepared as the Premium coals. The results suggest that the classic thermal drying method did not yield true moisture values for coals. One aspect of Finseth's study that is relevant to this study is that all exchangeable oxygen reservoir throughout the coal was contacted with the isotopically labeled water. This means that for chemical dehydration the same assumption can be made—that the dehydration agent will react with all the available water in the coal structure both internally and externally (surface water).

EXPERIMENTAL

Coal Samples

Of the six coals used in this study, four were obtained from the Pennsylvania State University Coal Research Section, and two were obtained from the Powder River Basin in Wyoming. The coals selected for study consisted of a lignite, three subbituminous, and two bituminous coals. Tables 1 and 2 list the coals and the results of the proximate and ultimate analyses, respectively. All data collected on Utah Blind Canyon and North Dakota Beulah coals were performed under DOE Grant Agreement DE-FG22-91PC91310. Experimental data collected on Illinois # 6, Wyoming Eagle Butte, Wyoming Black Thunder, and Texas Bottom coals were performed under DOE Contract DE-AC22-91PC91043. For a more meaningful discussion of the data, the results of the six coals were combined in this single report.

Reagents

Analytical reagent grade anhydrous magnesium sulfate from Mallinckrodt was used to dry the various reagents used in determining the amount of water in coals by the dehydration method. 2,2-Dimethoxypropane (98%) from Aldrich Chemicals was used as received except that it was dried with anhydrous magnesium sulfate. Gas

Table 1. Proximate Analyses of Six Coal Samples

PSU Number (Seam Name)	Proximate Analysis (As Received)					
	Location	Apparent Rank	Moisture wt %	Ash wt %	Volatile wt %	Fixed Carbon wt %
DECS-6 (Blind Canyon) ¹	Utah	hvAb	4.73	5.56	42.40	47.31
DECS-2 (Illinois #6) ¹	Illinois	hvCb	10.43	14.47	34.16	40.93
(Eagle Butte) ^{2,3}	Wyoming (Powder River Basin)	Sub	29.2	4.7	30.9	35.2
(Black Thunder) ^{2,4}	Wyoming (Powder River Basin)	Sub	27.63	4.49	31.78	36.10
DECS-1 (Bottom) ¹	Texas	Sub C	30.00	11.07	33.18	25.75
DECS-11 (Beulah) ¹	North Dakota	Lignite	33.38	6.37	37.36	22.89

¹ Data from Penn State Coal Data Base

² Mine Name

³ Boysen et al. 1990

⁴ Data from Wyoming Analytical Laboratory, Laramie, Wyoming

Table 2. Ultimate Analyses of Six Coal Samples

PSU Number (Seam Name)	Ultimate Analysis (As Received)							
	Location	Apparent Rank	Ash wt %	Carbon wt %	Hydrogen ¹ wt %	Nitrogen wt %	Total Sulfur wt %	Oxygen ¹ (Diff) wt %
DECS-6 (Blind Canyon) ²	Utah	hvAb	5.56	72.91	5.60	1.39	0.38	9.42
DECS-2 (Illinois #6) ²	Illinois	hvCb	14.47	58.66	4.08	0.99	4.05	7.31
(Eagle Butte) ^{3,4,5}	Wyoming (Powder River Basin)	Sub	6.6	67.4	5.1	0.9	0.6	19.4
(Black Thunder) ^{3,5,6}	Wyoming (Powder River Basin)	Sub	4.49	49.58	2.84	0.35	0.36	14.75
DECS-1 (Bottom) ²	Texas	Sub C	11.07	43.77	3.32	0.86	0.69	10.28
DECS-11 (Beulah) ²	North Dakota	Lignite	6.37	44.07	2.68	0.60	0.49	12.40

¹ Excludes Moisture

² Data from Penn State Coal Data Base

³ Mine Name

⁴ Boysen et al. 1990

⁵ Wt % on dry basis

⁶ Data from Wyoming Analytical Laboratory, Laramie, Wyoming

chromatographic analysis indicated the purity to be 99% with three impurity components of 0.16, 0.45, and 0.38 relative percent. The NMR spectrum of the reagent showed a small acetone peak. Methanol, HPLC grade, from J.T. Baker was dried with anhydrous magnesium sulfate and was used to prepare standard solutions of water in methanol. A 0.2 N solution of methanesulfonic acid in methanol was prepared using methanesulfonic acid (99%) from Aldrich Chemicals. Cycloheptane (> 98%), used as the analytical hydrogen standard, was also obtained from Aldrich Chemicals. Gas chromatographic analysis indicated the purity to be 97.63% with three impurity components of 1.27, 0.67, and 0.69 relative percent. All calculations of the hydrogen content were corrected for the percent purity. Type I distilled water was used to make the standard solutions of water in methanol. The reagents deuteriochloroform (CDCl_3 , 99.8 Atom %) and tetramethylsilane (TMS) used for liquid state NMR experiments were obtained from Wilmad Glass Co. Tetralin and methylene chloride (CH_2Cl_2) used in coal liquefaction experiments were obtained from Fluka Chemika (> 97%) and J.T. Baker Inc. (99.9%), respectively, and were used as received. The nitrogen gas used to pressurize the autoclave was 99.7% and was obtained from Praxair. Reagent grade 1,4-dioxane obtained from Allied Chemical was used in all coal swelling experiments.

Coal Preparation

In order to study the effects of different methods for drying coal, the coals were premoisturized. A master batch sample of each coal (~ 500 g) was prepared by grinding and screening to -20, +100 mesh particle size (except for Wyoming Black Thunder, which was prepared with a mesh size of -100). The ground coal was placed in a wide-mouth jar and allowed to equilibrate in an oven with a beaker of water at 30°C for 24 hours. The water-equilibrated coal sample was then removed from the oven and placed in a humidifier until aliquots were taken for the different experiments. The "moisture" value (used as the reference moisture content) for the coals used in the various drying tests was determined from the weight loss of 1 g of the coals in a nitrogen atmosphere at 105°C for 24 hours.

Drying Processes for Coals

Thermal Drying.

Coal samples used in coal liquefaction experiments were thermally dried by placing 20 g of coal in an oven that was set at 105°C and purged with nitrogen gas.

Generally, it took 24 hrs for the weight loss to stabilize to a given value. The coal samples were removed at different times and the weights obtained so that the amount of moisture removed in a given time could be determined. Liquefaction experiments were then conducted on coals that had been totally and partially dried to different moisture content.

The six coal samples were also heated to different final temperatures in order to determine at what temperature significant structural changes begin to occur that might affect the liquefaction behavior. These heating experiments are referred to as ballistic heating experiments. The ballistic heating experiments were performed with a small, vertically aligned furnace having a 12-centimeter long heated section and a 1.4-centimeter i.d. quartz liner. A stainless steel screen provides support for the coal and a steel wool pack heats the nitrogen sweep gas, which was introduced at the bottom of the quartz liner. In a typical experiment, the furnace was preheated to about 10°C above the desired final coal temperature. A 2-gram coal sample was then poured into the quartz liner and a thermocouple inserted into the coal sample bed. When this thermocouple reached the desired temperature, the quartz liner was removed from the furnace and allowed to cool. A dry nitrogen flow was maintained at all times. When the sample temperature fell below 50°C, the coal was poured into a sample vial, capped with dry nitrogen, and sealed. Heatup times with this system were typically from 15 to 20 minutes.

Microwave Drying.

Initially, microwave drying experiments were conducted using a CEM model MDS 81-D laboratory microwave oven. Temperature measurements of the coal as a function of microwave drying times were a problem. Samples of coal weighing 2 g were placed in a microwave digestion sample holder that was modified to accommodate the sample. The configuration was chosen because the same sample could be placed in the thermal drying unit to obtain moisture determinations for calibrating the microwave unit. After a given period of drying at a given microwave power level, the sample was removed and a fast-response thermocouple was placed in the coal bed to measure the temperature. However, preliminary measurements had indicated that there was a

significant variation in the coal bed temperature from the bottom to the top of the bed. The higher temperature at the top of the bed was attributed to additional heating of the coal by superheated water escaping the coal. Because of poor reproducibility, experiments with the laboratory microwave oven were discontinued.

The laboratory microwave oven was replaced by a commercial microwave oven. All microwave experiments described in this report were conducted using the commercial microwave oven. Microwave drying tests were conducted in the following manner: ~ 2 grams of premoisturized coal were placed in 25 mL beakers, and the beakers were placed at the center of the microwave oven. Separate samples were exposed to microwave radiation for one to five and one to 15 minutes at 225 and 540 watts, respectively. The samples were removed from the oven and a thermocouple inserted into the coal bed to determine an average temperature. The percent "moisture" was determined by the weight loss.

At 100% power (540 watts), 75% or greater of the moisture was removed in ~ 2 min., and removal of the remaining moisture caused the temperatures to increase rapidly (see Figure 4). Because of the rapid moisture removal at full power, a lower level of microwave power was used to obtain a more complete drying curve. At power levels of 225 watts, 25 to 75% moisture could be removed with microwave irradiation times of up to 15 min.

Chemical Drying.

Chemical dehydration of the coals before coal liquefaction was conducted using 2,2-dimethoxypropane (DMP) as a drying agent. Depending on the amount of moisture in the coal, between 22 and 72 grams of DMP, and between 6 and 25 mL of 0.2 N methanesulfonic acid in methanol were added to a 20-g sample of coal. The acid-methanol solution was added to the sample, followed by DMP. The contents of the flask were shaken to ensure good mixing and contact. The mixture was allowed to stand for 24 hours. The liquid was then decanted and a vacuum was applied to remove the remaining liquid (excess DMP and methanol).

Figure 4. Coal Temperature as a Function of Moisture Removed at 540 Watts of Power

Analysis of Water in Coal Using NMR

The ^1H NMR spectrum of a solution after the reaction of 2,2-dimethoxypropane with water in methanol containing the cycloheptane (the hydrogen reference) and tetramethylsilane (TMS, the chemical shift reference) is shown in Figure 5. Table 3 lists the ^1H chemical shift position for the various compounds. To determine the water content in standard water samples, the resonance areas were measured for acetone (2.18 ppm) and cycloheptane (1.55 ppm), using the Lab CalcTM curve-fitting software routine. Figure 6 shows the application of the curve-fitting routine to the hydrogen signals for acetone and cycloheptane. Using a Lorentzian curve-fitting routine increased the precision and accuracy of the convoluted area using the NMR method by eliminating distortion at the base of the peak and other instrumental artifacts which contribute to the shape of the peak. The amount of water in methanol was calculated using equation 1.

Figure 5. Hydrogen-1 NMR Spectrum of the Solution from the Reaction of Water with 2,2-dimethoxypropane (DMP)

Table 3. ^1H Chemical Shifts of Reactants, Products, and Reference Compounds

Compound	^1H Chemical Shift (ppm)
Tetramethylsilane (TMS)	0
2,2-Dimethoxypropane (DMP)	
CH ₃	1.34
CH ₃ O	3.41
Cycloheptane	1.55
Acetone	2.18
Methanol	
CH ₃ O	4.28
OH	3.20

Figure 6. Expanded Hydrogen-1 NMR Spectrum of the Solution from the Reaction of Water with DMP Illustrating the Use of the Curve-fitting Software for Determining the Areas of the Acetone and Cycloheptane Resonances

$$g_{H_2O} = (f_c n_c w_c A_A M_{H_2O}) / (n_A A_c M_c) \quad (1)$$

where:

- g_{H_2O} = grams of water
- f_c = fractional purity of cycloheptane
- n_c = number of hydrogens in cycloheptane molecule
- w_c = weight of cycloheptane (grams)
- A_A = convoluted area of acetone
- M_{H_2O} = molecular weight of water
- n_A = number of hydrogens in acetone molecule
- A_c = convoluted area of cycloheptane
- M_c = molecular weight of cycloheptane

The precision and accuracy of the ^1H NMR method to determine water content in a sample were investigated using known amounts of water in methanol. Various amounts of water (0.0, 0.05, 0.10, 0.20, and 0.30 g) were added to 2 mL of 0.2 N methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) in methanol. To this solution was added 4 mL of DMP and 0.7 mL of cycloheptane as the internal hydrogen standard. After a reaction time of five minutes, a one-half mL aliquot of the solution was removed, diluted with one-half mL of CDCl_3 containing TMS and the ^1H NMR spectrum recorded.

Three separate experimental runs using solutions of a known amount of water in methanol were used to determine the precision and accuracy of the method (Table 4). The amount of water in the blank solutions was found to be an average of 0.0107 ± 0.0004 g. The average relative error was found to be $< \pm 3\%$, and the absolute error was found to be better than ± 0.005 g for all solutions with a known amount of water. The percent recovery was determined to be $100 \pm 3\%$ over the concentration range of 0.0 to 0.3 g of water. Figure 7 shows the plot of the amount of water added to methanol versus the amount of water determined by the reaction with DMP and using ^1H NMR.

Table 4. Precision and Accuracy for Solutions of a Known Amount of Water by ^1H NMR

Run No.	Sample	Water, g		Recovery, %	Relative Error, %	Absolute Error, g
		Added	Found			
1	H651011	-	0.0103			
	H651012	0.0509	0.0495	97	-2.75	-0.0014
	H651013	0.1023	0.1065	104	4.11	0.0042
	H651014	0.2029	0.2026	100	-0.15	-0.0003
	H651015	0.3036	0.2995	99	-1.35	-0.0041
2	H651011A	-	0.0106			
	H651012A	0.0668	0.0662	99	-0.90	-0.0006
	H651013A	0.1323	0.1316	100	-0.53	-0.0007
	H651014A	0.2027	0.2008	99	-0.91	-0.0019
	H651015A	0.3079	0.2973	97	-3.40	-0.0106
3	H651001	-	0.0111			
	H651002	0.0578	0.0588	102	1.73	0.0010
	H651003	0.1070	0.1080	101	0.93	0.0010
	H651004	0.2040	0.1988	97	-2.55	-0.0052
	H651005	0.3098	0.3063	99	-1.13	-0.0035

Figure 7. A Plot of the Amount of Water Added to Methanol versus the Amount of Water Determined by the Reaction with DMP and Using ^1H NMR. Solid line represents a 1:1 correlation.

Moisture determinations were conducted on coals of various ranks using 2,2-dimethoxypropane as a drying agent. One-half gram of coal was weighed into a 10 mL centrifuge tube followed by 1 mL of 0.2 N $\text{CH}_3\text{SO}_3\text{H}$ in CH_3OH , 0.7 mL of the reference cycloheptane, and 2 mL of DMP. After 16 hours, the solution was stirred and centrifuged prior to removing the aliquots. One-half mL aliquot was removed and diluted with one-half mL CDCl_3 . This solution was then transferred to an NMR tube and the ^1H spectrum recorded. From the convoluted areas of the methyl hydrogens of acetone and the hydrogens of cycloheptane, the amount of water in the coal samples was determined using equation 2.

$$P_{H_2O} = (g_{H_2O} / W_{coal}) \times 100 \quad (2)$$

where:

$$\begin{aligned} P_{H_2O} &= \text{percent of water in coal} \\ g_{H_2O} &= \text{grams of water (equation 1)} \\ W_{coal} &= \text{weight of coal sample (grams)} \end{aligned}$$

Kinetics of Chemical Dehydration of Coal

To determine the kinetics of drying, the amount of coal and volumes of the reagents used were doubled. Aliquots of the reaction mixture were removed at 15 and 30 minutes, one, two, four, six, eight and 24 hours, were diluted in $CDCl_3$, and the 1H NMR spectra was recorded. In some cases, the aliquots removed had to be refrigerated until the NMR instrument was again available or operable.

The kinetic data from the chemical dehydration of coals were fitted to 1st and nth order kinetic equations (equations 3 and 4, respectively) (Frost and Pearson 1961).

For $n = 1$

$$M = C_i + M_{\infty} (1 - e^{-kt}) \quad (3)$$

For $n \neq 1$

$$M = C_i + M_{\infty} - \left[\frac{1}{(n-1)kt + 1/M_{\infty}^{n-1}} \right]^{\frac{1}{n-1}} \quad (4)$$

where: M = total percent moisture removed

C_i = percent moisture removed during the initial reaction

M_{∞} = percent moisture in coal at $t = \infty$ (not including the water removed during the initial reaction)

k = rate constant (hr^{-1})

t = time (hr)

n = order of reaction

Coal Liquefaction

Borgialli Microreactor

A modified "Borgialli" microreactor was obtained from the Wilsonville Two-Stage Advanced Coal Liquefaction Research Facility after it was shut down. The microreactor is a magnetically-stirred, microautoclave system developed at the University of Wyoming by Mr. Ron Borgialli under an Electric Power Research Institute (EPRI) coal liquefaction contract (Silver and Frazee 1985). The key features of this reactor system are rapid heating through submergence in a fluidized sandbath; pneumatic control of the extent of autoclave submergence; and continuous stirring using a magnetically coupled stirrer.

The autoclave has a capacity of 200 cc with an inside diameter of 1.75 cm. The original system was modified at the Wilsonville Advanced Coal Liquefaction Research and Development Facility to increase the volume (original volume was 75 cc) and, as a result, improve material balances. The improved system, called VaSTeC for Variable Submergence Temperature Control, was developed by Catalytic Inc. (1986) and has been used extensively and reliably to predict and augment test results from the thermal liquefaction unit at the Wilsonville Direct Liquefaction facility. The VaSTeC system is large enough to provide adequate materials for post-experiment analyses, yet is small enough to provide the rapid heating and cooling required for kinetic experiments. A schematic of the VaSTeC autoclave system is shown in Figure 8. The repeatability of product yields from the VaSTeC autoclave is excellent, as is shown in Table 5 (Catalytic, Inc. 1986).

Shakedown experiments to evaluate the performance of the system and to test and establish operating procedures were performed with the microautoclave system at WRI using undried coal and tetralin. The results from one of the shakedown experiments are shown in Table 6. In this experiment a 1:1 mixture of Caballo Rojo coal and tetralin was heated for one hour at 400°C in a helium atmosphere. The initial helium charge pressure was 1000 psig. After cooldown, product gases were collected in 5-liter containers and analyzed by gas chromatography. The gas analysis results are also shown in Table 6. The trace of argon in the analysis is a remnant of a volume calibration performed immediately prior to the experiment. Liquid and solid products were removed from the reactor by a combination of decanting and dicloromethane wash. The material balance for this coal liquefaction experiment, as shown in Table 6 was 98.8 wt %. This value was typical of all coal liquefaction experiments conducted.

Source: Catalytic, Inc., 1986

Figure 8. Schematic of VaSTec Autoclave System

Table 5. VaSTeC Autoclave Repeatability Data¹

Product	Repeatability, 1 standard deviation
H ₂	± 0.08%
H ₂ O	± 1.%
H ₂ S	± 0.01%
CO ₂ + CO	± 0.3%
C ₁ -C ₃	± 0.3%
C ₄ -1000°F	± 2.4%
Resid	± 2.1%
UC ²	± 0.5%

¹ Catalytic, Inc. 1986

² UC = Unconverted Carbon

Table 6. Coal Liquefaction Experiment Conditions and Material Balance for Caballo Rojo Coal

<u>Run Conditions</u>		<u>Material Recovered</u>	
Run Number	CLF3	Paste	37.5 g
Temperature	400 C	Spindle Wash	0.5 g
Duration	60 minutes	Gas	1.6 g
Coal Type	Caballo Rojo	<u>Gas composition, wt %</u>	
Solvent	Tetralin	Hydrogen	0.0
Charge Gas	Helium	Nitrogen	11.4
Charge Pressure	1000 psig	Argon	1.5
<u>Material Charged</u>		Carbon Monoxide	5.6
Coal	19.9 g	Methane	5.9
Tetralin	20.1 g	Carbon Dioxide	60.8
		Ethene	1.2
		Ethane	4.2
		Water in gas	2.9
		Hydrogen Sulfide	0.0
		Carbonyl Sulfide	0.0
		Propane	5.1
		iso Butane	0.4
		normal Butane	1.0
		Total Material Recovered	98.8 wt %

Additional experiments were conducted using a 1:1 weight ratio of Eagle Butte coal to tetralin. The initial coal sample had a weight of 20 g and was screened to a -20 +100 mesh particle size. The autoclave was pressurized with hydrogen at 900 psig. Liquefaction experiments were conducted at 425°C for a period of 30 minutes. Typical temperature profiles for the sand bath, coal slurry, and vapor are shown in Figure 9.

Figure 9. Temperature Profiles in Coal Liquefaction Reactor using Eagle Butte Subbituminous Coal

Based on the results of the shakedown experiments, liquefaction experiments on premoisturized and dried coals were carried out using a 2:1 weight ratio of tetralin to coal. The initial coal had a weight of 15 g and was screened to a -20 +100 mesh size. The autoclave was pressurized with nitrogen to 900 psig. Liquefaction experiments were carried out at 425°C for 30 minutes. Instead of using tetrahydrofuran (THF) solubles as a measure of coal conversion, conversion was based on CH_2Cl_2 solubles. Methylene chloride was chosen because it can be easily removed from the coal residue and coal liquid products.

A search for experimental conditions that would provide the greatest yields of any given product was not conducted because the objectives were to determine the effects of different drying methods on coal structure and liquefaction behavior. Liquefaction and extraction experiments conducted under the same conditions were considered acceptable to meet the objectives of the project.

Gas Analysis

The gases produced during the coal liquefaction process were collected in a gas bomb and analyzed using an Hewlett-Packard 5890 Series II Gas Chromatograph fitted with both a flame ionization detector (FID) and a thermal conductivity detector (TCD). A 6-ft, Porapak N, packed column was used to separate the gases. Helium was used as the carrier gas at a pressure of 20 psig at 160°C and a flow rate of 16 cc/min. The analyses were performed with an oven temperature ranging from -45 to 160°C. The instrument was calibrated using a standard gas mixture of known volume percent.

Liquid and Solid Extraction

Upon completion of the coal liquefaction experiment, the reactor was opened, and the soluble coal products and residue were rinsed using CH_2Cl_2 into a Soxhlet thimble. Soxhlet extraction was carried out for 30 hours at the refluxing temperature of CH_2Cl_2 . Nitrogen gas was bubbled through the CH_2Cl_2 . The CH_2Cl_2 was removed using a rotary evaporator at 40°C and at the atmospheric pressure in Laramie (typically 585 mm of Hg). The extracted material consisted of the CH_2Cl_2 , soluble product and tetralin. The extract was analyzed for soluble products above and below the retention time of tetralin, using a Hewlett-Packard 5890 Gas Chromatograph with flame ionization detector. The amount of material eluting at a retention time less and greater than that of tetralin (14 minutes) was considered to be an indicator of product quality. That is, the greater the fraction eluting before tetralin, the better the product quality.

The Soxhlet thimble and the solid residue in it were placed into a furnace set at ~ 100°C for 20 hours to remove solvent. The coal residues were characterized using solid-state carbon-13 NMR and ultimate analyses. The ultimate analyses of the dried coals (Table 7), and coal residues (Table 8) from coal liquefaction experiments were obtained from Wyoming Analytical Laboratory in Laramie, Wyoming.

Table 7. Ultimate Analysis of Coals Totally and Partially Dried by Thermal, Microwave, and Chemical Methods

Utah Blind Canyon

Ultimate Analysis	Drying Method									
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed	
	0	-	-	100	0	-	-	100	0	100
Moisture As Received	4.73			2.67	4.73			1.49	4.73	3.59
Ash										
As Received	5.56			7.07	5.56			4.94	5.56	5.08
Moisture Free	5.84			7.26	5.84			5.01	5.84	5.27
Carbon										
As Received	72.91			71.23	72.91			75.44	72.91	69.48
Moisture Free	76.53			73.18	76.53			76.58	76.53	70.51
Moisture-Ash Free	81.28			78.91	81.28			80.62	81.28	80.46
Hydrogen ¹										
As Received	5.60 ²			5.22	5.60 ²			5.48	5.60 ²	5.79
Moisture Free	5.88			5.06	5.88			5.39	5.88	5.59
Moisture-Ash Free	6.24			5.46	6.24			5.67	6.24	5.90
Nitrogen										
As Received	1.39			1.66	1.39			1.79	1.39	1.35
Moisture Free	1.46			1.71	1.46			1.82	1.46	1.40
Moisture-Ash Free	1.55			1.84	1.55			1.92	1.55	1.48
Sulfur										
As Received	0.38			0.97	0.38			0.49	0.38	0.79
Moisture Free	0.40			1.00	0.40			0.50	0.40	0.82
Moisture-Ash Free	0.42			1.08	0.42			0.53	0.42	0.87
Oxygen ^{1,3}										
As Received	9.42 ²			13.85	9.42 ²			11.86	9.42 ²	12.10
Moisture Free	9.89			11.79	9.89			10.70	9.89	9.24
Moisture-Ash Free	10.50			12.71	10.50			11.26	10.50	9.75

¹ Hydrogen and oxygen values include hydrogen and oxygen in the free moisture associated with the sample.

² Excludes Moisture ³ By difference

Table 7 continued.

Illinois # 6

Ultimate Analysis	Drying Method									
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed	
	0	13	89	100	0	33	79	100	0	100
Moisture As Received	10.43	4.59	1.75	2.66	10.43		IS ¹	1.59	10.43	3.17
Ash										
As Received	14.47	14.56	12.45	15.57	14.47		IS	13.21	14.47	12.61
Moisture Free	16.16	15.26	12.67	16.00	16.16		IS	13.42	16.16	13.02
Carbon										
As Received	58.66	65.58	68.18	66.85	58.66		65.15	65.85	58.66	66.45
Moisture Free	65.49	68.73	69.39	68.68	65.49		IS	66.91	65.49	68.43
Moisture-Ash Free	78.11	81.11	79.46	81.76	78.11		IS	77.28	78.11	78.90
Hydrogen ²										
As Received	4.08 ³	5.07	4.83	4.63	4.08 ³		4.75	4.45	4.08 ³	4.88
Moisture Free	4.56	4.78	4.72	4.45	4.56		IS	4.34	4.56	4.67
Moisture-Ash Free	5.44	5.64	5.40	5.30	5.44		IS	5.01	5.44	5.37
Nitrogen										
As Received	0.99	1.17	1.51	1.33	0.99		1.48	1.44	0.99	1.37
Moisture Free	1.11	1.23	1.54	1.37	1.11		IS	1.46	1.11	1.41
Moisture-Ash Free	1.32	1.45	1.76	1.63	1.32		IS	1.69	1.32	1.62
Sulfur										
As Received	4.05	3.66	3.64	4.47	4.05		3.35	3.98	4.05	4.18
Moisture Free	4.52	3.84	3.70	4.59	4.52		IS	4.04	4.52	4.32
Moisture-Ash Free	5.39	4.53	4.24	5.46	5.39		IS	4.67	5.39	4.97
Oxygen ^{2,4}										
As Received	7.31 ³	9.96	9.39	7.15	7.31 ³		25.27	11.07	7.31 ³	10.51
Moisture Free	8.16	6.16	7.98	4.91	8.16		IS	9.83	8.16	7.95
Moisture-Ash Free	9.73	7.27	9.14	5.85	9.73		IS	11.35	9.73	9.14

¹ IS = Insufficient Sample ² Hydrogen and oxygen values include hydrogen and oxygen in the free moisture associated with the sample.³ Excludes Moisture ⁴ By difference

Table 7 continued.
Wyoming Eagle Butte

Ultimate Analysis	Drying Method									
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed	
	0	14	82	100	0	32	73	100	0	100
Moisture As Received	29.2	6.70	3.19	5.64	29.2	12.29	4.32	1.59	29.2	10.77
Ash										
As Received	4.7	4.75	5.01	4.85	4.7	4.34	4.75	13.21	4.7	5.12
Moisture Free	6.6	5.09	5.18	5.14	6.6	4.95	4.96	13.42	6.6	5.74
Carbon										
As Received		65.38	65.46	68.00		61.09	65.21	65.85		63.31
Moisture Free		70.08	67.62	72.06		69.65	68.15	66.91		70.95
Moisture-Ash Free	67.4	73.84	71.31	75.96	67.4	73.28	71.71	77.28	67.4	75.27
Hydrogen ¹										
As Received		4.65	4.35	4.67		4.91	4.37	4.45		4.73
Moisture Free		4.18	4.12	4.28		4.03	4.06	4.34		3.95
Moisture-Ash Free	5.1	4.40	4.35	4.51	5.1	4.24	4.27	5.01	5.1	4.19
Nitrogen										
As Received		1.39	1.52	1.15		0.96	1.18	1.44		1.18
Moisture Free		1.49	1.57	1.22		1.09	1.23	1.46		1.32
Moisture-Ash Free	0.9	1.57	1.66	1.29	0.9	1.15	1.29	1.69	0.9	1.40
Sulfur										
As Received		0.23	0.26	0.15		0.27	0.32	0.30		0.67
Moisture Free		0.25	0.27	0.16		0.31	0.33	0.33		0.75
Moisture-Ash Free	0.6	0.26	0.28	0.17	0.6	0.33	0.35	0.35	0.6	0.80
Oxygen ^{1,2}										
As Received		23.60	23.40	21.18		28.43	24.17	22.15		24.99
Moisture Free		18.91	21.24	17.14		19.97	21.27	15.33		17.29
Moisture-Ash Free	19.4	19.93	22.40	18.07	19.4	21.00	22.38	16.12	19.4	18.34

¹ Hydrogen and oxygen values include hydrogen and oxygen in the free moisture associated with the sample. ² By difference

Table 7 continued.
Wyoming Black Thunder

Ultimate Analysis	Drying Method											
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed			
	0	23	70	100	0	30	73	100	0	100	0	100
Moisture As Received	27.63	7.70	2.98	5.77	27.63		2.37	4.02	27.63		4.79	
Ash As Received Moisture Free	4.49 6.21	7.45 8.07	7.76 8.00	7.86 8.34	4.49 6.21		8.03 8.22	6.46 6.73	4.49 6.21		7.30 7.67	
Carbon As Received Moisture Free Moisture-Ash Free	49.58 68.51 73.05	62.97 68.22 74.21	64.66 66.65 72.45	65.25 69.25 75.55	49.58 68.51 73.05		67.00 68.63 74.78	65.11 67.84 72.74	49.58 68.51 73.05		63.55 66.75 72.30	
Hydrogen As Received Moisture Free Moisture-Ash Free	2.84 3.92 4.18	4.52 3.96 4.31	4.18 3.96 4.30	4.23 3.80 4.15	2.84 3.92 4.18		4.13 3.96 4.31	4.38 4.09 4.39	2.84 3.92 4.18		4.28 3.93 4.26	
Nitrogen As Received Moisture Free Moisture-Ash Free	0.35 0.48 0.51	0.66 0.72 0.78	0.77 0.79 0.86	0.61 0.65 0.71	0.35 0.48 0.51		0.75 0.77 0.84	1.02 1.06 1.14	0.35 0.48 0.51		1.41 1.48 1.60	
Sulfur As Received Moisture Free Moisture-Ash Free	0.38 0.41 0.44	0.30 0.33 0.36	0.33 0.34 0.37	0.30 0.32 0.35	0.38 0.41 0.44		0.40 0.41 0.45	0.42 0.44 0.47	0.38 0.41 0.44		0.81 0.85 0.92	
Oxygen ¹ As Received Moisture Free Moisture-Ash Free	18.25 12.97 13.81	24.10 18.70 20.34	22.30 20.26 22.02	21.75 17.64 19.24	18.25 12.97 13.81		19.69 18.01 19.62	22.61 19.84 21.26	18.25 12.97 13.81		22.65 19.32 20.92	

¹ By difference

Table 7 continued.

Texas

Ultimate Analysis	Drying Method									
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed	
	0	38	75	100	0	30	78	100	0	100
Moisture As Received	30.00	5.46	2.65	2.44	30.00	15.03	6.35	1.27	30.00	7.69
Ash										
As Received	11.07	11.24	12.14	12.33	11.07	9.91	11.65	13.79	11.07	13.08
Moisture Free	15.81	11.89	12.47	12.64	15.81	11.66	12.44	13.97	15.81	14.17
Carbon										
As Received	43.77	59.37	59.73	61.74	43.77	57.07	59.41	62.09	43.77	57.14
Moisture Free	62.53	62.80	61.36	63.28	62.53	67.16	63.44	62.89	62.53	61.90
Moisture-Ash Free	74.27	71.27	70.10	72.44	74.27	76.02	72.45	73.10	74.27	72.12
Hydrogen ¹										
As Received	3.32 ²	4.44	4.11	4.23	3.32 ²	5.05	4.59	4.02	3.32 ²	4.49
Moisture Free	4.75	4.05	3.92	4.06	4.75	3.96	4.14	3.93	4.75	3.93
Moisture-Ash Free	5.64	4.60	4.48	4.65	5.64	4.48	4.73	4.57	5.64	4.58
Nitrogen										
As Received	0.86	1.20	1.51	1.21	0.86	0.66	1.22	1.43	0.86	0.97
Moisture Free	1.23	1.27	1.55	1.24	1.23	0.78	1.30	1.45	1.23	1.05
Moisture-Ash Free	1.46	1.44	1.77	1.42	1.46	0.88	1.48	1.69	1.46	1.22
Sulfur										
As Received	0.69	0.98	0.88	0.80	0.69	0.75	0.78	0.96	0.69	1.41
Moisture Free	0.99	1.04	0.90	0.82	0.99	0.88	0.83	0.97	0.99	1.53
Moisture-Ash Free	1.18	1.18	1.03	0.94	1.18	1.00	0.95	1.13	1.18	1.78
Oxygen ^{1,3}										
As Received	10.28 ²	22.77	21.63	19.69	10.28 ²	26.56	22.35	17.71	10.28 ²	22.91
Moisture Free	14.69	18.95	19.80	17.96	14.69	15.56	17.85	16.79	14.69	17.42
Moisture-Ash Free	17.45	21.51	22.62	20.55	17.45	17.62	20.39	19.51	17.45	20.30

¹ Hydrogen and oxygen values include hydrogen and oxygen in the free moisture associated with the sample.² Excludes Moisture ³ By difference

Table 7 continued.
North Dakota Beulah

Ultimate Analysis	Drying Method									
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed	
	0	-	-	100	0	-	-	100	0	100
Moisture As Received	33.38			0.63	33.38			1.61	33.38	10.69
Ash										
As Received	6.37			8.28	6.37			7.57	6.37	6.75
Moisture Free	9.56			8.33	9.56			7.69	9.56	7.56
Carbon										
As Received	44.07			64.06	44.07			63.41	44.07	60.40
Moisture Free	66.15			64.47	66.15			64.45	66.15	67.63
Moisture-Ash Free	73.14			70.33	73.14			69.82	73.14	73.16
Hydrogen ¹										
As Received	2.68 ²			3.99	2.68 ²			4.08	2.68 ²	4.90
Moisture Free	4.03			3.94	4.03			3.96	4.03	4.15
Moisture-Ash Free	4.46			4.30	4.46			4.29	4.46	4.49
Nitrogen										
As Received	0.60			1.82	0.60			1.69	0.60	1.65
Moisture Free	0.90			1.83	0.90			1.72	0.90	1.85
Moisture-Ash Free	1.00			2.00	1.00			1.86	1.00	2.00
Sulfur										
As Received	0.49			0.71	0.49			0.73	0.49	0.88
Moisture Free	0.74			0.71	0.74			0.74	0.74	0.99
Moisture-Ash Free	0.82			0.77	0.82			0.80	0.82	1.07
Oxygen ^{1,3}										
As Received	12.40 ²			21.14	12.40 ²			22.52	12.40 ²	25.42
Moisture Free	18.62			20.72	18.62			21.44	18.62	17.82
Moisture-Ash Free	20.59			22.60	20.59			23.23	20.59	19.28

¹ Hydrogen and carbon values include hydrogen and oxygen in the free moisture associated with the sample.

² Excludes moisture ³ By difference

Table 8. Ultimate Analysis of Coal Liquefaction Residues from Coals Totally and Partially Dried by Thermal, Microwave, and Chemical Methods

Utah Blind Canyon

Ultimate Analysis	Drying Method									
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed	
	0	-	-	100	0	-	-	100	0	100
Moisture As Received	1.67			2.49 (1.53) ¹	1.67			1.84	1.67	1.79 (1.46)
Ash										
As Received	14.69			17.28 (18.26)	14.69			18.32	14.69	16.77 (12.19)
Moisture Free	14.94			17.72 (18.91)	14.94			18.66	14.94	17.08 (12.37)
Carbon										
As Received	74.19			70.83 (74.18)	74.19			72.17	74.19	68.61 (69.48)
Moisture Free	75.45			72.64 (75.33)	75.45			73.52	75.45	69.86 (70.51)
Moisture-Ash Free	88.70			88.28 (92.90)	88.70			90.39	88.70	84.25 (80.46)
Hydrogen ²										
As Received	4.30			4.12 (4.25)	4.30			4.20	4.30	4.22 (4.08)
Moisture Free	4.18			3.94 (4.14)	4.18			4.07	4.18	4.09 (3.97)
Moisture-Ash Free	4.91			4.79 (5.11)	4.91			5.00	4.91	4.93 (4.53)
Nitrogen										
As Received	1.66			1.68 (1.73)	1.66			1.14	1.66	1.33 (1.51)
Moisture Free	1.69			1.72 (1.76)	1.69			1.16	1.69	1.35 (1.53)
Moisture-Ash Free	1.99			2.09 (2.17)	1.99			1.43	1.99	1.63 (1.75)
Sulfur										
As Received	0.52			1.19 (1.02)	0.52			1.09	0.52	1.60 (1.19)
Moisture Free	0.53			1.22 (1.04)	0.53			1.11	0.53	1.63 (1.21)
Moisture-Ash Free	0.62			1.48 (1.28)	0.62			1.36	0.62	1.97 (1.38)
Oxygen ^{3,4}										
As Received	4.64			4.90 (2.34)	4.64			3.08	4.64	7.47 (11.55)
Moisture Free	3.21			2.76 (0.99)	3.21			1.48	3.21	5.99 (10.41)
Moisture-Ash Free	3.78			3.36 (1.22)	3.78			1.82	3.78	7.22 (11.88)

¹ Values in parentheses are from repeated experiments.

² Hydrogen and oxygen values include hydrogen and oxygen in the free moisture. ³ By difference

Table 8 continued.

Illinois # 6

Ultimate Analysis	Drying Method									
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed	
	0	13	89	100	0	33	79	100	0	100
Moisture As Received	3.23 (1.93) ¹	1.65	2.68	2.72	3.23 (1.93)		1.28	1.20	3.23 (1.93)	1.40
Ash										
As Received	31.83 (37.95)	37.47	33.61	38.88	31.83 (37.95)		36.04	37.87	31.83 (37.95)	36.67
Moisture Free	32.89 (38.70)	38.10	34.54	39.97	32.89 (38.70)		36.51	38.33	32.89 (38.70)	37.19
Carbon										
As Received	53.53 (48.96)	52.87	53.32	48.49	53.53 (48.96)		51.61	51.02	53.53 (48.96)	51.18
Moisture Free	55.32 (49.92)	53.76	54.79	49.85	55.32 (49.92)		52.28	51.64	55.32 (49.92)	51.91
Moisture-Ash Free	82.43 (81.44)	86.85	83.70	83.04	82.43 (81.44)		82.34	83.74	82.43 (81.44)	82.65
Hydrogen ²										
As Received	3.24 (2.78)	3.18	3.35	2.68	3.24 (2.78)		3.01	2.97	3.24 (2.78)	2.89
Moisture Free	2.97 (2.61)	3.05	3.13	2.44	2.97 (2.61)		2.90	2.87	2.97 (2.61)	2.77
Moisture-Ash Free	4.43 (4.26)	4.93	4.78	4.06	4.43 (4.26)		4.57	4.65	4.43 (4.26)	4.41
Nitrogen										
As Received	1.03 (0.77)	0.77	1.01	0.84	1.03 (0.77)		0.98	1.23	1.03 (0.77)	1.20
Moisture Free	1.06 (0.79)	0.78	1.04	0.86	1.06 (0.79)		0.99	1.24	1.06 (0.79)	1.22
Moisture-Ash Free	1.58 (1.29)	1.26	1.59	1.43	1.58 (1.29)		1.56	2.01	1.58 (1.29)	1.94
Sulfur										
As Received	3.83 (4.70)	4.36	3.64	5.21	3.83 (4.70)		4.43	5.22	3.83 (4.70)	5.14
Moisture Free	3.96 (4.79)	4.41	3.74	5.36	3.96 (4.79)		4.49	5.28	3.96 (4.79)	5.21
Moisture-Ash Free	5.90 (7.81)	7.13	5.71	8.93	5.90 (7.81)		7.07	8.56	5.90 (7.81)	8.29
Oxygen ^{2,3}										
As Received	6.54 (4.84)	1.14	5.07	3.90	6.54 (4.84)		3.93	1.69	6.54 (4.84)	2.92
Moisture Free	3.80 (3.19)	0.06	2.76	1.52	3.80 (3.19)		2.83	0.64	3.80 (3.19)	1.70
Moisture-Ash Free	5.66 (5.20)	0.10	4.22	2.54	5.66 (5.20)		4.46	1.04	5.66 (5.20)	2.71

¹ Values in parentheses are from repeated experiments.² Hydrogen and oxygen values include hydrogen and oxygen in the free moisture.³ By difference

Table 8 continued.
Wyoming Eagle Butte

Ultimate Analysis	Drying Method									
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed	
	0	14	82	100	0	32	73	100	0	100
Moisture As Received	2.44 (2.16) ¹	3.23	2.62	1.82	2.44 (2.16)	2.26	2.50	2.48	2.44 (2.16)	3.27
Ash										
As Received	16.55 (19.47)	16.23	12.76	10.67	16.55 (19.47)	13.87	11.95	11.34	16.55 (19.47)	21.88
Moisture Free	16.96 (19.90)	16.77	13.10	10.87	16.96 (19.90)	14.19	12.26	11.63	16.96 (19.90)	22.62
Carbon										
As Received	69.28 (69.96)	67.61	69.17	75.00	69.28 (69.96)	69.56	71.36	73.91	69.28 (69.96)	62.44
Moisture Free	71.01 (71.50)	69.87	71.03	76.39	71.01 (71.50)	71.17	73.19	75.70	71.01 (71.50)	64.55
Moisture-Ash Free	85.51 (89.26)	83.95	81.74	85.71	85.51 (89.26)	82.94	83.42	85.76	85.51 (89.26)	83.42
Hydrogen ²										
As Received	3.70 (3.71)	3.58	3.76	3.61	3.70 (3.71)	3.79	3.87	3.65	3.70 (3.71)	3.52
Moisture Free	3.51 (3.54)	3.33	3.56	3.47	3.51 (3.54)	3.62	3.68	3.46	3.51 (3.54)	3.26
Moisture-Ash Free	4.23 (4.42)	4.00	4.10	3.89	4.23 (4.42)	4.22	4.19	3.92	4.23 (4.42)	4.21
Nitrogen										
As Received	1.44 (1.36)	1.53	1.61	1.53	1.44 (1.36)	1.63	1.66	1.64	1.44 (1.36)	1.34
Moisture Free	1.48 (1.39)	1.58	1.65	1.56	1.48 (1.39)	1.67	1.70	1.68	1.48 (1.39)	1.39
Moisture-Ash Free	1.78 (1.74)	1.90	1.90	1.75	1.78 (1.74)	1.95	1.94	1.90	1.78 (1.74)	1.80
Sulfur										
As Received	0.53 (0.34)	0.53	0.42	0.39	0.53 (0.34)	0.37	0.38	0.42	0.53 (0.34)	1.85
Moisture Free	0.54 (0.35)	0.55	0.43	0.40	0.54 (0.35)	0.38	0.39	0.43	0.54 (0.35)	1.91
Moisture-Ash Free	0.65 (0.44)	0.66	0.49	0.45	0.65 (0.44)	0.44	0.44	0.49	0.65 (0.44)	2.47
Oxygen ^{2,3}										
As Received	8.50 (5.16)	10.52	12.28	8.80	8.50 (5.16)	10.78	10.78	9.04	8.50 (5.16)	8.97
Moisture Free	6.50 (3.32)	7.90	10.23	7.31	6.50 (3.32)	8.97	8.78	7.01	6.50 (3.32)	6.27
Moisture-Ash Free	7.83 (4.14)	9.49	11.77	8.20	7.83 (4.14)	10.45	10.01	7.93	7.83 (4.14)	8.10

¹ Values in parentheses are from repeated experiments.

² Hydrogen and oxygen values include hydrogen and oxygen in the free moisture.

³ By difference

Table 7 continued.
Wyoming Black Thunder

Ultimate Analysis	Drying Method									
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed	
	0	23	70	100	0	30	73	100	0	100
Moisture As Received	27.63	7.70	2.98	5.77	27.63		2.37	4.02	27.63	4.79
Ash										
As Received	4.49	7.45	7.76	7.86	4.49		8.03	6.46	4.49	7.30
Moisture Free	6.21	8.07	8.00	8.34	6.21		8.22	6.73	6.21	7.67
Carbon										
As Received	49.58	62.97	64.66	65.25	49.58		67.00	65.11	49.58	63.55
Moisture Free	68.51	68.22	66.65	69.25	68.51		68.63	67.84	68.51	66.75
Moisture-Ash Free	73.05	74.21	72.45	75.55	73.05		74.78	72.74	73.05	72.30
Hydrogen										
As Received	2.84	4.52	4.18	4.23	2.84		4.13	4.38	2.84	4.28
Moisture Free	3.92	3.96	3.96	3.80	3.92		3.96	4.09	3.92	3.93
Moisture-Ash Free	4.18	4.31	4.30	4.15	4.18		4.31	4.39	4.18	4.26
Nitrogen										
As Received	0.35	0.66	0.77	0.61	0.35		0.75	1.02	0.35	1.41
Moisture Free	0.48	0.72	0.79	0.65	0.48		0.77	1.06	0.48	1.48
Moisture-Ash Free	0.51	0.78	0.86	0.71	0.51		0.84	1.14	0.51	1.60
Sulfur										
As Received	0.38	0.30	0.33	0.30	0.38		0.40	0.42	0.38	0.81
Moisture Free	0.41	0.33	0.34	0.32	0.41		0.41	0.44	0.41	0.85
Moisture-Ash Free	0.44	0.36	0.37	0.35	0.44		0.45	0.47	0.44	0.92
Oxygen ¹										
As Received	18.25	24.10	22.30	21.75	18.25		19.69	22.61	18.25	22.65
Moisture Free	12.97	18.70	20.26	17.64	12.97		18.01	19.84	12.97	19.32
Moisture-Ash Free	13.81	20.34	22.02	19.24	13.81		19.62	21.26	13.81	20.92

¹ By difference

Table 8 continued.

Texas

Ultimate Analysis	Drying Method									
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed	
	0	38	75	100	0	30	78	100	0	100
Moisture As Received	1.93	1.78	2.22	2.24	1.93	2.27	2.03	2.15	1.93	1.92
Ash										
As Received	36.04	37.06	30.77	29.02	36.04	33.31	31.19	29.75	36.04	41.67
Moisture Free	36.75	37.73	31.47	29.68	36.75	34.08	31.84	30.04	36.75	42.49
Carbon										
As Received	51.35	50.68	55.62	53.23	51.35	51.29	50.68	57.86	51.35	47.36
Moisture Free	52.36	51.60	56.88	54.45	52.36	52.48	51.73	59.13	52.36	48.29
Moisture-Ash Free	82.78	82.86	83.00	77.43	82.78	79.61	75.89	84.96	82.78	83.97
Hydrogen ¹										
As Received	2.96	2.82	3.25	3.11	2.96	2.93	2.82	3.11	2.96	2.86
Moisture Free	2.80	2.67	3.07	2.92	2.80	2.74	2.65	2.93	2.80	2.70
Moisture-Ash Free	4.43	4.29	4.48	4.15	4.43	4.16	3.89	4.21	4.43	4.69
Nitrogen										
As Received	0.66	0.70	0.85	1.09	0.66	0.84	0.70	0.92	0.66	0.56
Moisture Free	0.67	0.71	0.87	1.11	0.67	0.86	0.71	0.94	0.67	0.57
Moisture-Ash Free	1.06	1.14	1.27	1.58	1.06	1.30	1.04	1.35	1.06	0.99
Sulfur										
As Received	0.82	0.95	0.97	0.95	0.82	0.82	0.95	1.02	0.82	1.98
Moisture Free	0.74	0.97	0.99	0.97	0.74	0.84	0.97	1.04	0.74	2.02
Moisture-Ash Free	1.33	1.56	1.44	1.38	1.33	1.27	1.42	1.49	1.33	3.51
Oxygen ^{1,2}										
As Received	8.17	7.79	8.54	12.60	8.17	10.81	13.66	7.34	8.17	5.57
Moisture Free	6.58	6.32	6.72	10.87	6.58	9.00	12.10	5.56	6.58	3.93
Moisture-Ash Free	10.40	10.15	9.81	15.46	10.40	13.66	17.76	7.99	10.40	6.84

¹ Hydrogen and oxygen values include hydrogen and oxygen in the free moisture. ² By difference

Table 8 continued.
North Dakota Beulah

Ultimate Analysis	Drying Method									
	Thermal % Water Removed				Microwave % Water Removed				Chemical % Water Removed	
	0	-	-	100	0	-	-	100	0	100
Moisture As Received	1.61			1.90 (2.77) ¹	1.61			1.94	1.61	2.68 (1.64)
Ash										
As Received	24.83			14.67 (16.79)	24.83			15.34	24.83	15.30 (21.26)
Moisture Free	25.24			14.95 (17.27)	25.24			15.64	25.24	15.72 (21.61)
Carbon										
As Received	62.45			71.74 (67.42)	62.45			70.99	62.45	73.45 (63.91)
Moisture Free	63.47			73.13 (69.34)	63.47			72.39	63.47	75.47 (64.98)
Moisture-Ash Free	84.90			85.98 (83.81)	84.90			85.81	84.90	89.55 (82.89)
Hydrogen ²										
As Received	3.47			3.55 (3.87)	3.47			3.56	3.47	3.72 (3.77)
Moisture Free	3.34			3.40 (3.66)	3.34			3.41	3.34	3.51 (3.65)
Moisture-Ash Free	4.47			4.00 (4.42)	4.47			4.04	4.47	4.16 (4.66)
Nitrogen										
As Received	1.22			1.53 (1.61)	1.22			1.69	1.22	1.66 (1.59)
Moisture Free	1.24			1.56 (1.66)	1.24			1.72	1.24	1.71 (1.62)
Moisture-Ash Free	1.66			1.83 (2.01)	1.66			2.04	1.66	2.03 (2.07)
Sulfur										
As Received	1.19			1.05 (1.07)	1.19			0.96	1.19	1.57 (2.26)
Moisture Free	1.21			1.07 (1.10)	1.21			0.98	1.21	1.61 (2.30)
Moisture-Ash Free	1.62			1.26 (1.33)	1.62			1.16	1.62	1.91 (2.93)
Oxygen ^{2,3}										
As Received	6.84			7.46 (9.24)	6.84			7.46	6.84	4.30 (7.21)
Moisture Free	5.50			5.89 (6.97)	5.50			5.86	5.50	1.98 (5.84)
Moisture-Ash Free	7.35			6.93 (8.43)	7.35			6.95	7.35	2.35 (7.45)

¹ Values in parentheses are from repeated experiments.

² Hydrogen and oxygen values include hydrogen and oxygen in the free moisture. ³ By difference

Calculations

The calculations of the percent of coal liquefaction products and percent conversion are based upon known procedures given in the literature and adapted to the specific experiments using the Borgialli microreactor. Equations 5 to 8 give the weight percent of residue, gas, conversion yield (MAF), and liquids, respectively.

$$MAF \text{ Coal Residue (wt \%)} = \frac{10^4 R - (100 - M) A_p C}{(V_p + C_p^{fix}) C} \quad (5)$$

$$MAF \text{ Coal Converted into Gas (wt \%)} = \frac{10^4 (A + B) \sum_{i=N_2} [(Mw_i m_i) / \Sigma (Mw_i m_i)]}{(V_p + C_p^{fix}) C} \quad (6)$$

$$MAF \text{ Coal Conversion (wt \%)} = 10^2 - \left[\frac{10^4 R - (100 - M) A_p C}{(V_p + C_p^{fix}) C} \right] \quad (7)$$

$$MAF \text{ Coal Converted into Liquid (wt \%)} = MAF \text{ Coal Conversion (wt \%)} - MAF \text{ Coal Converted into Gas (wt \%)} \quad (8)$$

- where R = weight of residue (grams)
 C = weight of coal (grams)
 A = weight of gas in Bomb A (grams)
 B = weight of gas in Bomb B (grams)
 Mw_i = molecular weight of component gas i
 m_i = mole percent of component gas i
 M = weight percent of moisture
 V_p = weight percent of volatiles from proximate analysis
 C_p^{fix} = weight percent of fixed carbon from proximate analysis
 A_p = weight percent of ash from proximate analysis

Coal Swelling

The purpose of the swelling experiment was to obtain some measure of cross-linking during drying. Solvent swelling of the coal samples was conducted using the procedure described by Green et al. (1984). Swelling experiments were done on the initial coals and coals dried using thermal, microwave energy, and chemical dehydration methods. The coal mesh size was -20 +100. A 1/2-g sample of coal was weighed in a centrifuge tube, centrifuged for five minutes at 1700 rev/min, and the resulting height of the coal measured in millimeters. Four milliliters of the swelling solvent, 1,4 dioxane, was added, the mixture stirred, and let stand for 42 hours. After 42 hours, the mixture was again stirred and centrifuged and the height measured. It was not necessary to change solvent during the swelling experiment because little extraction of the coals was observed using 1,4-dioxane. The volumetric ratio, $Q_{v, dry}$, was calculated from the ratio of the measured heights of the coal in the solvent (h_2) and the height of the initial coal (h_1) (Equation 9).

$$Q_{v, dry} = h_2/h_1 \quad (9)$$

NMR Instrumentation

Hydrogen-1 (^1H) NMR spectra were obtained on a JEOL GSX-270 NMR spectrometer. The experimental conditions for recording a ^1H spectrum were eight scans, a pulse width of 5.4 μs (45°), an acquisition time of 1.5 s, a pulse delay of 20 s, and 16 K time-domain data points. In some experiments the ^1H NMR spectra were obtained on a JEOL GS-400 NMR spectrometer. The experimental conditions for recording a ^1H spectrum using this spectrometer were eight scans, a pulse width of 9.9 μs , an acquisition time of 1.0 s, a pulse delay of 20 s., and 16 K time-domain data points. A line broadening factor of 2 Hz was used to obtain the transformed spectra. Resonance areas for acetone and cycloheptane were performed on a Gateway 2000 Personal Computer using Lab CalcTM software curve-fitting routine (Galactic Industries Corporation). Line width at half-height of 0.010 ppm was used for curve-fitting. Twenty iterations of a Lorentzian line shape give quite acceptable agreement between the experimental and fitted resonance.

Solid-state ^{13}C NMR measurements were made using a Chemagnetics 100/200 solids NMR spectrometer. Carbon aromaticity measurements were made at 25 MHz using the technique of cross-polarization (CP) with magic-angle spinning (MAS) and high-power decoupling. These measurements were made using either a large-volume sample spinner (2.1 mL) at a spinning rate of ~ 3.8 kHz or a 7.5 mm (o.d.) sample spinner at a spinning rate of 4.5 kHz. Between 3,600 and 7,200 transients were recorded. Other instrument parameters were a pulse delay of 1 s, a contact time of 1 ms, a 6.2 μs (large volume spinner) and 5 μs (7.5 mm spinner) pulse widths, a sweep width of 16 kHz, and 1 K data acquisition points. A 25 or 50 Hz exponential multiplier was applied to the free induction decay of each ^{13}C spectrum before integration.

Differential Scanning Calorimetry of Coals

A TA instruments 2910 Differential Scanning Calorimeter (DSC) with a liquid nitrogen cooling accessory (LNCA) was used in this study to determine what solvents were retained by the coals after chemical dehydration. A helium purge of 20 cc/min through the cell provided an inert operating environment. Nitrogen at 100 cc/min was directed through the vacuum port of the system. The DSC was temperature-calibrated using indium at 156.61°C and mercury at -38.87°C. Heat flow was calibrated using the indium heat of fusion (28.42 J/g). All DSC tests were performed at ambient pressure, typically about 0.78 bar.

A weighed aliquot (~ 5 mg) of coal was encapsulated in an aluminum hermetic pan with a laser-drilled aluminum hermetic lid. The precision pinhole in these lids has a 75 μm diameter. Total exposure time from opening the nitrogen-capped coal storage vial to inserting the DSC pan into the helium-swept instrument cell was typically about two minutes. An empty pan and lid were used for reference.

The DSC was programmed to heat the coal sample at 10°C per minute from -20°C to 225°C, cool the sample at 10°C per min to -20°C, and then reheat to 225°C at 10°C per minute. After the test was completed, the sample was removed and weighed. Total mass loss was obtained by difference. Transition energies were obtained by integration of the endothermic peaks seen during the first heating ramp. A visual

comparison between the baseline produced during the second heating ramp and the baseline selected for peak integration ensured reasonable integration endpoints.

The weight loss of the coal sample during the DSC experiments was calculated from the original, C_o , and final, C_f , coal weights (see equation 10).

$$\% \text{ Weight Loss} = [(C_o - C_f) / C_o] 100 \quad (11)$$

If all the weight loss is due to water, the % weight is the weight percent water in the original sample.

DSC measurements of the transition energies were done in two ways to identify the material lost during the tests. First, if the lost material was assumed to be water, the percent water in the original sample was calculated using equation 11.

$$H_2O \% = [H_{vap}(\text{sample}) / H_{vap}(H_2O)] 100 \quad (12)$$

where

$H_{vap}(\text{sample})$ = the measured transition energy in J/g and
 $H_{vap}(H_2O)$ = the heat of vaporization of water, 2257 J/g.

If the result of equation 11 does not match the result of equation 10, the heat of vaporization of the lost material was calculated using equation 12.

$$H_{vap}(\text{lost material}) = [H_{vap}(\text{sample}) / (C_o - C_f)] C_o \quad (13)$$

where all variables have been defined above. The result is in units of Joules/gram. This value was then used in conjunction with knowledge of the history of the coal sample and thermodynamic properties tables to indicate probable vaporized materials. The assumption involved in this approach is that only one compound contributes to the weight loss and to the DSC endotherms for a given sample. This is certainly valid in the premoisturized coals where most of the weight loss is known to be water. For the chemically dried coals, methanol and acetone were components of the weight loss, although methanol most likely predominates.

D₂O Exchange Studies

Preliminary exchange studies with D₂O were conducted on the Utah Blind Canyon coal and on the Texas Bottom coal. One-half gram of raw coal was placed into a centrifuge tube to which 2 mL of D₂O was added. The sample was mixed and allowed to stand for two hours. After two hours, the sample was centrifuged and an aliquot removed for ¹H NMR analysis.

Two other types of experiments also were performed to study the D₂O exchange with the H₂O in coal. The first D₂O-H₂O exchange experiment involved repeated washings of the coal with D₂O. The samples were prepared by taking about 0.5 g of coal and covering it with about 2 mL of D₂O. After 20 minutes, an aliquot of D₂O was drawn off and put in an NMR tube, and the rest of the D₂O was discarded. This process was repeated twice more. For the last aliquot, the D₂O was removed after one week in contact with the coal sample. The second of these experiments involved taking aliquots of D₂O from coal-D₂O slurry (0.5 g coal, 5 mL D₂O). Every two hours an aliquot of D₂O was removed and put into an NMR tube, except for the last aliquot, which was removed from the coal slurry after one week. The samples were then run on the liquid state ¹H NMR spectrometer.

RESULTS AND DISCUSSION

A. Effects of Different Drying Processes on the Structure of Coals

Thermal Drying

The expected changes in the coal structure during thermal drying at 105°C for 24 hours are the loss of moisture and possibly some highly volatile components. Any structural changes due to low temperature oxidation were presumed to be minimized by using a nitrogen atmosphere. Samples of coals were also ballistically heated in a nitrogen atmosphere to different final temperatures in order to determine if, and at what temperature, significant structural changes begin to occur that might affect the liquefaction behavior. Table 9 gives the percent weight loss for the six coal samples

during ballistic heating to 250°C. The data show that the weight losses after heating are greater than the moisture content of the unheated coals, indicating a loss of material and, presumably, structural changes in the coals.

Table 9. Coal Weight Loss During Ballistic Heating to 250°C

Coal	Wt % Moisture (thermal heating) ¹	% Weight Loss (ballistic heating)
Utah Blind Canyon	4.04	5.85
Illinois # 6	9.79	11.63
Wyoming Eagle Butte	18.54	19.81
Wyoming Black Thunder	23.22	24.02
Texas Bottom	28.73	26.88
North Dakota Beulah	35.44	35.38

¹ 105°C for 24 hrs

a. ¹³C Solid-State NMR of Coals. Solid-state ¹³C NMR spectra were obtained on the coals that were thermally heated to 105°C and ballistically heated to 250°C and 300°C. Figures 10 to 15 are the ¹³C NMR spectra of the initial, thermally heated, and the ballistically heated coals. Overall, there were not any dramatic changes in the carbon structure as a result of thermal heating to 105°C or ballistic heating to 250°C and 300°C. The most noticeable change in the NMR spectra is in the carboxyl region (~ 180 ppm) of the ballistic heated Wyoming Eagle Butte, Wyoming Black Thunder, and North Dakota Beulah coal samples, where there is evidence of some decarboxylation having taken place during heating (see Figures 12c, 13c, and 15c). Utah Blind Canyon coal shows a dramatic reduction in the aliphatic carbons content relative to the aromatics between 250°C and 300°C. (Compare Figures 10c and 10d.) Some narrowing of the aliphatic band in the spectrum of the Eagle Butte coal is observed (Figure 12c). These results are also in agreement with data in Table 9, which show that the weight losses after heating are greater than the moisture content of the unheated coals.

Figure 10. Carbon-13 NMR Spectrum of Utah Blind Canyon Coal: (a) Initial Coal, (b) Thermally Dried at 105°C, (c) Ballistically Heated to 250°C, and (d) Ballistically Heated to 300°C

Figure 11. Carbon-13 NMR Spectra of Illinois #6 Coal: (a) Initial Coal, (b) Thermally Dried at 105°C, and (c) Ballistically Heated to 250°C

Figure 12. Carbon-13 NMR Spectra of Wyoming Eagle Butte Coal: (a) Initial Coal, (b) Thermally Dried at 105°C, and (c) Ballistically Heated to 250°C

Figure 13. Carbon-13 NMR Spectra of Wyoming Black Thunder Coal: (a) Initial Coal, (b) Thermally Dried at 105°C, and (c) Ballistically Heated to 250°C

Figure 14. Carbon-13 NMR Spectra of Texas Bottom Coal: (a) Initial Coal, (b) Thermally Dried at 105°C, (c) Ballistically Heated to 250°C, and (d) Ballistically Heated to 300°C

Figure 15. Carbon-13 NMR Spectra of North Dakota Beulah Lignite: (a) Initial Lignite, (b) Thermally Dried at 105°C, (c) Ballistically Heated to 250°C, and (d) Ballistically Heated to 300°C

Table 10 gives the apparent carbon aromaticity values for the initial coals and the coal dried by the various methods. The apparent carbon aromaticity values for the thermally dried coals are slightly less than those for the initial coals (within ± 0.03 units) except for Wyoming Black Thunder coal and North Dakota Beulah lignite. The slight decrease in aromaticity values may be the result of small structural changes in the aromatic structure of the coal, possibly due to low-temperature decarboxylation or loss of volatile components.

Table 10. Apparent Carbon Aromaticity Values for Initial Coal and Coal Dried Using Thermal, Microwave, and Chemical Methods

Coal	Apparent Carbon-Aromaticity Values ¹			
	Initial Coal	Dried Coal		
		Thermal Heating	Microwave Heating	Chemical Dehydration
Utah Blind Canyon	0.618	0.610	0.638	0.637
Illinois # 6	0.694	0.665	0.701	0.663
Wyoming Eagle Butte	0.629	0.617	0.662	0.638
Wyoming Black Thunder	0.596	0.626	0.639	0.613
Texas Bottom	0.542	0.439	0.528	0.552
North Dakota Beulah	0.745	0.751	0.728	0.684

¹ includes contribution from carboxylate carbons (~ 180 ppm) if present

b. Swelling Index. Table 11 gives the results of coal swelling measurements using 1,4-dioxane as the swelling reagent for premoisturized coals (initial) and coals dried thermally, chemically, and with microwave radiation. The swelling ratio indicates the extent of cross-linking in the coal (Solomon et al. 1988; Bockrath et al. 1987). An increase in the ratio indicates a decrease in the number of cross-links. Solomon et al. (1990), in their study of the cross-linking reactions during coal conversion, described a swelling index profile defined as $1-X$, where X is the change in solvent swelling ratio between the initial coal and char, normalized by the maximum change. Their expression was adapted in this study to describe coals dried by the three methods. The modified expression is given in equation 13.

Table 11. Swelling Index for Initial Coals and the Thermally, Microwave, and Chemically Dried Coals

Coal	Swelling Index Using 1,4-Dioxane			
	Initial Coal	Dried Coal		
		Thermal	Microwave	Chemical
Utah Blind Canyon	1.23	1.15	1.12	1.37
Illinois # 6	1.62	1.54	1.45	1.59
Wyoming Eagle Butte	1.46	1.26	1.31	1.55
Wyoming Black Thunder	1.45	1.34	1.33	1.68
Texas Bottom	1.49	1.28	1.33	1.41
North Dakota Beulah	1.40	1.15	1.13	1.44

$$X = \frac{Q_{coal} - Q_{v,dry}}{Q_{coal} - 1} \quad (14)$$

where X = swelling index
 Q_{coal} = swelling ratio of the initial coal
 $Q_{v,dry}$ = swelling ratio of the dried coal

When $1 - X = 1$, this profile parameter represents the cross-linking structure of the initial coal normalized to one. For $1 - X = 0$, the parameter corresponds to a fully cross-linked coal and for $1 - X > 1$, the parameter represents a cross-linking coal structure less than the initial coal.

Table 12 lists the $1 - X$ parameter for the initial coals and dried coals. As shown in the table, the swelling index profile parameters ($1 - X$) for the thermally dried coals are all less than for the initial coals, indicating an increase in the cross-linking structure due to thermal heating of the coals. In general, the lower rank coals (Texas Bottom and North Dakota Beulah) demonstrated a greater degree of cross-linking during thermal drying than did the higher rank coals. For the thermally dried coals, some degree of cross-linking had occurred with the loss of moisture and at the relatively low temperature of 105°C. The change in coal structure as a result of cross-linking is probably due to partial devolatilization and decarboxylation processes.

Table 12. Solvent Swelling Profile Parameter of Initial Coals and the Microwave, Thermally, and Chemically Dried Coals

Coal	Swelling Parameter (1-X) using 1,4-Dioxane			
	Microwave Dried	Thermally Dried	Initial Coal	Chemically Dried
Utah Blind Canyon	0.52	0.65	1.0	1.61
Illinois # 6	0.73	0.87	1.0	0.95
Wyoming Eagle Butte	0.67	0.56	1.0	1.50
Wyoming Black Thunder	0.73	0.76	1.0	1.51
Texas Bottom	0.67	0.57	1.0	0.84
North Dakota Beulah	0.32	0.37	1.0	1.10

Microwave Drying

a. Model Compounds. Some microwave heating experiments were performed on model compounds to determine whether microwaves interact with certain functional groups in coals, particularly OH groups which have a strong dipole moment. Exploratory experiments were performed on model compounds: phenol (C_6H_5OH), benzoic acid (C_6H_5COOH), stearic acid ($CH_3(CH_2)_{16}COOH$), and stearyl alcohol ($CH_3(CH_2)_{16}COH$). All materials are solids at room temperature. About 2 g of the model compounds was placed in the microwave oven and irradiated for one hour at 100% power, after which the % weight loss was determined. The results are summarized in Table 13.

Table 13. Percent Weight Loss of Model Compounds Due to Microwave Heating

Compound	mp, °C	bp, °C	Weight Loss, %
Benzoic Acid	122-123	249	0.053
Phenol	40-42	182	13.07
Stearic Acid	67-69	183-184	0.345
Stearyl Alcohol	60-61	170-171	0.186

Except for benzoic acid, which showed the smallest weight loss, all compounds melted during microwave heating, indicating absorption of energy. In addition, phenol appeared to have undergone a chemical reaction as evidenced by a color change from white to red. The other compounds resolidified to their original colors when returning to room temperature. No further work was done on the effects of microwave radiation on model compounds.

b. Coals. The general features of coal drying using microwave radiation are shown in Figure 16, which is a master plot of the superposition of the drying curves for all six coals. Each drying curve is normalized to the percent moisture in that coal. In general, there is a very rapid temperature rise after ~ 10% of the inherent moisture is removed. This is followed by removal of the bulk of the moisture (10 to 80%) at temperatures approaching the boiling point of water (~ 93°C at the 7,200-ft elevation of Laramie, Wyoming). The rapid increase in temperature after removal of about 80% of the moisture seems to be a general characteristic of microwave heating of subbituminous coals. This behavior was also observed by Silver and Frazee (1985) and Silver et al. (1986), who also noted a decreased reactivity toward liquefaction for greater than 75% moisture removal.

Figure 16. Superposition of the Microwave Drying Curve for the Six Coals

The moisture removed at higher temperatures could be from water in the gel or that which is strongly hydrogen bonded to coal within the internal pore structure of the coal. These water molecules are more tightly bound and would have a more difficult time aligning and realigning with the radiation field. This could cause heating of the coal to higher temperatures, with possible disruption of part of the coal matrix enabling some retrograde reactions to take place that diminish the reactivity toward liquefaction. To test these ideas, a microwave drying curve was also measured for a Linde 13X molecular sieve containing 30.6% moisture in its pores. The microwave drying curve for the molecular sieve (Figure 17) is similar to that of the coals. Thus, it appears that the increase in temperature after about 80% of the moisture removal is due to removal of the "free" water in the internal pore structure of coal and not water that is hydrogen bonded, or in a gel-like phase.

Figure 17. Microwave Drying Curve for Linde 13X (1/16 in. Pellets) Molecular Sieve. Initial Moisture Content 30.59 wt %.

c. ^{13}C NMR. Solid-state ^{13}C CP/MAS NMR spectra of microwave-heated coals (Figures 18 to 23) do not show any significant carbon structural changes relative to the initial coal as a result of moisture removal using microwaves, even though temperatures greater than 100°C were produced and greater than 100% of the moisture was removed relative to thermal drying at 105°C . However, small changes in the resolution and intensity of the resonances are noted in the region from 180 to 220 ppm for Wyoming Eagle Butte (Figure 20b), Wyoming Black Thunder (Figure 21b), Texas Bottom (Figure 22b), and North Dakota Beulah (Figure 23b) coals. These changes suggest that some decarboxylation could have occurred during microwave heating. As noted previously, organic acids melted from the absorption of microwaves. Therefore, similar functional groups in coal can absorb microwaves, become heated and possibly decarboxylate. Figure 24 shows the ^{13}C NMR spectrum of Wyoming Eagle Butte coal and percent weight loss when subjected to microwave heating for different periods of time. In general, it appears that microwave drying behavior reflects mostly the drying behavior of water in different sized pores, and heating with microwaves under these conditions does not cause any major changes in carbon structure of the coals except for possibly some loss of phenolic groups at ~ 155 ppm.

The NMR carbon aromaticity values for the coals dried using microwave radiation are given in Table 10. The values for Texas and North Dakota coals reflect the possible loss of carbon due to decarboxylation. In general, little change in coal structure is noted for the coals dried using microwave heating.

d. Swelling Index. Microwave drying decreased the swelling index profile parameter of the coals relative to the coals before heating (Table 12). The parameters are less than those measured for the thermally dried coals with the exception of Wyoming Eagle Butte and Texas Bottom coals. Thus, microwave radiation induces still more cross-linking in the coal structure than thermal heating. These changes do not appear to affect the overall carbon distribution significantly, as major changes are not observed in the NMR spectra. It is assumed that microwave radiation produces intense localized heating in the coals, causing some loss of phenolic groups and more devolatilization and decarboxylation than thermally heating the coals at 105°C , and thus it promotes additional cross-linking.

Figure 18. Carbon-13 NMR Spectra of Utah Blind Canyon Coal: (a) Initial Coal and (b) Microwave Heated at 100% Power for 15 Minutes.

Figure 19. Carbon-13 NMR Spectra of Illinois # 6 Coal: (a) Initial Coal and (b) Microwave Heated at 100% Power for 12 Minutes

Figure 20. Carbon-13 NMR Spectra of Wyoming Eagle Butte Coal: (a) Initial Coal and (b) Microwave Heated at 50% Power for 1 Hour

Figure 21. Carbon-13 NMR Spectra of Wyoming Black Thunder Coal: (a) Initial Coal and (b) Microwave Heated at 100 % Power for 15 Minutes

Figure 22. Carbon-13 NMR Spectra of Texas Bottom Coal: (a) Initial Coal and (b) Microwave Heated at 100% Power for 15 Minutes

Figure 23. Carbon-13 NMR Spectra of North Dakota Beulah Lignite: (a) Initial Lignite and (b) Microwave Heated at 100% Power for 15 Minutes.

Figure 24. Solid-State Carbon-13 NMR Spectra of Eagle Butte Coal Subjected to Microwave Drying for Different Periods of Time (total weight loss from thermal drying = 22.5%)

Chemical Drying

a. Moisture in Coal. The results for determining the water content for six coals using the chemical dehydration method are summarized in Table 14. The data given here are for illustrating the precision of the chemical dehydration method. As shown in the table, the Texas Bottom subbituminous coal has the largest standard deviation of all the coals investigated. From another set of experiments, thermally drying the Texas coal gives a moisture value of 29.17% with a standard deviation of $\pm 0.61\%$. The standard deviation for the other coals are about $\pm 1\%$ or less, which is better than what one can obtain by many other moisture determination methods for coals.

Table 14. Moisture Determination in Coals of Various Rank Using 2,2-Dimethoxypropane and ^1H NMR

Coal	Run 1	Run 2	Run 3A	Run 3B	Run 4	Ave.	SD ¹
UtahBlind Canyon	3.95	4.56	3.97			4.16	0.35
Illinois #6	10.89	11.35	10.79			11.01	0.30
Wyoming Eagle Butte	22.35	20.66	20.18			21.06	1.14
Wyoming Black Thunder	24.88	22.39	23.16			23.48	1.27
Texas Bottom	31.02	(44.16) ²	24.96	(44.21)	29.81	28.60	3.21
North Dakota Beulah	(40.73)	34.71	34.34	33.26	32.09	33.60	1.18

¹ One Standard Deviation

² Samples in parenthesis were thrown out based on the fact that they lie more than two standard deviations from the mean of the remaining runs.

Figure 25 shows a least squares regression plot of the water content determined chemically versus the water content determined thermally for coals of different rank. It can be seen that for the high rank coals (Utah Blind Canyon and Illinois #6) the errors in the methods are about the same. For the low-rank coals (Texas Bottom and North Dakota Beulah), the chemical method is less precise than the thermal method for determining moisture content. For the four medium- and high-rank coals, the average moisture content for each falls on a straight line slightly higher than the line representing a 1:1 correlation. This difference may signify that (for the medium- or higher-rank coals) the chemical method is indeed determining water that is more tightly bound or accessible through diffusion in the pore structure of the coals. Using different coals and the isotope dilution method, Finseth (1987) also found that the water content measured by isotopic dilution is greater than when measured by the thermal method (Figure 26).

Figure 25. A Comparison of the Water Content in Coals as Measured by Chemical and Thermal Drying Methods: (a) ——— Solid Line Represents 1:1 Correlation; (b) - - - - , 4 pts; and (c) - - - - , 6 pts

Figure 26. A Comparison of the Water Content in Coals as Measured by Isotopic Exchange and by ASTM Thermal Drying Method (Finseth 1987). Solid line represents 1:1 correlation.

b. Chemical Drying Kinetics. Plots of the weight percent of moisture removed from the coal samples as a function of time in which the coals are in contact with DMP are shown in Figures 27 through 32. In all cases, a significant amount of moisture is removed in the first minute of the reaction. The initial reaction is DMP with physisorbed surface water and free water in the pores near the surface of the coal. Removal of the remaining moisture requires longer times and is due to diffusion control of DMP into the smaller pores within the coals.

The chemical drying data after the fast initial reaction were fit to 1st- and nth-order kinetic equations (equations 3 and 4, respectively). The kinetic parameters are listed in Table 15.

The initial concentration, C_i , shown in the table is defined as the percent of physisorbed and free surface moisture removed from the coal during the initial reaction of water and DMP. This reaction occurs almost instantaneously. The value of C_i for both the first order and nth order reactions increases with decreasing coal rank. That is, the higher rank coals are generally less porous and have less adsorbed water than the lower rank coals. Wyoming Black Thunder coal C_i value is higher than expected and may be due to the smaller mesh size of the coal sample compared to the other coals.

The percent of moisture in coal at $t = \infty$, but not including the water removed during the initial reaction, is M_∞ . The sum of C_i and M_∞ gives the total amount of water in each coal sample. These values greatly exceed their respective thermal moisture values, especially for the low-rank coals. Figures 33 and 34 show the first and nth order plots of the total amount of water in coal at $t = \infty$ as determined by chemical dehydration method versus moisture content determined by the standard thermal method. These figures are similar to Figure 25 except that the chemical dehydration data in Figure 25 were obtained for $t = 16$ hours and the total moisture content determined directly from NMR data.

Table 15 also lists the percent of readily accessible water (sorbed surface water) for each coal. As shown in the table, the percent of loosely bound surface water increases with decreasing rank of the coal. Based on a first-order kinetics analysis of the data, the Utah Blind Canyon coals have the lowest amount of surface water (12.2%), whereas the Texas Bottom coal and North Dakota Beulah lignite have almost two-thirds of the total water near or on the surface and readily accessible to react with DMP (62.0 and 64.4%, respectively).

Figure 27. Weight Percent of Water Removed by DMP for Utah Blind Canyon Coal as a Function of Time

Figure 28. Weight Percent of Water Removed by DMP in Illinois # 6 Coal as a Function of Time

Figure 29. Weight Percent of Water Removed by DMP in Eagle Butte Coal as a Function of Time

Figure 30. Weight Percent of Water Removed by DMP in Black Thunder Coal as a Function of Time

Figure 31. Weight Percent of Water Removed by DMP in Texas Coal as a Function of Time

Figure 32. Weight Percent of Water Removed by DMP for North Dakota Beulah Lignite as a Function of Time

Table 15. Kinetic Parameters for the Chemical Dehydration of Coals

Coal		Kinetic Parameters					
		Order n	Rate Constant k, hr ⁻¹	Initial Concentration of water, C _i (%)	Final Concentration of water, M _∞ (%)	Total Concentration of Water (%) C _i + M _∞	Percent of Surface Water C _i /(C _i + M _∞)
Utah Blind Canyon	1st order	1	3.59 x 10 ⁻³	0.89	6.41	7.3	12.2
	nth order	0.893	4.15 x 10 ⁻³	0.94	6.31	7.3	13.0
Illinois # 6	1st order	1	1.93 x 10 ⁻²	4.6	6.5	11.1	41.4
	nth order	1.07	2.49 x 10 ⁻²	4.5	6.6	11.1	40.5
Wyoming Eagle Butte	1st order	1	2.17 x 10 ⁻³	12.5	11.5	24.0	52.1
	nth order	3.62	0.157	11.2	18.8	30.0	37.3
Wyoming Black Thunder	1st order	1	1.85 x 10 ⁻³	19.9	2.2	22.1	90.1
	nth order	0.943	1.62 x 10 ⁻²	15.3	7.1	22.4	68.3
Texas Bottom	1st order	1	8.39 x 10 ⁻³	18.4	11.3	29.7	62.0
	nth order	5.61	12.8	13.0	23.6	36.6	35.5
North Dakota Beulah	1st order	1	1.11 x 10 ⁻³	24.6	13.6	38.2	64.4
	nth order	1.32	4.29 x 10 ⁻⁴	24.6	15.4	40.0	63.1

Figure 33. Total Water Content Determined for Chemical Dehydrated Coals (1st order kinetics) versus the Water Content Determined for Thermally Dried Coals. Solid line represents a 1:1 correlation.

Figure 34. Total Water Content Determined for Chemical Dehydration Coals (nth order kinetics) versus the Water Content Determined for Thermally Dried Coals. Solid line represents a 1:1 correlation.

Figure 35 is a plot of the percent of surface water as a function of the rank of coal based on the fixed carbon content. The data for the Wyoming Black Thunder coal was discarded because of the different mesh size of this coal. Wroblewski and Verkade (1992) also measured the different types of moisture in coals using several extraction solvents and measuring the moisture content in the extracts over an eight-hour period. These authors found that of the total moisture content in coals, the higher-rank coals have less surface water than the lower-rank coals, in qualitative agreement with the results shown in Figure 35.

The chemical drying method may provide a method to obtain the relative percentages of external surface and internal pore water in coals. The amount of external (surface) and internal (pore and hydrogen bonded) water in coal is essential to the study of the role of water in coal liquefaction or any other type of process.

c. ^{13}C NMR. The ^{13}C CP/MAS NMR spectra of the chemically dried coals are shown in Figures 36 through 41. There appears to be enhanced resolution in the aromatic (100-210 ppm) and aliphatic (0-80 ppm) carbon regions of the spectra. Decarboxylation in the aromatic region is not apparent. The enhanced resolution in the aliphatic carbon region may be due to (1) the tightly bound residual solvents and/or reaction products such as CH_3OH that had replaced the water and (2) increased mobility of some coal components because of fewer secondary interactions resulting from the loss of the strongly hydrogen bonded water. Additional vacuum drying of the chemically dried North Dakota lignite altered the aliphatic carbon region extensively (Figure 41c) but the enhanced resolution remained unaffected. The carbon aromaticity values of the chemically dried coals are given in Table 10. Only slight changes (with experimental error) are noted for the chemically dried coals relative to the initial coals. Thus, chemical drying had little or no effect on the organic composition of the coals. However, the extent of physical association of the coal molecule had been altered due to the loss of water, which may have affected the overall coal structure (Nishioka 1994).

d. Differential Scanning Calorimetry of Coals. The solid-state ^{13}C NMR spectra of chemically dried coals showed additional carbon resonances and/or increased resolution in the aliphatic carbon region. The changes in the spectra were assumed

Figure 35. A Plot of the Percent Surface Water for Coals as a Function of the Coal Rank (wt % of fix carbon)

Figure 36. Carbon-13 NMR Spectra of Utah Blind Canyon Coal: (a) Initial Coal and (b) Chemically Dried

Figure 37. Carbon-13 NMR Spectra of Illinois # 6 Coal: (a) Initial Coal and (b) Chemically Dried

Figure 38. Carbon-13 NMR Spectra of Wyoming Eagle Butte Coal: (a) Initial Coal and (b) Chemically Dried

Figure 39. Carbon-13 NMR Spectra of Wyoming Black Thunder Coal: (a) Initial Coal and (b) Chemically Dried

Figure 40. Carbon-13 NMR Spectra of Texas Bottom Coal: (a) Initial Coal and (b) Chemically Dried

Figure 41. Carbon-13 NMR Spectra of North Dakota Beulah Lignite: (a) Initial Lignite, (b) Chemically Dried, and (c) Chemically Dried Followed by Vacuum

to be due to sorbed solvents and/or reaction products occupying surface and pore sites previously held by water. DSC was used to identify and quantify the sorbed species for the chemically dehydrated coals. Initial DSC experiments showed little weight loss from -20°C to 225°C on the microwave-dried and thermally dried coals. Thus, no further tests were performed on coals treated by either of these methods. The DSC experiments were focused on the premoisturized and chemically dried coals, and Table 16 summarizes these results. The coal source and treatment method are identified in the first two columns of the table. The original sample weight, final sample weight, and the weight loss percent (see equation 10) are listed in the next columns. Integrating the vaporization endotherm produces the transition energy per gram of original sample listed in the sixth column of the table. When converted to energy per gram of material lost (column 7) as described in equation 12, the type of material lost during the scan might be deduced.

Obviously, losses from the premoisturized coal samples are primarily caused by vaporization of water. For the chemically dried coal samples, however, losses could conceivably be from vaporization of methanol, acetone, water, or a combination of the three. Fortunately, the heats of vaporization of the three materials are significantly different, and a tentative identification of the material is possible if it is assumed that only one material is lost. For all chemically dried coals, except Utah Blind Canyon, the material lost appears to be methanol with an average heat of vaporization of 1136 J/g and a standard deviation of 100 J/g . The literature value is 1224.5 J/g (see reference in table). The measured heat of vaporization for the Utah coal is close to the literature value for acetone, however, the weight loss for this material and the transition energy are small, decreasing the accuracy of both measurements and placing the identification of the material in some doubt.

It is possible to use the measured transition energy and the published values for the heats of vaporization to estimate the amount of material lost. This calculated value for each of the samples is listed in the last column of Table 16. Plotting the calculated values against the measured weight loss percent (Figure 42) shows the consistency of the data and the validity of selecting methanol as the material vaporized in all but one of the chemically treated coals.

Table 16. Differential Scanning Calorimetry of Thermally, Microwave, and Chemically Dried Coals

Material	Treatment	Original wt, mg	Final wt, mg	Weight loss, wt %	Transition energy, J/g-sample	Measured heat of vaporization, J/g-lost	Predicted material	Calculated loss, wt %
Utah Blind Canyon	Premoisturized	4.50	4.34	3.6	54.96	1546	Water	2.4
	Chemically dried	4.52	4.27	5.5	36.89	667	Acetone	6.7
	Microwave dried ¹	5.45	5.41	0.7	1.88	256	Water	0.1
	Microwave dried ¹	2.95	2.93	0.7	4.32	637	Water	0.2
Illinois #6	Premoisturized	5.39	4.85	10.0	235.90	2355	Water	10.5
	Premoisturized	3.09	2.73	11.7	217.50	1867	Water	9.6
	Chemically dried	4.33	4.09	5.5	63.92	1153	Methanol	5.2
Wyoming Eagle Butte	Premoisturized	3.41	2.84	16.7	368.30	2203	Water	16.3
	Chemically dried	5.46	4.41	19.2	229.90	1195	Methanol	18.8
Wyoming Black Thunder	Premoisturized	3.87	3.15	18.6	361.80	1945	Water	16.0
	Chemically dried	4.76	4.35	8.6	106.70	1239	Methanol	8.7
Texas Bottom	Premoisturized	5.66	4.35	23.1	479.50	2072	Water	21.2
	Chemically dried	3.67	3.11	15.3	164.40	1077	Methanol	13.4
North Dakota Beulah	Premoisturized	4.26	2.95	30.8	631.80	2055	Water	28.0
	Chemically dried	3.70	3.36	9.2	91.58	997	Methanol	7.5
	Microwave dried ¹	6.33	6.26	1.1	21.72	1964	Water	1.0
	Thermally dried ¹	4.22	4.11	2.6	12.37	475	Water	0.5

Heats of vaporization

Water	2257 J/g @ 373.15 K, Table A.6 in Fundamentals of Heat and Mass Transfer, 3rd edition, Incropera and De Witt
Methanol	1224.5 J/g, pg C-733 in CRC Handbook of Chemistry and Physics, 57th edition
Acetone	550.5 J/g, pg C-734 in CRC Handbook of Chemistry and Physics, 57th edition

¹ These samples were heated at 5°C per minute from 20°C to 200°C.

Figure 42. A Plot of the Calculated Weight Loss versus the DSC Measured Weight Loss for Chemically Dehydrated Coals (♦ Water, ■ Methanol). Solid line represents a 1:1 correlation

e. Swelling Index. The swelling index profile parameters of the chemically dehydrated coals are given in Table 11. This parameter for Illinois # 6 and Texas Bottom coals shows a small decrease relative to the swelling index parameter of the initial coals, whereas, Utah Blind Canyon, Wyoming Eagle Butte, Wyoming Black Thunder, and North Dakota Beulah coals show a significant increase. The data suggest that only a small increase or no change in the cross-linking internal structure for the Illinois # 6 and Texas Bottom coals occurred as a result of chemical dehydration. However, a significant decrease in the cross-linking structure ($1 - X > 1$) is observed for the other four coals due to chemical dehydration. Water in coal can form extensive hydrogen bonding, and its incorporation into the coal structure has been postulated for the strained state of coal (Nishioka 1994). This author suggests that the removal of water from coal changes its structural conformation below the glass transition temperature level observed in the initial state of coal and suggests that the mobility of coal molecules may be a strong function of the water content.

It was shown by NMR and DSC data that the solvent, CH_3OH , is incorporated into the coal structure of the chemically dehydrated coals. It is possible that the solvent and products resulting from the chemical dehydrating (acetone and methanol) occupy the surface sites that water had before the reaction. The incorporation of CH_3OH at the sites previously occupied by water molecules would decrease the extent of relatively strong secondary interactions involving ionized groups, charge-transfer complexes and π - π interactions as well as hydrogen bonding and weak van der Waal's forces (Nishioka 1992). A decrease in these interactions, in effect, would reduce the cross-linking due to physical association relative to the initial coal.

B. Effects of Different Drying Processes and Moisture Content on the Reactivity of Coals

Coal Liquefaction Yield

Tables 17a through 17c give the results of the coal liquefaction of the six coals that were dried using various methods. The table contains data on the percentage of gas, liquid, and residue produced, and the percent conversion for different drying techniques. Relative to the premoisturized coals, drying coals thermally and with microwave radiation decreased the percent conversion for all coals except for Utah

Blind Canyon and Illinois # 6 coals. Both of these coals are of high rank and low moisture content, with most of the moisture tightly bound in the internal structure of the coal. Drying the coals by chemical dehydration, in general, increased the conversion yield. Utah Blind Canyon and North Dakota Beulah coals showed little or no change in the conversion yield.

Table 17a. Percentages of Gas, Liquid, Residue, and Conversion from the Liquefaction of Coals Dried using the Thermal Method

Coal	Percent Water Removed	Thermal			
		Percent Gas	Percent Liquid	Percent Residue	Percent Conversion
Utah Blind Canyon	0	9.1	61.0	30.0	70.0
	100	1.9	67.9	30.2	69.8
Illinois # 6	0	4.4 (3.4)	49.0 (64.3)	46.5 (32.4)	53.6 (67.6)
	13	3.6	70.6	25.8	74.2
	89	3.8	67.5	28.7	71.3
	100	4.7	61.3	34.0	66.0
Wyoming Eagle Butte	0	10.9	62.3	26.8	73.2
	14	12.7	59.9	27.5	72.5
	82	10.8	56.8	32.4	67.6
	100	12.9	42.1	45.0	55.0
Wyoming Black Thunder	0	11.4	67.6	21.0	79.0
	23	10.3	54.6	35.1	64.9
	70	9.5	57.0	33.6	66.4
	100	11.1	56.0	32.9	67.1
Texas Bottom	0	12.4	70.0	17.6	82.4
	38	11.0	74.1	14.9	85.1
	75	10.8	59.5	29.7	70.3
	100	10.6	62.7	26.7	73.3
North Dakota Beulah	0	35.6	38.8	25.6	74.4
	100	1.3 (12.6)	51.0 (45.7)	47.7 (41.6)	52.3 (58.4)

Table 17b. Percentages of Gas, Liquid, Residue, and Conversion from the Liquefaction of Coals Dried using the Microwave Method

Coal	Percent Water Removed	Microwave			
		Percent Gas	Percent Liquid	Percent Residue	Percent Conversion
Utah Blind Canyon	0	9.1	61.0	30.0	70.0
	100	1.7	72.6	25.6	74.4
Illinois # 6	0	4.4 (3.4)	49.0 (64.3)	46.5 (32.4)	53.6 (67.6)
	33	3.6	66.5	30.0	70.0
	79	3.6	67.3	29.1	70.9
	100	3.8	62.6	33.7	66.3
Wyoming Eagle Butte	0	10.9	62.3	26.8	73.2
	32	11.4	57.8	30.8	69.2
	73	10.9	51.3	37.8	62.2
	100	12.3	46.5	41.2	58.8
Wyoming Black Thunder	0	11.4	67.6	21.0	79.0
	30	10.7	58.6	30.7	69.3
	73	10.1	52.9	37.0	63.0
	100	10.0	58.3	31.7	68.3
Texas Bottom	0	12.4	70.0	17.6	82.4
	30	11.8	68.1	20.1	79.9
	78	10.4	66.4	23.2	76.8
	100	12.5	51.0	36.5	63.5
North Dakota Beulah	0	35.6	38.8	25.6	74.4
	100	14.4	38.6	47.0	53.0

Table 17c. Percentages of Gas, Liquid, Residue, and Conversion from the Liquefaction of Coals Dried using the Chemical Method

Coal	Percent Water Removed	Chemical			
		Percent Gas	Percent Liquid	Percent Residue	Percent Conversion
Utah Blind Canyon	0	9.1	61.0	30.0	70
	100	4.0 (4.0)	65.0 (63.7)	31.0 (32.3)	69.0 (67.7)
Illinois # 6	0	4.4 (3.4)	49.0 (64.3)	46.5 (32.4)	53.6 (67.6)
	-	-	-	-	-
	-	-	-	-	-
	100	5.3	74.4	20.2	79.8
Wyoming Eagle Butte	0	10.9	62.3	26.8	73.2
	-	-	-	-	-
	-	-	-	-	-
	100	10.0	75.1	14.9	85.1
Wyoming Black Thunder	0	11.4	67.6	21.0	79.0
	-	-	-	-	-
	-	-	-	-	-
	100	9.7	72.4	17.9	82.1
Texas Bottom	0	12.4	70.0	17.6	82.4
	-	-	-	-	-
	-	-	-	-	-
	100	10.2	77.2	12.6	87.4
North Dakota Beulah	0	35.6	38.8	25.6	74.4
	100	14.1 (12.1)	46.9 (62.1)	39.0 (25.8)	61.0 (74.2)

Except for the chemically dried coals, the conversions are generally less for the dried coals. These results are in agreement with the results obtained by others (Silver and Frazee 1985; Silver et al. 1986; Serio et al. 1993; Saini et al. 1993; and Song et al. 1994). The reason for the differences in liquefaction behavior of the chemically dried and the thermally and microwave-dried coals appears to be due to the retention of the reaction products and solvents by the chemically dried coals. DSC has shown that some of the methanol was incorporated into the coal pore structure in place of the water, thus possibly preventing collapse of the pore structure during the dehydration reaction. This would allow for greater diffusion of tetralin during liquefaction and hence greater conversion.

The percent coal liquefaction conversion for Illinois # 6, Wyoming Eagle Butte, Wyoming Black Thunder, and Texas Bottom coals which have been partially dried using thermal and microwave methods is shown in Table 17. The percent conversion of Illinois # 6 coal is hardly affected by the moisture content of the coal. However, Wyoming Eagle Butte, Wyoming Black Thunder, and Texas Bottom all show a general trend of decreasing percent conversion with increasing percent of water removed. The percent conversion of the coals does not depend on the heating method (thermal or microwave) used to dry the coals. These results are in agreement with those of Silver and Frazee (1985) and extend their results by including coals of rank other than subbituminous.

Liquid Analysis

The percentages of liquid product obtained from the coal liquefaction of the six coals dried by the various methods are given in Table 17. Relative to the premoisturized initial coal, the thermally and microwave-dried subbituminous Wyoming Eagle Butte, Wyoming Black Thunder, and Texas Bottom coals show a decrease in the amount of liquid produced, whereas Utah Blind Canyon coal gave an increase in liquid yield. Both for the dried Illinois # 6 coal and dried North Dakota Beulah lignite, the liquid yield was about the same as for the premoisturized coals. All chemical dried coals show an increase in the coal liquid yield. This increase may be the result of replacement of water by CH_3OH , which might prevent collapse of the pore structure, allowing for greater diffusion and interaction of the tetralin with the coal components.

Table 17 also gives the percent of liquid produced from the coal liquefaction of the Illinois # 6, Wyoming Eagle Butte, Wyoming Black Thunder, and Texas Bottom coals, which have been partially dried thermally or with microwave heating. For any given coal, thermal and microwave heating of the partially dried coals gives essentially the same liquid product yield. Except for Illinois # 6 coal, the percentage of liquid formed during coal liquefaction, in general, decreases with increasing percentage of water removed.

Gas chromatographic analyses of the coal liquids from each liquified coal are reported in Table 18. The analysis is reported as the percent of oil below and above a retention time (RT) of 14 minutes. The amount of oil below an RT of 14 minutes is defined as a light oil and above an RT of 14 min as a heavy oil.

Except for the premoisturized Utah Blind Canyon coal (0% H₂O removed), the percent of light oil produced from the other premoisturized coals decreases slightly with decreasing rank (increasing moisture content) of the coals. Conversely, the percent of heavy oil increases with increasing moisture content. In addition, the percentages of light oil and heavy oil produced from partially and totally dried coals were found to be independent of the drying method and rank of coal except for the Utah Blind Canyon coal.

Relative to the premoisturized coals, complete drying of the coals (100% H₂O removed) increased the percent of light oil and decreased the heavy oil produced during the coal liquefaction, except for the Utah coal for which the percent of light oil decreased (heavy oil increased). The light oil produced for the completely dried coals varied from 82.1 to 89.7 percent, and the heavy oil produced varied from 10.3 to 17.9 percent.

In general, the premoisturized coals and partially dried coals (Illinois # 6, Wyoming Eagle Butte, Wyoming Black Thunder, and Texas Bottom) produced about the same amount of light oil. That is, water tends to not only decrease slightly the formation of light oil components for coals relative to coals that have been totally dried thermally or with microwave radiation, but increase the overall percent of coal converted to liquid (Table 17).

Table 18. Gas Chromatographic Analyses¹ of the Coal Liquids from the Liquefaction Coals Dried Using Thermal, Microwave, and Chemical Methods

Coal	Thermal			Microwave			Chemical		
	% H ₂ O Removed	Light Oil ²	Heavy Oil ³	% H ₂ O Removed	Light Oil ²	Heavy Oil ³	% H ₂ O Removed	Light Oil ²	Heavy Oil ³
Utah Blind Canyon	0 100	71.6 67.3	28.4 32.7	0 100	71.6 66.0	28.4 34.0	0 100	71.6 69.9 (79.6)	28.4 30.1 (20.4)
Illinois # 6	0 13 89 100	86.6 (84.3) 87.2 86.3 88.4	13.4 (15.7) 12.8 13.7 11.6	0 33 79 100	86.6 (84.3) 79.3 85.2 87.5	13.4 (15.7) 20.7 14.8 12.5	0 - - 100	86.6 (84.3) - - 89.7	13.4 (15.7) - - 10.3
Wyoming Eagle Butte	0 14 82 100	83.1 82.8 83.9 89.4	16.9 17.2 16.1 10.6	0 32 73 100	83.1 85.5 86.4 88.6	16.9 14.5 13.6 11.4	0 - - 100	83.1 - - 86.9	16.9 - - 13.1
Wyoming Black Thunder	0 23 70 100	83.3 81.9 82.4 85.0	16.7 18.1 17.6 15.0	0 30 73 100	83.3 80.9 80.6 85.3	16.7 19.1 19.4 14.7	0 - - 100	83.3 - - 84.5	16.7 - - 15.5
Texas Bottom	0 38 75 100	79.0 81.5 79.0 82.2	21.0 18.5 21.0 17.8	0 30 78 100	79.0 81.0 80.8 84.2	21.0 19.0 19.2 15.8	0 - - 100	79 - - 84.7	21 - - 15.3
North Dakota Beulah	0 100	78.5 87.4 (84.5)	21.5 12.6 (15.5)	0 100	78.5 82.1	21.5 17.9	0 100	78.5 84.1(84.6)	21.5 15.9 (15.4)

¹ Expressed as a percentage of the total liquid product

² Light oil – gas chromatographic retention time is less than 14 minutes.

³ Heavy oil – gas chromatographic retention time is greater than 14 minutes.

Gas Analysis

The total percent of gas formed during liquefaction for the six premoisturized coals and the six coals dried using thermal, microwave, and chemical methods are given in Table 17. In general, there is an increase in total percent of gas produced with decreasing rank of the premoisturized coals (Utah to North Dakota). Both the Utah and North Dakota coals show a significant decrease in gas produced when completely dried using the three methods. The total amount of gas produced from the other four dried coals is essentially the same as from their corresponding premoisturized coals. The moisture content of the partially dried coals (Illinois # 6, Wyoming Eagle Butte, Wyoming Black Thunder, and Texas Bottom) has little or no effect on the total amount of gas produced during coal liquefaction regardless of the drying method.

The types and relative amounts of gases produced during the coal liquefaction for the six coals are given in Table 19. Even though the total amount of gas produced during liquefaction is independent of the moisture content (Table 17), the relative amount of any component in the total gas is a function of the moisture content. The premoisturized coals upon liquefaction, in general, produced the least amount of any component gas, whereas, the totally dried coals produced the highest amount. This is true whether the gases are CO and CO₂ or hydrocarbons. Thus, the initial amount of water present in the coal during coal liquefaction appears to determine the relative amounts of CO, CO₂ and gaseous hydrocarbons produced.

The amount of CO, CO₂, methane, ethane and propane depend on the method of drying. In general, the production of CO upon liquefaction of the coals increases for the thermally and microwave-dried coals relative to the premoisturized initial coals. The amounts of CO produced for the chemical dried coals are about the same as for the premoisturized coals. Generally, the amount of CO produced for the partially dried coals lies between the moisturized (zero percent water removed) and the totally dried coals (100 percent water removed).

Only the amount of CO₂ produced during liquefaction of the premoisturized coals appears to be dependent on the coal rank. As expected, the percent of CO₂ increases with decreasing coal rank (increasing moisture content). Relative to the premoisturized coals, the amount of CO₂ produced increased for thermally and microwave-dried coals and decreased for the chemically dehydrated coals. The increase in CO₂ produced for the thermally and microwave dried coals supports the conclusion that cross-linking of the coal structure had occurred.

Table 19. Relative Amount of Gases Produced during the Coal Liquefaction of Coals Dried using Thermal, Microwave, and Chemical Methods

Coal	% H ₂ O Removed	Nitrogen	CO	CO ₂	Methane	Ethane	Propane	Isobutane	n-butane
<u>Utah Blind Canyon</u>	0	93.0	0.58	2.57	2.50	0.69	0.41	0.05	0.10
Premoisturized	100	97.8	0	0.39	1.46	0.20	0.15	0.01	0.04
Thermal	100	98.0	0	0.37	1.31	0.19	0.14	0.01	0.02
Microwave	100	95.4 (95.7) ¹	0.13 (0.16)	1.00 (1.08)	2.86 (2.32)	0.36 (0.40)	0.25 (0.28)	0.01 (0.02)	0.03 (0.03)
Chemical									
<u>Illinois # 6</u>									
Premoisturized	0	97.4	0.09	0.85	1.14	0.38	0.15	0.01	0.02
Thermal	13	97.2	0.09	0.95	1.16	0.38	0.15	0.01	0.02
	89	96.8	0.12	1.11	1.34	0.45	0.18	0.01	0.03
	100	96.1	0.17	1.53	1.42	0.50	0.22	0.01	0.04
Microwave	33	97.2	0.09	1.00	1.10	0.40	0.15	0.01	0.02
	79	96.9	0.11	1.03	1.34	0.45	0.19	0.01	0.03
	100	96.7	0.10	1.07	1.38	0.46	0.21	0.01	0.04
Chemical	100	94.0	0.06	0.78	4.48	0.39	0.28	0.01	0.03
<u>Wyo Eagle Butte</u>									
Premoisturized	0	93.3	0.51	4.86	0.92	0.29	0.12	0.01	0.01
Thermal	14	92.3	0.61	5.44	1.04	0.37	0.18	0.01	0.03
	82	92.5	0.66	5.23	1.08	0.35	0.18	0.01	0.03
	100	90.3	0.79	6.04	1.87	0.64	0.27	0.02	0.04
Microwave	32	92.8	0.56	5.10	0.97	0.34	0.17	0.01	0.03
	73	92.2	0.63	5.38	1.15	0.40	0.20	0.01	0.03
	100	90.4	0.82	5.75	1.97	0.66	0.28	0.02	0.06
Chemical	100	90.9	0.57	3.85	4.10	0.36	0.22	0.01	0.03

¹ Values in parentheses are from repeat experiments.

Table 19 continued.

Coal	% H ₂ O Removed	Nitrogen	CO	CO ₂	Methane	Ethane	Propane	Isobutane	n-butane
<u>Wyo Black Thunder</u>									
Premoisturized	0	93.2	0.50	4.73	0.98	0.36	0.18	0.01	0.03
Thermal	23	93.7	0.35	4.50	0.94	0.33	0.16	0.01	0.02
	70	93.4	0.66	4.35	1.01	0.35	0.18	0.01	0.03
	100	91.8	0.80	5.40	1.27	0.45	0.23	0.02	0.04
Microwave	30	93.6	0.52	4.40	0.92	0.34	0.16	0.01	0.03
	73	93.0	0.68	4.45	1.17	0.43	0.26	0.02	0.04
	100	92.6	0.71	4.75	1.26	0.44	0.21	0.02	0.05
Chemical	100	91.5	0.58	3.66	3.72	0.35	0.21	0.01	0.03
<u>Texas Bottom</u>									
Premoisturized	0	93.4	0.50	4.65	0.97	0.34	0.15	0.01	0.02
Thermal	38	93.8	0.31	4.49	0.92	0.30	0.16	0.01	0.03
	75	93.4	0.59	4.49	1.02	0.32	0.18	0.01	0.03
	100	92.6	0.60	4.92	1.29	0.40	0.19	0.01	0.03
Microwave	30	93.5	0.49	4.61	0.92	0.31	0.17	0.01	0.04
	78	93.3	0.52	4.46	1.08	0.38	0.20	0.02	0.03
	100	91.3	0.68	5.06	1.89	0.65	0.32	0.03	0.08
Chemical	100	91.6	0.53	3.34	3.93	0.35	0.21	0.01	0.04
<u>North Dakota Beulah</u>									
	0	83.9	1.09	10.1	2.14	0.57	0.33	0.19	0.08
Premoisturized	100	98.3 (91.4) ¹	0.00 (0.64)	0.07 (0.63)	1.52 (1.15)	0.06 (0.33)	0.05 (0.00)	0.01 (0.01)	0.01 (0.02)
Thermal	100	89.9	0.64	5.91	2.51	0.69	0.26	0.02	0.04
Microwave	100	89.4(91.0)	0.69(0.50)	5.43 (5.46)	3.53 (2.39)	0.63 (0.34)	0.29 (0.12)	0.02 (0.01)	0.42 (0.03)
Chemical									

¹ Values in parentheses are from repeat experiments.

The amount of CH_4 produced increases for the coals dried thermally, with microwave radiation, and with chemical dehydration. The chemically dried coals produced more methane than the premoisturized or the thermally and microwave-dried coals (Table 19). The greater amount of produced methane is attributed to the methanol retained by the coal during chemical drying. In the presence of the tetralin donor solvent, the methanol could be converted to methane, although the mechanistic details are not known. It has been reported (Solomon et al. 1990) that an increase in CH_4 produced can result from the reactivity of the coals leading to an extensive cross-linking structure. However, the swelling experiments indicate little or no cross-linking structural change for the chemically dehydrated coals at room temperature.

The amount of ethane produced shows a slight increase when the coals are thermally or microwave-dried, whereas the chemically dried coals produce about the same amount of ethane upon liquefaction as the premoisturized coals. The amount of propane produced, in general, increased slightly upon liquefaction of the coals relative to the premoisturized coals. The exception being the Utah and North Dakota coals. In addition, the amount of propane produced is independent of the drying method.

Residue Analysis

The percentages of residue produced during the liquefaction of the premoisturized, partially dried and completely dried coals are given in Table 17. The amount of coal residue produced during liquefaction of the premoisturized coals decreases with the increase in the moisture content of the coal (decrease in coal rank). In most cases, the amounts of residue from the thermally dried, microwave-dried, and partially dried coals are greater than the amount of residue from the premoisturized coal. This is reflected in the lower conversion of the totally and partially dried coals (Table 17). It is of interest to note that the amounts of residue from the liquefaction of the chemically dried Illinois # 6, Wyoming Eagle Butte, Wyoming Black Thunder, and Texas Bottom coals are significantly less than from their respective premoisturized coals as well as from their respective thermally dried and microwave-dried coals. Because of the lower residue yield, the percent conversion for the chemically dried coals is higher than for the thermally dried and microwave-dried coals.

The ^{13}C CP/MAS NMR spectra of the coal liquefaction CH_2Cl_2 extracted residues from the premoisturized coals and the thermally, chemically, and microwave-dried coals are shown in Figures 43 to 48. The spectra of the residues from the thermal partially dried coals are given in Figures 49 to 52, and the microwave partially dried coals are given in Figures 53 to 56. In all cases, when compared to the starting coal spectrum, the NMR spectra of the residues show a significant reduction in the aliphatic component relative to the aromatic component.

Figure 43. Carbon-13 NMR Spectra of Utah Blind Canyon Coal Residues from Coal Liquefaction of (a) Premoisturized Coal, (b) Thermally Dried Coal, (c) Microwave Dried Coal, and (d) Chemically Dried Coal

Figure 44. Carbon-13 NMR Spectra of Illinois #6 Coal Residues from Coal Liquefaction of (a) Premoisturized Coal, (b) Thermally Dried Coal, (c) Microwave Dried Coal, and (d) Chemically Dried Coal

Figure 45. Carbon-13 NMR Spectra of Wyoming Eagle Butte Coal Residues from Coal Liquefaction of (a) Premoisturized Coal, (b) Thermally Dried Coal, (c) Microwave Dried Coal, and (d) Chemically Dried Coal

Figure 46. Carbon-13 NMR Spectra of Wyoming Black Thunder Coal Residues from Coal Liquefaction of (a) Premoisturized Coal, (b) Thermally Dried Coal, (c) Microwave Dried Coal, and (d) Chemically Dried Coal

Figure 47. Carbon-13 NMR Spectra of Texas Bottom Coal Residues from Coal Liquefaction of (a) Premoisturized Coal, (b) Thermally Dried Coal, (c) Microwave Dried Coal, and (d) Chemically Dried Coal

Figure 48. Carbon-13 NMR Spectra of North Dakota Beulah Lignite Residues from Coal Liquefaction of (a) Premoisturized Coal, (b) Thermally Dried Coal, (c) Microwave Dried Coal, and (d) Chemically Dried Coal

Figure 49. Carbon-13 NMR Spectra of Illinois #6 Coal Residues from Coal Liquefaction of Thermal Partially Dried Coals: (a) 0% Water Removed, (b) 13% Water Removed, (c) 89% Water Removed, and (d) 100% Water Removed

Figure 50. Carbon-13 NMR Spectra of Wyoming Eagle Butte Coal Residues from Coal Liquefaction of Thermal Partially Dried Coals: (a) 0% Water Removed, (b) 14% Water Removed, (c) 82% Water Removed, and (d) 100% Water Removed

Figure 51. Carbon-13 NMR Spectra of Wyoming Black Thunder Coal Residues from Coal Liquefaction of Thermal Partially Dried Coals: (a) 0% Water Removed, (b) 23% Water Removed, (c) 70% Water Removed, and (d) 100% Water Removed

Figure 52. Carbon-13 NMR Spectra of Texas Bottom Coal Residues from Coal Liquefaction of Thermal Partially Dried Coals: (a) 0% Water Removed, (b) 38% Water Removed, (c) 75% Water Removed, and (d) 100% Water Removed

Figure 53. Carbon-13 NMR Spectra of Illinois #6 Coal Residues from Coal Liquefaction of Microwave Partially Dried Coals: (a) 0% Water Removed, (b) 33% Water Removed, (c) 79% Water Removed, and (d) 100% Water Removed

Figure 54. Carbon-13 NMR Spectra of Wyoming Eagle Butte Coal Residues from Coal Liquefaction of Microwave Partially Dried Coals: (a) 0% Water Removed, (b) 32% Water Removed, (c) 73% Water Removed, and (d) 100% Water Removed

Figure 55. Carbon-13 NMR Spectra of Wyoming Black Thunder Coal Residues from Coal Liquefaction of Microwave Partially Dried Coals: (a) 0% Water Removed, (b) 30% Water Removed, (c) 73% Water Removed, and (d) 100% Water Removed

Figure 56. Carbon-13 NMR Spectra of Texas Bottom Coal Residues from Coal Liquefaction of Microwave Partially Dried Coals: (a) 0% Water Removed, (b) 30% Water Removed, (c) 78% Water Removed, and (d) 100% Water Removed

In addition, there is a substantial narrowing of the aromatic resonance band as carbons substituted on aromatic rings (~ 140 ppm), phenolic (~ 155 ppm), and carboxylic carbons (~ 180 ppm) evolve as liquid products during conversion. There is also a shift in the resonance position from ~ 30 ppm to ~ 20 ppm for the aliphatic carbons. The residual aliphatic component at ~ 20 ppm could be due to methyl groups attached to aromatic rings that would not be cleaved during liquefaction at 425°C. It's also possible that some of the aromatic carbon in the residues resulted from aromatization of a fraction of the aliphatic carbon. However, without NMR measurements of the liquid fractions and elemental analyses, the extent of aromatization could not be ascertained.

The significant difference in the residue NMR spectra shown in the figures for the six coals is the enhanced resolution of the aliphatic carbons for the coals dried via chemical dehydration. This enhanced resolution of the aliphatic carbons in the ^{13}C NMR spectra was also noted in the NMR spectra of the chemically dried coals before liquefaction. It is unlikely that the carbon resonances observed are due to solvent and reaction products of the chemical drying technique, unless the methanol is strongly adsorbed, even at the liquefaction temperature of 425°C. It may be that the methanol solvent removed some of the soluble aliphatic carbon substituents (decreasing the chemical shift dispersion) thus, in effect, giving higher resolution of the remaining carbons types.

The apparent carbon aromaticity values for the liquefaction residues for the six coals dried by the three methods are listed in Table 20. As shown in the table, the aromaticity values for the liquefaction residues from coals that were completely dried are nearly the same (0.82 ± 0.04), being independent of the coal rank and the method of drying. One exception is the residues from the North Dakota lignite after being completely dried using thermal, microwave, and chemical methods. These have aromaticity values of about 0.880.

C. H_2O - D_2O Exchange Studies on Coals

Regarding the liquefaction of coal, there does not appear to have been any systematic chemical study of the role water plays in enhancing or lessening coal reactivity toward liquefaction.

Table 20. Apparent Carbon Aromaticity Values for the Liquefaction Residues from Thermally, Microwave, and Chemically Dried Coals

Coal	Percent Water Removed	Thermal	Percent Water Removed	Microwave	Percent Water Removed	Chemical
Utah Blind Canyon	0 100	0.809 0.809	0 100	0.809 0.775	0 100	0.809 0.754 (0.781) ¹
Illinois # 6	0 13 89 100	0.833 0.826 0.840 0.813	0 33 79 100	0.833 0.833 0.807 0.807	0 - - 100	0.833 - - 0.855
Wyoming Eagle Butte	0 14 82 100	0.840 0.820 0.826 0.862	0 32 73 100	0.840 0.855 0.833 0.870	0 - - 100	0.840 - - 0.813
Wyoming Black Thunder	0 23 70 100	0.825 0.800 0.787 0.807	0 30 73 100	0.825 0.806 0.794 0.794	0 - - 100	0.825 - - 0.794
Texas Bottom	0 38 75 100	0.807 0.794 0.781 0.813	0 30 78 100	0.807 0.794 0.806 0.787	0 - - 100	0.807 - - 0.800
North Dakota Beulah	0 100	0.892 0.886 (0.840)	0 100	0.892 0.894	0 100	0.892 0.880 (0.794)

¹ Values in parentheses are from repeat experiments.

Ruether et al. (1985) using non-deuterated water studied the effects of water during direct hydroliquefaction on coal in uncatalyzed systems. They observed that at a substantial water partial pressure, coal conversion increases. Water was not considered to be a reactant (Ruether et al. 1986), however, the mechanism through which it aids conversion is unknown. Mikita and Fish (1986) suggested that water acts to open new ionic reaction pathways through its solvation effect. In a later study, Ruether et al. (1987) investigated hydroliquefaction coal conversion in the presence of catalysts and found that highest conversions are obtained without added water. They concluded that for reaction systems with the catalyst deposited from solution onto the coal particles, the resultant particles are highly reactive and that water retains a role as a solvent for the catalyst. In all studies, non-deuterated water was used, the percent coal conversion was measured by tetrahydrofuran (THF) solubles, and no product analyses were conducted. Thus, the role of water could not be ascertained.

One method of studying the chemical reactions occurring during the liquefaction of coal is to use deuterium-labeled compounds and to follow the incorporation of the deuterium into the coal-derived products. The coal liquefaction process can be divided into three distinct chemical reaction steps: (1) the reaction of pressurized H_2 gas with the coal, (2) the hydrogen exchange reactions of the hydrogen donor solvents with the coal, and (3) the hydrogen exchange reactions of the water associated with the coal. In each of these steps the hydrogen can be replaced with deuterium to study the mechanism of the exchange reactions.

A number of deuterium exchange studies using deuterated hydrocarbon and D_2 gas under various experimental conditions have been conducted (Kuznetsov et al. 1991 and literature cited therein). In all of these studies, the alkyl group α to aromatic rings is shown to be important in coal liquefaction and that under coal liquefaction conditions deuterium is thoroughly scrambled.

Schweighardt et al. (1976) determined the distribution of deuterium incorporated among the various organic constituents of the liquid products resulting from coal liquefaction in a D_2 gas atmosphere, at 1600 psig, 450°C, for 15 minutes. The analysis of the product gases (H_2 , HD, and D_2) using mass spectrometry indicated that approximately 45% of the hydrogen originally present in the coal liquid had been replaced by deuterium. Deuterium NMR was used to determine the hydrogen and deuterium distribution in the deuterated coal liquid and several fractions. Deuterium was found in all fractions at both aromatic and nonaromatic sites of the organic constituents. Schweighardt et al. (1976) found that a degree of specificity for the

incorporation of deuterium at the α -alkyl and aromatic positions prevailed. Hydrogen bonded to carbons β or further removed from aromatic ring appeared to be least susceptible to deuterium labeling under the experimental conditions employed.

Hydrogen transfer reactions during coal liquefaction processes using deuterium-labeled tetralin was studied by Ratto et al. (1979, 1980). They measured the deuterium incorporated into the coal-derived products by ^2H NMR and found that deuterium was preferentially incorporated into the α -alkyl position in the soluble products. Considerable isotopic exchange occurred between the deuterated tetralin at the α -position and the coal. Franz (1979) and Franz and Camaioni (1981) conducted similar studies and found that at times longer than 10 minutes the deuterium was incorporated into the aromatic structure as well as at the α -alkyl position. The transfer of deuterium after five minutes at 427°C from deuterated tetralin to coal resulted in 80 to 85% of the deuterium appearing in the aliphatic structures (Franz and Camaioni 1981). The highest concentration occurred in benzylic and tertiary aliphatic sites.

The incorporation of deuterium into coal liquefaction products from D_2O has not been studied. The extent of deuterium scrambling from D_2O during coal liquefaction is unknown. However, Kuznetsov et al. (1991) studied the liquefaction of Kansk-Achinsk lignite in the presence of deuterated alcohols. From the analyses of the products obtained from the liquefaction process, they found that deuterium distribution in maltenes, asphaltenes, and solid residues increased in the order: solid residues > asphaltenes > maltenes. In all cases, deuterium was detected mainly in the aliphatic structural groups and to a small extent in the aromatic rings. The deuterium distribution differs considerably from that observed by previous authors for coal liquefaction in deuterated tetralin or in the presence of gaseous deuterium. Kuznetsov et al. (1991) suggest that the apparent differences in deuterium distribution in tetralin and alcohol-derived coal products are connected with the initial exchange mechanism. For coal liquefaction in deuterated tetralin or gaseous deuterium, deuterium is transferred into the products through hydrogenation and exchange. For coal liquefaction in the presence of alcohol, the deuterium transfer is apparently made by alkylation.

Lewan (1992) used D_2O in hydrous pyrolysis of Woodford shale to better understand the role of water in petroleum formation. Deuterium NMR analyses of the pyrolyzate products showed that the expelled immiscible oil as well as the bitumen and kerogen retained in the rock contained significant quantities of deuterium. Deuterium

substitution for hydrogen was found to be approximately 40% for the expelled oil and 33% for the extracted bitumen. Quantification for the kerogen was not performed. Lewan interprets the high degree of deuterium substitution to be the result of free radical sites being terminated by deuterium atoms derived from the oxidation of carbonyl groups by D_2O . Thus, under hydrous conditions, the free radical sites formed on the bitumen molecule are terminated with water-derived hydrogen before β -scission of the molecule occurs. Under anhydrous conditions, the lack of water-derived hydrogen for terminating free-radical sites that occur on the bitumen molecule results in frequent β -scissions.

Figure 57 shows the 1H NMR spectra of the solutions of D_2O after exchange with the H_2O in the Texas Bottom coal (a) and the Utah Blind Canyon coal (b). The observed signals are that of HDO. The water content of the Texas coal is about 29 wt % and the Utah coal contains ~ 4 wt % of water. As shown in Figure 54, the corresponding HDO resonance is directly related to the moisture content. That is, the HDO peak for the Texas coal is much larger than that observed for the Utah Blind Canyon coal. Figure 57c is the residue HDO signal in the blank D_2O solvent.

A series of D_2O exchange experiments on coal samples has been performed. The first series involved repeated washing of the lignite with D_2O . As shown in Figure 58, the four successive washings of the North Dakota Beulah lignite with D_2O replaces essentially all H_2O in a short period as measured by the decrease in the 1H NMR of the HDO signal in D_2O . The second series of the exchange experiments involved the kinetics of D_2O - H_2O exchange for the North Dakota Beulah lignite and Utah Blind Canyon bituminous coal. The coals were treated with D_2O and aliquots removed over several hours. The replacement of surface H_2O , as measured by the HDO 1H NMR signal, is rapid, followed by the replacement of the diffusion controlled pore H_2O . This is shown in Figure 59a and b as an increase in signal height with time. After a significant length of time a decrease in HDO signal is observed. Additional experiments are needed to confirm that the decrease in signal is real and to determine the exchange mechanism which can explain the observations.

The successive exchange of H_2O in coal with D_2O should provide D_2O -hydrated coal samples for coal liquefaction. It is suggested that by comparing the liquefaction data for H_2O -hydrated coals and D_2O -hydrated coals, additional information can be obtained about the chemistry of water in the coal liquefaction process.

Figure 57. Hydrogen-1 NMR Spectra of Single D_2O Exchange of H_2O in (a) Texas Bottom Coal, (b) Utah Blind Canyon Coal, and (c) Residual H_2O in D_2O Blank

Figure 58. Hydrogen-1 NMR Spectra of the HDO Resonance for Successive D₂O-H₂O Exchange for the North Dakota Beulah Lignite

Figure 59. Hydrogen-1 NMR Spectra of HDO Resonance as a Function of Exchange Time: (a) North Dakota Beulah Lignite and (b) Utah Blind Canyon Coal

CONCLUSIONS

During microwave drying of coals, there is a rapid rise in temperature close to the boiling point of water, followed by a plateau in temperature, followed by a plateau in temperature. This temperature is maintained until about 80% of the coal moisture is removed, after which the temperature rises rapidly during removal of the remaining moisture. These water molecules are more tightly bound and require more energy for removal. However, solid-state ^{13}C NMR measurements did not show any significant changes in the general chemical structure of the coal, save for some possible decarboxylation in the low-rank coals.

Solid-state ^{13}C NMR measurements also showed that, other than partial decarboxylation, there was little change in the chemical structure of a subbituminous coal (Eagle Butte) when heated ballistically to a temperature of 250°C . Little change was observed in the aliphatic and aromatic carbon regions.

There were, however, changes in the chemical structure of the coals that were dried chemically using 2,2-dimethoxypropane. In particular, there was enhanced resolution in the aliphatic region of the spectra. This enhanced resolution was attributed to CH_3OH , which could have been adsorbed onto the coal, and to greater mobility of coal molecules because of reduced hydrogen bonding with the removal of the water.

Chemical dehydration using 2,2-dimethoxypropane gave moisture values that were about 10% greater than those determined by simple heating. Drying kinetics showed that a significant fraction of the moisture is removed in the first minute of the reaction. Removal of the remaining moisture required longer. Analysis of the drying kinetics data suggested that chemical drying provides a method to discriminate quantitatively between surface and readily accessible water from tightly bound internal pore water in coals.

Swelling ratios were determined on the premoisturized and dried coals to obtain an assessment of cross-linking during drying. The results showed that there was less cross-linking in the chemically dried coals than in the coals dried thermally or with microwaves, suggesting that the pore structure increased when the water molecules were removed (less hydrogen bonding to contract the pores).

The liquefaction behavior of the microwave-dried and thermally dried coals was similar. That is, the extent of conversion was lower for coals partially and completely dried using microwaves or thermal drying than for the premoisturized coals. For the chemically dried coals, the conversions were the same or greater than for the premoisturized coals. This is attributed to retention of some of the solvent and reaction products by the coal, which would have the effect of preventing collapse of the pore structure, enabling donor solvent penetration into the pores.

Relative to the premoisturized coals, the low-rank coals that were thermally and microwave-dried showed a decrease in the amount of liquids produced during liquefaction. Liquid yields were greater for the chemically dried coals. In general, the quality of the liquids produced was better for the coals that were completely dried, even though the overall conversions were lower.

^1H NMR studies have shown that the water molecules in coal can be easily and completely exchanged with D_2O . It is suggested that coals that have been completely hydrated with D_2O can, by incorporating deuterium in the coal liquefaction products, provide additional information about the chemistry of water in the coal liquefaction process.

DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand.

REFERENCES

- Adams, R.F., 1974, Determination of Amino Acid Profiles in Biological Samples by Gas Chromatography. *J. Chromatogr.*, 95: 189-212.
- Bockrath, B.C., E.G. Illig, D.H. Finseth, and R.F. Sprecher, 1984, Coal Liquefaction and Hydrogen Utilization at Low Temperatures, *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 29(5): 76.
- Bockrath, B.C., E.G. Illig, W.D. Wassell-Bridger, 1987, *Energy and Fuels*, 1: 227.
- Boysen, J.E., C.Y. Cha, F.A. Barbour, T.F. Turner, T.W. Kwang, M.H. Berggren, R.F. Hogsett, and M.C. Jha, 1990, Development of an Advanced Process for Drying Fine Coal in an Inclined Fluidized Bed. Laramie, WY, DOE Report in press, WRI Report WRI-90-R031.
- Catalytic Inc., 1986, Development of VaSTeC Autoclave Technique and Applications to Pilot Plant Guidance, Catalytic Inc. Wilsonville, AL, April Topical Report prepared for USDOE (Contract No. DE-AC22-82PC50041 and EPRI (Contract No: RP12324-1-2).
- Chatterjee, I., and M. Misra, 1991, Electromagnetic and Thermal Modeling of Microwave Drying of Fine Coals, *Minerals and Metallurgical Processing*, 8: 110.
- Critchfield, F.E., and E.T. Bishop, 1961, Water Determination by Reaction with 2,2-Dimethoxypropane. *Anal. Chem.*, 33: 1034-1033.
- Davidson, R.M, Nuclear Magnetic Resonance Studies of Coal, 1986, London, IEA Coal Research Report ICTIS/TR32.
- Deshpande, G.V., P.R. Solomon, and M.A. Serio, 1988, Crosslinking Reactions in Coal Pyrolysis. *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 33(2): 310-321.
- Donoghue, J.T., and R.S. Drago, 1962, Non-aqueous Coordination Phenomena--Complexes of Hexamethylphosphoramide. I. Preparation and Properties of Tetrahedral $[\text{Zn}\{\text{PO}[\text{N}(\text{CH}_3)_2]_3\}_4]^{+2}$, $[\text{Co}\{\text{PO}[\text{N}(\text{CH}_3)_2]_3\}_4]^{+2}$, and $[\text{Ni}\{\text{PO}[\text{N}(\text{CH}_3)_2]_3\}_4]^{+2}$ Compounds. *Inorg. Chem.*, 1: 866-872.
- Evans, D.G., 1973, The Brown-Coal/Water System: Part 4. Shrinkage on Drying. *Fuel*, 52: 186-190.

- Finseth, D., D.L. Cillo, R.F. Sprecher, H.L. Retcofsky, and R.G. Lett, 1985, Changes in Hydrogen Utilization with Temperature During Direct Coal Liquefaction. *Fuel*, 64: 1718.
- Finseth, D., 1987, An Isotope Dilution Study of Exchangeable Oxygen in Premium Coal Samples. *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 32(4): 260-265.
- Foster, N.R., M.A. Wilson, R.G. Weiss, and K.N. Clark, 1983, Isothermal Studies of the Liquefaction of Liddell Coal. *Industrial and Engineering Chemistry, Product Research and Development*, 22(3): 479-482.
- Franz, J.A., 1979, *Fuel*, 58: 405-412.
- Franz, J.A., and D.M. Camaioni, 1981, Proceedings of the International Conference on Coal Science, Duesseldorf, FRG, 7-9 Sept. Essen, FRG Verlag Glueckauf, pp. 327-331.
- Frost, A.A., and R.G. Pearson, 1961, "Kinetics and Mechanism," John Wiley & Sons, Inc. New York, N.Y., p. 14.
- Gethner, J.S., 1986, Coal Oxidation and Thermal Chemistry. *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 31(4): 103-110.
- Green, T.K., J. Kovac, and J.W. Larsen, 1984, A rapid and convenient method for measuring the swelling of coals by solvents, *Fuel*, 63, 935-938.
- Ibarra, J.V., I. Cervero, M. Garcia, and R. Moliner, 1990, Influence of Cross-Linking on Tar Formation During Pyrolysis of Low-Rank Coals. *Fuel Process. Technol.*, 1990, 24: 19-25.
- Kuznetsov, P.N., N.G. Bereyovtsova, A.I. Rubaylo, E.D. Korniyets, and N.I. Pavlenko, 1991, *Fuel*, 70: 559-563.
- Lewan, M.D., 1992, *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 37: 1643-1648.
- McMillen, D.F., R. Malhotra, G.P. Hum, and S.-J. Chang, 1987, Hydrogen-Transfer-Promoted Bond Scission Initiated by Coal Fragments. *Energy and Fuels*, 1: 193-198.
- Mikita, M.A., and H.T. Fish, 1986, *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 31: 56-63.
- Miknis, F.P., 1988, Solid State ^{13}C NMR in Coal Research: Selected Techniques and Applications, in *New Trends in Coal Science*, Yürüm, Y., Ed., NATO ASI Series C., Kluwer Academic Publishers, Boston, MA, pp. 117-158.

- Muller, L.L., and T.J. Jacks, 1975, Rapid Chemical Dehydration of Samples for Electron Microscopic Examinations. *J. of Histochemistry and Cytochemistry*, 23: 107-110.
- Neuworth, M.B., and D. Gray, 1985, Fundamental Aspects of Primary Liquefaction, Albuquerque, NM, Sandia National Laboratory Report SAND85-7211.
- Nishioka, M., 1992, The Associated Molecular Nature of Bituminous Coal, *Fuel*, 71: 941.
- Nishioka, M., 1994, Molecular Mobility of High-Volatile Bituminous Coals Accompanying Drying, *Fuel*, 73: 57.
- Okuma, O., M. Masuda, K. Murakoshi, S. Yanai, and T. Matsumura, 1990, Effects of Moisture Content on Liquefaction of Victorian Brown Coal. *Nenryo Kyokaishi*, 69: 259.
- Rao, S.N., H.D. Schindler, and G.V. McGurl, 1988, Advances and New Directions in Direct Liquefaction. *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 33(3): 145-156.
- Ratto, J.R., L.A. Heredy, and R.P. Skowronski, 1979, *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 24: 155-165.
- Ratto, J.R., L.A. Heredy, and R.P. Skowronski, 1980, ACS Symposium Series, 139: 347-370.
- Ruether, J.A., S. Friedman, E.G. Illig, and B.C. Bockrath, 1985, *Proc. Int. Conf. Coal Sci.* 1985, 1: 51-54.
- Ruether, J.A., R.G. Lett, and J.A. Mima, 1986, *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 31: 140-151.
- Ruether, J.A., J.A. Mima, R.M. Kornosky, and B.C. Ha, 1987, *Energy & Fuels*, 1: 198-202.
- Saini, A.K., C. Song, and H. Shobert, 1993, ACS Div. Fuel Chem. Preprints, 38 (2): 593.
- Schweighardt, F.K., B.C. Bockrath, R.A. Friedel, and H.L. Retcofsky, 1976, *Anal. Chem.*, 48: 1254-1255.
- Serio, M.A., P.R. Solomon, E. Kroo, R. Bassilakis, R. Malhotra, and D. McMillen, 1990, Studies of Coal Pretreatment in Direct Liquefaction. *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 35(1): 61-69.

- Serio, M., E. Kroo, H. Teng, and P.R. Solomon, 1993, *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 38 (2): 577.
- Shin, S.-C., R.M. Baldwin, and R.L. Miller, 1989, Correlation of Bituminous Coal Hydroliquefaction Activation Energy with Fundamental Coal Chemical Properties. *Energy and Fuels*, 3: 193-199.
- Silver, H.F., and W.S. Frazee, 1985, Integrated Two-Stage Coal Liquefaction Studies, University of Wyoming, Laramie, WY, August 1985, EPRI Report AP-4193, 460 p.
- Silver, H.F., P.J. Hallinan, and W.S. Frazee, 1986, Effect of Water on Liquefaction Reactivity of Low Rank Coals. *Amer. Chem. Soc. Div. Fuel Chem. Prepr.*, 31(3): 755-760.
- Snape, C.E., 1987, Characterization of Organic Coal Structure for Liquefaction. *Fuel Proc. Technol.*, 15: 257.
- Solomon, P.R., D.G. Hamblen, R.M. Carangelo, M.A. Serio, and G.V. Deshpande, 1988, *Energy and Fuels*, 2: 405.
- Solomon, P.R., M.A. Serio, G.V. Deshpande, and E. Kroo, 1990, Cross-Linking Reactions During Coal Conversion, *Energy and Fuels*, 4: 42.
- Song, C., A.K. Saini, and H.H. Schobert, 1994, Effects of Drying and Oxidation of Wyodak Subbituminous Coal on Its Thermal and Catalytic Liquefaction Spectroscopic Characterization and Products Distribution. *Energy and Fuels*, 8: 301.
- Suuberg, E.M., D. Lee, and J.W. Larsen, 1985, Temperature Dependence on Cross-Linking Processes in Pyrolysing Coals. *Fuel*, 64: 1668-1671.
- Suuberg, E.M., P.E. Unger, and J.W. Larsen, 1987, Relation Between Tar and Extractables Formation and Cross-Linking During Coal Pyrolysis. *Energy and Fuels*, 1: 305-308.
- Suuberg, E.M., Y. Otake, Y. Yun, and S.C. Deevi, 1993, Role of Moisture in Coal Structure and the Effects of Drying upon the Accessibility of Coal Structure, *Energy and Fuels*, 7: 384.
- U. S. Department of Energy, March 1989, Coal Liquefaction: A Research & Development Needs Assessment, Volume 1: DOE/ER-0400.
- Vassallo, A.M., M.A. Wilson, and J. Edwards, 1987, ^{13}C NMR Aromaticity Balance on the Products from Flash Pyrolysis of Five Australian Coals, *Fuel*, 66: 622.

- Whitehurst, D.D., ed., 1980, *Coal Liquefaction Fundamentals*. American Chemical Society: Washington, DC, Symposium Series 139.
- Whitehurst, D.D., T.O. Mitchell, and M. Farcasiu, 1980, *Coal Liquefaction: The Chemistry and Technology of Thermal Processes*. Academic Press: New York, NY.
- Wilson, M.A., R.J. Pugmire, A.M. Vassallo, D.M. Grant, P.J. Collin, and K.W. Zilm, 1982, Changes in Aromaticity During Coal Liquefaction. *Ind. Eng. Chem. Prod. Res. Dev.*, 21: 477.
- Wroblewski, A.E., K. Reinartz, and J.G. Verkade, 1991, Moisture Determination of Argonne Premium Coal Extracts by ^{31}P NMR Spectroscopy. *Energy and Fuels*, 5: 786-791.
- Wroblewski, A.E., and J.G. Verkade, 1992, Moisture Release from Argonne Premium Coal Samples. A Qualitative ^{31}P NMR Spectroscopic Study, 6: 331.