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

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EXECUTIVE SUMMARY

In this quarter, progress has been made in the following two aspects: 1) effects of drying and mild oxidation on conversion and product distribution during non-catalytic and catalytic liquefaction of a Montana subbituminous coal (DECS-9); and 2) effects of solvent and catalyst on conversion and structural changes of a Texas subbituminous coal (DECS-1).

Influence of drying and mild oxidation on catalytic and non-catalytic liquefaction (at 350 °C for 30 min with 6.9 MPa (cold) H₂) was studied using Wyodak subbituminous coal. For non-catalytic runs, fresh raw coal gave higher conversion and higher oil yield than both the vacuum- and air-dried coals, regardless of the solvent. Compared to the vacuum-dried coal, the coal dried in air at 100 °C for 2 h gave a better conversion in the presence of either a hydrogen-donor tetralin or a non-donor 1-methylnaphthalene (1-MN) solvent. Catalytic runs were performed using in-situ generated molybdenum sulfide catalyst from ammonium tetrathiomolybdate (ATTM) precursor impregnated on either raw coal or predried coal samples. The solvent-free runs using ATTM loaded on the raw coal gave higher conversion and higher oil yield than loading ATTM on vacuum- or air-dried coals. In the presence of either tetralin or 1-MN, however, the runs using ATTM loaded on air-dried coal afford better conversions and oil yields as compared to the runs using vacuum-dried coal. This may be due to the moderate increase in surface functionality contributing to decreased surface hydrophobicity, representing a case where negative effect of drying is offset by the positive effect of mild oxidation-induced increase in surface functionality contributing to better ATTM dispersion. Upon drying coal in air at 150 °C for 20 h, the conversion significantly decreased to a lower value than that of the vacuum-dried coal in the non-catalytic runs, and the same trend was observed in the runs of the dried coals loaded with ATTM. Such a clearly negative impact of severe oxidation on coal liquefaction is considered to arise from significantly increased oxygen functionality which enhances the cross-link formation in the early stage of coal liquefaction. Physical, chemical, and surface chemical aspects of effects of drying and oxidation

and the role of water are also discussed in this report.

Liquefaction of a Big Brown Texas subbituminous coal was studied in the temperature range 250°C to 450°C. Tetralin and 1-MN were used as reaction solvents to compare with the reactions without solvent. Ammonium tetrathiomolybdate was used as the catalyst precursor. In thermal (i.e., non-catalytic) experiments, tetralin, an H-donor solvent, was beneficial not only in providing high conversion but, most importantly, also in gaining a high yield of oil at temperatures higher than 350°C. In catalytic experiments, conversions are very similar regardless of solvent used at temperatures up to 400°C, and tetralin does not provide any advantage. However, at 450°C, conversions with 1-MN or with no solvent dropped, while that with tetralin increased as well as did the oil yield. The gas yields appear to be independent of solvent and catalyst, but dependent on temperature. Cross polarization magic angle spinning (CPMAS) ^{13}C NMR was performed to obtain aromaticities of reaction residues. It is found that in plotting aromaticity versus conversion, the data fall into two sets: the thermal reactions and the catalytic reactions. At the same conversion, a residue from a catalytic reaction always has the lower aromaticity. This is because in a catalytic reaction, more aromatic carbon has been reacted. The study of the amount of aliphatic carbon converted from the coal to THF solubles shows that neither the catalyst nor the solvents has influence, but it is a function of temperature. In the conversion of aromatic carbon from coal to THF solubles, both the catalyst and the solvents have strong effects. For thermal reactions, tetralin gave much higher conversions of aromatic carbon than 1-MN or no solvent. For catalytic reactions, there is no difference among the solvents, or no solvent, at temperatures up to 400°C. At higher temperatures, tetralin again gave a much higher conversion than the other two cases, indicating that the solvent donation of hydrogen played a significant role. As for 1-MN and no solvent, compared with results at 400°C, the conversion of aromatic carbon at 450°C did not increase, but in fact decreased drastically, suggesting that retrogressive reactions occur in these situations.

INTRODUCTION

The conventional concept for high-severity conversion of coal is that coal must be heated to high temperatures (400-450°C) causing thermal cleavage of bonds in organic matrix of coal to yield free radicals, which are capped by hydrogen to form low-molecular-weight products. However, recent fundamental research in coal liquefaction and pyrolysis has revealed that coal is more reactive than had been thought previously. The thermally initiated reactions of coal can take place very rapidly and, especially for low-rank coals, can occur at lower temperatures. We have performed the temperature-programmed pyrolysis (TPP) of different coals ranging from brown to bituminous coals, and the results clearly showed that more bonds in low-rank coals are thermally broken at lower temperatures as compared to bituminous coals, and a concept of bond energy distribution has been developed from TPP (Song et al., 1991a; Song and Schobert, 1992). Considerable prior work at Penn State (Davis et al., 1986, 1989; Derbyshire et al., 1986a, 1986b, 1989; Stansberry et al., 1987; Burgess and Schobert, 1990; Burgess et al., 1991) has demonstrated that the combination of low-temperature catalytic reaction followed by the high temperature catalytic reaction using dispersed molybdenum catalysts significantly enhanced coal conversion and oil production. More recent work in this laboratory has shown that temperature-programmed liquefaction using programmed heat-up is more effective for converting low-rank coals (Song et al., 1991b; Song and Schobert, 1992; Huang et al., 1992; Song et al., 1993). All these results point to the beneficial effects of reactions at lower temperatures as compared to conventional high-severity processes.

The above results strongly suggest that low-temperature catalytic pretreatment or preconversion is a promising approach and deserves further detailed study. This work is a fundamental study on effects of pretreatments on coal structure and reactivity in liquefaction. The main objectives of this project are to study the coal structural changes induced by low-temperature catalytic and thermal pretreatments by using

spectroscopic techniques; and to clarify the pretreatment-induced changes in reactivity or convertibility of coals in the subsequent liquefaction. This report describes the recent progress of our work.

PROJECT OBJECTIVES

This work is a fundamental study of catalytic pretreatments as a potential preconversion step to low-severity liquefaction. The ultimate goal of this work is to provide the basis for the design of an improved liquefaction process and to facilitate our understanding of those processes that occur when coals are initially dissolved. The main objectives of this project are to study the effects of low-temperature pretreatments on coal structure and their impacts on the subsequent liquefaction. The effects of pretreatment temperatures, catalyst type, coal rank and influence of solvent will be examined.

The specific objectives are to identify the basic changes in coal structure induced by catalytic and thermal pretreatments by using spectroscopic, thermochemical and chemical techniques; and to determine the reactivity of the catalytically and thermally treated coals for coal liquefaction. Combining the two lines of information will allow us to identify the pretreatment-induced desirable or undesirable basic changes in coal structure; to clarify the impacts of pretreatments on coal liquefaction; to identify the structures responsible for retrograde reactions; to evaluate the structural differences resulting from different catalytic actions in relation to the overall catalytic effects in liquefaction; and ultimately, to develop a structure-reactivity relationship for liquefaction associated with catalyst type, coal rank and solvent. Furthermore, this research will contribute greatly to the development of effective pretreatment procedures which will allow coals to be liquefied more efficiently than the current practice. Finally, much of the knowledge to be generated from this research is not only critical for developing advanced hydroliquefaction processes, but also very useful to development of coal/petroleum resid co-processing, pyrolysis and hydropyrolysis processes.

TECHNICAL PROGRESS

1. EFFECTS OF DRYING OF WYODAK SUBBITUMINOUS COAL ON ITS THERMAL AND CATALYTIC LIQUEFACTION.

INTRODUCTION

Low-rank coals, including subbituminous coals and lignites, are characterized by low aromaticities, high oxygen functionalities, and high moisture contents.¹ Because many low-rank coals contain 20–35 wt % of moisture, an extensive amount of fundamental research has been done to develop an understanding of the occurrence of moisture in low-rank coals and their drying behavior.²⁻¹⁶ Moisture in the coal has been classified¹⁶ into four major forms: 1) superficial free water, 2) capillary condensed water, 3) sorbed water associated with polar groups and cations, and 4) water released only by chemical decomposition of organic or inorganic matter. Wroblewski and Verkade¹⁶ have shown that the differentiation of surface water from pore water is possible by using some reagents in combination with ³¹P NMR technique. Several methods, including thermal drying under vacuum and in air, microwave drying, chemical drying, or drying under a stream of dry inert gases, have been proposed and their impacts on coal structure have been studied.¹³⁻²¹ It has been well established that low-rank coal has a colloidal gel-like structure that can shrink and swell in response to moisture loss and gain.^{2,18,19} Suuberg et al.¹⁸ pointed out that water is retained tightly in coal in several forms; coal behaves like a swellable colloid in the presence of water. A drying process, with minimal effect on the reactivity of a coal, is the ultimate goal of several coal conversion studies.^{14,19-22} The changes caused by drying could be physical, chemical, or both, depending upon the drying method applied. Vorres et al. studied^{13,14} the drying kinetics of Beulah-Zap lignite in detail. They have found that the lignite dehydration follows a unimolecular rate law which is first order in the water in the sample; there are two segments in the dehydration kinetics: the first includes about 80–85% of the water loss and the second covers most of the

remaining water. Recently, Vorres¹⁵ also reported that the behavior of a Wyodak subbituminous coal on drying is very similar to that of the Beulah-Zap lignite; there is a transition after about 80 % of moisture loss to a slower unimolecular process.

For thermal liquefaction (i.e., reaction without added catalyst), several groups have examined the effects of drying or oxidation on coal conversion.^{14,17,19-22} Some experiences have shown that drying of coal has negative impact on its conversion reactivity,¹⁹⁻²² while there are also evidence to the contrary in non-catalytic liquefaction.¹⁴ It has been indicated that drying can cause an irreversible change in the pore structure, such as collapse of pores,¹³ which could limit accessibility of the reacting components during liquefaction and thus limit the rate of reaction. The oxidative drying of coal has been reported to have very detrimental effect on the coal conversion.¹⁹⁻²² Atherton²⁰ pointed out that commercial coal-drying techniques (i.e., thermal) make low-rank coals prone to self-heating and cause a decline in reactivity for subsequent conversion. Neavel²¹ reported a significant reduction in the yield of benzene-soluble products from a hvC bituminous coal as a result of oxidation. Cronauer et al.²² found that partial drying of subbituminous coal in a mixture of nitrogen and oxygen or even in nitrogen alone reduced the conversion as compared to that of the raw coal. Serio et al.¹⁷ observed that drying has a negative impact on the liquefaction of a lignite and a subbituminous coal but has little impact on the reaction of a bituminous coal. On the other hand, Vorres et al.¹⁴ recently reported that the oil yield in liquefaction of a lignite sample was highest for the dried sample, lowest for the partially dried and intermediate for the starting material.

For liquefaction of coal loaded with dispersed catalysts, there is little published information about the effects of predrying and mild oxidation. If a drying step has to be included in a catalytic liquefaction process, it would be desirable that the drying operation has minimal negative impact on both process economics and the reactivity of the coal. We also recognize that, when one considers the overall economics of a coal conversion complex, there may be reasons, other than conversion achieved in liquefaction reactors, to consider drying the coal. Examples of such reasons might be the reduction of coal transportation costs, lowering of the pressure in the reactors by eliminating the contribution from the partial

pressure of water vapor, or reducing the amount of waste water generated. In addition to deliberate drying of the coal carried out as part of a process, some inadvertent drying may occur during storage or transportation. For example, drying and oxidation may occur simultaneously during natural weathering.

In the present study we examined the effects of drying of Wyodak subbituminous coal in vacuum (non-oxidative drying) and in air (mild oxidation) on its thermal (non-catalytic) and catalytic liquefaction. To monitor the reactivity changes, we used low-severity liquefaction conditions such as 350 °C for 30 min. To detect the difference in physical changes (affecting diffusion) induced by drying under different conditions, we performed the reactions both in the absence of solvent and in the presence of either a hydrogen donor tetralin or a non-donor 1-methylnaphthalene (1-MN) solvent. This report describes our results on the effects of drying and mild oxidation on 1) non-catalytic liquefaction, 2) catalytic liquefaction using in-situ generated dispersed molybdenum sulfide, and 3) on the consumption of gas-phase H₂ and hydrogen transfer from donor solvent. Also presented in this report are the physical, chemical, and surface chemical considerations of drying effects and the physicochemical role of original moisture in the coal.

EXPERIMENTAL

Materials

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

Drying Treatment

The drying of coal was conducted under vacuum and in air. The non-oxidative drying (VD) was performed by placing a flask containing the coal into an oven which was then evacuated at room temperature (to minimize any possible oxidation due to the presence of air) and gradually heated within one hour to 100 °C followed an isothermal holding for 2 h and subsequent cooling in the oven. The air drying (AD) was done in an oven maintained at 100 °C for 2–100 h and at 150 °C for 20 h, with the door partially open to the atmosphere. Fresh as-received coal, with minimum possible exposure to air, was used as the raw coal.

Catalyst Loading

Reagent grade ammonium tetrathiomolybdate (ATTM, from Aldrich Chemical Company with 99.97 % purity) was used as the precursor for the dispersed molybdenum sulfide catalyst. ATTM $[(\text{NH}_4)_2\text{MoS}_4]$ was dispersed onto the raw coal or dried coal samples by the incipient wetness impregnation method from the aqueous solution. The same impregnation method was used in previous studies in this laboratory, but with different solvents.²³ The metal loading was kept at 1 wt % Mo on dmmf coal. The ATTM-impregnated coal was dried in a vacuum oven at 100 °C for 2 h before liquefaction.

Liquefaction and Product Work-up

The liquefaction experiments were carried out in 25 mL microautoclaves with 4 grams of coal at 350 °C for 30 minutes (plus 3 minutes for the reactor heat-up time to attain the reaction temperature). When a solvent was used, the ratio of solvent to coal was 1 to 1 by weight. The reactor was purged with H_2 at least three times, and finally pressurized with 6.9 MPa (cold) H_2 . A fluidized sandbath was used as heater. After the reaction, the reactor was brought down to temperature below 200 °C by quickly immersing it in cold water and then letting it cool to room temperature in air. The total volume of the gaseous product was measured by the water displacement method and was collected for further analysis. The liquid and solid products were separated by sequential Soxhlet extraction with hexane to obtain oil; with toluene to obtain

asphaltene; and with tetrahydrofuran (THF) to obtain preasphaltene. The THF-insoluble residues obtained after extraction were washed first with acetone and then with pentane in order to remove all the THF, followed by drying at 110 °C for 6 h under vacuum. The conversion of the coal into soluble products and gases was calculated on the basis of THF-insoluble residues. More experimental details may be found elsewhere.^{24,25} All the liquefaction experiments were at least duplicated in order to obtain reliable data. The deviations in conversions and products yields are generally within ± 3 wt% and most results reported here are average of two runs.

The gas analysis was performed using a Perkin Elmer Auto-System gas chromatograph. The yields of CO and CO₂ were determined using a Carboxen-1000, 60/80 mesh column (1.7 mm x 4.5 m) with a thermal conductivity detector. C₁-C₄ hydrocarbon gases were determined using Chemipack C18 column (3.2 mm x 1.8 m) with flame ionization detector. Helium was used as a carrier gas for all the gas analysis. Hydrogen consumption from the gas phase H₂ was calculated from the difference between the amount of hydrogen initially charged to the reactor and that found by GC analysis of the gas recovered after reaction. The dominant component of gases is CO₂, and the experimental errors for CO₂ yields are usually within ± 0.5 wt% on a dmmf basis. Tetralin and naphthalene present in the spent solvent (mixed with the hexane-soluble fraction) were analyzed using a Hewlett Packard gas chromatograph equipped with Rtx-50 capillary column (0.25 mm i.d. x 30m). The net hydrogen consumption (transfer) from tetralin was calculated from the naphthalene to tetralin ratio after reaction.²⁶ The experimental errors for hydrogen consumption are usually within ± 0.2 wt% on a dmmf basis, and most data reported here are average of two runs.

RESULTS AND DISCUSSION

Effects of Drying on Non-catalytic Liquefaction

Table I presents the results for thermal liquefaction runs (i.e., without added catalyst) in the absence of solvent and in the presence of either 1-MN or tetralin solvent. It is clear from Table I that the drying of

coal, whether oxidative (air drying) or non-oxidative (vacuum drying), has a significant effect on the yields of gases and liquid products. Among the gaseous products, CO_2 and CO are the main constituents, and C_1 to C_4 hydrocarbon gases make up the remainder. The effect of drying on gas yields is manifested primarily by the changes in CO_2 yield and secondarily by CO yield. The yields of C_1 – C_4 hydrocarbon gases in all the thermal runs were essentially constant; among the C_1 – C_4 gases the yields of methane and ethane were always higher than the others.

As can be seen from Table I, the vacuum-dried coal gives lower gas yield compared to the raw coal and air-dried coal. The higher gas yield from the air-dried coal is mainly due to the increase in CO_2 yield. The CO_2 yield increases with the severity of drying in air. Relative to CO_2 , the CO yield is much less sensitive to the severity of oxidative drying, although it creeps up slightly after very severe drying such as 100 h at 100 °C and 20 h at 150 °C. The drying in air can cause oxidation of the coal, increasing the carboxylic and carbonyl functionalities,²⁷ which produce CO_2 and CO gases, respectively, upon thermolysis. The gas composition data in Table I clearly show that increased oxidation of coal has a greater impact on CO_2 production, and a lesser impact on CO formation. Probably decarboxylation (formation of CO_2) can occur readily at lower temperature compared to decarbonylation (formation of CO). The severity of drying in air does not seem to have any marked effect on the yields of C_1 – C_4 gases in thermal reactions.

With respect to the effects of drying on coal conversion, several trends are apparent from Table I. First, using the fresh raw coal always affords the highest conversions and the highest oil yields, regardless of the solvents. Second, predrying the coal under either non-oxidative (vacuum drying) or oxidative (air drying) conditions decreased coal conversion and the yields of oil, asphaltene, and preasphaltene. Third, relative to vacuum drying, air drying at 100 °C for 2 h tends to afford higher coal conversions and oil yields, and this trend becomes more apparent when either an H-donor tetralin or a non-donor 1-MN solvent was used. However, the oil yield in thermal runs drops sharply when the time of predrying at 100 °C in air is increased from 20 to 100 h. Fourth, under the given drying conditions, the coal conversion generally increases in the order of solvent-free < 1-MN < tetralin. Relative to the non-donor 1-MN, the advantage of

H-donor tetralin is more apparent for liquefying the coals that have been dried in air at 100 °C for 2–100 h. Finally, after drying in air under high-severity conditions such as 20 h at 150 °C, conversion of the dried coal decreased to less than 50% of that of the fresh raw coal on a dmmf basis. In this case, the advantage of using a H-donor solvent disappears, as there is no major difference in coal conversions and oil yields between runs with H-donor and non-donor solvents. In fact, such an oxidative drying caused significant increase in oxygen functional groups in the coal, as revealed by the spectroscopic characterization.²⁸ However, the runs of the highly oxidized coal using a solvent still gave better conversions (18.0–19.9 wt%) than the solvent-free run (10.9 wt%), as can be seen from Table I.

We have confirmed the above results by duplicating all the experiments. The data in Table I are also consistent with earlier findings of Neavel,²¹ Cronauer et al.²² and Serio et al.¹⁷ Combination of these results indicates that both non-oxidative and oxidative drying have negative impacts on non-catalytic liquefaction of low-rank coals including lignites and subbituminous coals. However, these results are in contrast with the recent results of Vorres et al.¹⁴ who reported that drying improves oil yields from liquefaction of a North Dakota lignite in thermal run with H-donor solvent. The reason for this discrepancy is not known yet. Nevertheless, from our data and literature results, it seems to be a general trend that using fresh raw coal gives higher oil yield and higher conversion than using dried or oxidized samples in non-catalytic liquefaction of low-rank coals, in most cases. These observations will be rationalized based on physicochemical considerations, as we further describe below.

Effects of Drying on Catalytic Liquefaction

ATTM is known to decompose at ≥ 275 °C to form MoS_3 , which subsequently transforms to MoS_2 ; this transformation occurs readily under H_2 pressure.²⁹ In the present work, catalytic liquefaction was conducted using in-situ generated molybdenum sulfide from ATTM. The ATTM precursor was impregnated onto raw coal or dried coal samples from its aqueous solution and the ATTM-loaded coal sample was dried in vacuum before reaction. Therefore, unlike the thermal reactions which also involve raw coal whose moisture (28.4 wt%) is present in the reaction system, the catalytic reactions discussed below involve the ATTM-impregnated dry

samples.

Table II presents the data for low-severity catalytic liquefaction at 350 °C. For solvent-free catalytic runs, using fresh raw coal for impregnation of ATTM afforded significantly higher conversion and higher oil yield, which were also accompanied by higher H₂ consumption (see below), than using the vacuum-dried and air-dried coal. This fact suggests that the water originally present in the coal affects either the catalyst impregnation or the catalyst dispersion, even when aqueous solution is used for ATTM impregnation. Loading ATTM onto the coals that were predried at 100 °C for 2 h under vacuum and in air gave similar results in the absence of a solvent. However, the coal conversion and oil yield decreased and CO₂ yield increased with further increase in the severity of air drying from 20 to 100 h at 100 °C and from 100 to 150 °C.

For catalytic runs in the presence of either an H-donor tetralin (Table II) or a non-donor 1-MN solvent, dispersing ATTM on air-dried coal leads to higher conversion and oil yield, especially in tetralin, than loading ATTM on vacuum-dried coal. These results indicate that, relative to the non-oxidative drying in vacuum, air drying at 100°C, which induces mild oxidation of coal surface, has some beneficial effect when ATTM is used together with a reaction solvent. This may be attributed to the mild oxidation-induced increase in surface functionality and hence increased hydrophilicity, which contributed to increasing catalyst dispersion in the impregnation process. In fact, with a predrying time of 2 h at 100 °C, the use of air-dried coal seems to be slightly better than using the fresh raw coal in terms of higher conversion in the catalytic runs with either tetralin or 1-MN solvent.

Similar to the thermal runs, the yields of gases in the catalytic runs also vary significantly due to predrying. The variations in gas yields are mainly manifested by the changes of CO₂ yield (Table II), which increases with increasing severity of drying in air. Apparently, this reflects the occurrence of oxidation of the coal in air. The presence of a solvent appears to slightly increase CO₂ yield in many cases in the catalytic runs, but using a solvent does not have any marked effect on the production of hydrocarbon gases both in thermal and catalytic runs. In collateral work in this laboratory, it was found that for a given subbituminous coal sample, the gas yields are a function of temperature but are independent of

solvent.³⁰ It should be noted from Table I that the yield of CO₂ is always higher in the run of the raw coal than in the run of the vacuum-dried coal. This trend suggests that the water present as moisture in the raw coal contributes to the increase in the CO₂ formation, probably by the interaction with the carbonyl functionalities in the coal.³¹ Both Serio et al.³² and Song et al.²⁵ have noticed a significant increase in CO₂ yield when water was added back to the vacuum-dried coal. In the runs using ATTM loaded on the raw coal, water was not present during the reaction, but still a higher CO₂ yield was obtained compared to that with ATTM loaded on the vacuum-dried coal (Table II).

As can be seen by comparison of Table II with Table I, there are some considerable differences in gas composition between thermal and catalytic runs. In general, the total gases yields in the thermal runs of the raw and the dried coal (Table I) are always higher than those in the corresponding catalytic runs (Table II). This is due mainly to the lower yields of CO₂ in all the catalytic runs than all the corresponding non-catalytic runs. Relative to the thermal runs, catalytic runs reduced CO₂ yield by more than 35 % when ATTM was loaded on raw coal, and by more than 20 % when ATTM was loaded on the air-dried coal. This observation clearly indicates the occurrence of hydrogenation of the oxygen-functional groups in the presence of a dispersed Mo sulfide catalyst at 350 °C. On the other hand, the yields of hydrocarbon gases are always higher in the catalytic runs of the dried coal or the raw coal than in the thermal runs, suggesting that parts of the hydrocarbon gases from catalytic liquefaction resulted from catalytic hydrogenolysis of C–C bond or dealkylation of alkylaromatics. However, the extent of decrease in CO₂ yield due to the use of catalyst at 350 °C is much higher than that of the increase in C₁–C₄ gas make.

Effects of Drying on Hydrogen Consumption

Figure 1 shows the effect of predrying of the coal on hydrogen consumption from gas-phase H₂ and on net hydrogen transfer from tetralin in the thermal and catalytic liquefaction. In the absence of an added catalyst, the runs of the raw coal gave higher consumptions of gas-phase H₂ than the runs of the coal that has been dried at 100 °C for 2 h under vacuum or in air, both in the absence and presence of a solvent

(tetralin or 1-MN). This is consistent with the fact that the dried coals gave lower conversions and lower total yields of liquid products (Table I). In the solvent-free thermal runs, relative to the vacuum-dried coal, air-dried coal consumed slightly more H_2 , and increasing the severity of air drying increased H_2 consumption (Figure 1A). For the thermal runs using 1-MN solvent, increasing predrying time in air at 100 °C from 2 h to 20 h resulted in a decrease in H_2 consumption but further increase in predrying severity in air led to increased H_2 consumption. A similar trend in H_2 consumption is observed when tetralin is used in the thermal reaction. In this case, the net amount of hydrogen transferred from tetralin increased with increasing severity of drying in air. This may be attributed to the increased hydrogen abstraction from reactive radicals resulting from decomposition of oxygen functional groups formed from oxidation of the coal during air drying.

A general trend from all the thermal runs is that H_2 consumption and the extent of hydrogen transfer from tetralin clearly increased with severity of oxidative drying: 100 °C - 20 h < 100 °C-100 h < 150 °C - 20 h. In fact, this parallels qualitatively with the increase in CO_2 formation (Table I). For thermal liquefaction of dried coals under the low-severity conditions (350 °C) used in this work, it is likely that the hydrogen is consumed mainly in stabilizing the free radicals formed upon thermolysis of relatively weak bonds. It is generally true that the coal conversion and oil yield strongly depend on hydrogen consumption.^{29,33-36} In spite of the highest hydrogen consumption being observed in the thermal runs of the coal dried in air at 150 °C, the conversions and the yields of liquid products are the lowest. This indicates that only a part of the hydrogen consumed in the runs of the highly oxidized coal is related to the coal conversion or oil formation. The oxidation of coal increases the surface and bulk functionalities, which upon thermolysis can increase the number of free radicals. These considerations point to the conclusion that, relative to the vacuum-dried coal, a significantly higher number of bonds in the highly oxidized coal (air dried at 100 °C for 100 h or at 150 °C for 20 h) are broken during liquefaction at 350 °C, but increased population of such weak bonds contributes to enhanced retrogressive crosslinking, rather than the enhanced dissolution of coal.

In all the catalytic runs, the consumption of gas-phase H_2 is

significantly higher than that for the corresponding thermal runs (Figure 1), regardless of the presence of solvent (Figures 1B and 1C). This clearly shows that, at 350 °C, the dispersed Mo sulfide catalyst facilitates the dissociation of molecular H_2 , thus making hydrogen atoms readily available for the free radicals formed during liquefaction, resulting in higher conversion (Table II). It seems possible that the hydrogen atoms from catalytic dissociation of molecular H_2 have also induced bond cleavage by attacking the C-C bonds. This consideration is supported by the facts that using catalyst enhanced C_1 - C_4 hydrocarbon gas make as compared to the corresponding thermal runs, but using H-donor solvent had little impact on C_1 - C_4 hydrocarbon gas make.

The maximum hydrogen consumption (1.9 wt %, dmmf) is observed in the solvent-free catalytic run using ATTM impregnated on raw coal. As compared to this run, the gas-phase H_2 consumption is significantly lower in the corresponding catalytic runs using either 1-MN (1.2 wt %, dmmf) or tetralin solvent (1.2 wt %, dmmf). When the coal is predried either under vacuum or in air before ATTM impregnation, the catalytic runs consumes considerably less hydrogen in the solvent-free run. In general, the severity and type of predrying (vacuum or air) do not have any significant impacts on the consumption of gas-phase H_2 in the catalytic runs with either 1-MN or tetralin solvent.

The predrying of the coal also affects the hydrogen transfer from tetralin during liquefaction (Figure 1C). Comparatively, the hydrogen transfer from tetralin in thermal runs of the vacuum- and air-dried coals is slightly higher than that of the raw coal; for the air-dried coal it appears to increase with the severity of air drying. It is very interesting to note from Figure 1C that in the thermal run of the raw coal, the consumption of gas-phase H_2 is higher than the amount of hydrogen transferred from tetralin. For thermal liquefaction generally radical reactions are dominant and the hydrogen transfer from tetralin is usually more efficient than that from gas-phase H_2 . However, if non-radical reaction pathways exist in the presence of moisture, then the gas-phase H_2 consumption being higher than the hydrogen transfer from tetralin in the run of the raw coal may not be an unusual phenomenon. Clarification of this issue requires further study.

In the catalytic runs, the hydrogen transfer from tetralin is lower

than that for the corresponding thermal runs. Similar to the thermal runs, increasing the severity of predrying in air also appears (with one exception) to increase the hydrogen transfer from tetralin in the catalytic runs. The observation that net hydrogen transfer from tetralin decreases upon the use of added catalyst is in good agreement with the earlier findings from the work using Lewis acid catalysts²⁶ and dispersed metal sulfide catalysts.³⁵ Both Song et al.^{26, 37} and Artok et al.³⁵ observed that, when a dispersed catalyst is present, most of the hydrogen utilization comes from the gas-phase H_2 and only a small part from the H-donor solvent. The mechanisms of hydrogen transfer in catalytic reactions have been discussed elsewhere.^{26, 38}

Physical and Chemical Considerations of Drying Effects

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

Apparently, the first effect, the removal of water, was neglected in most previous work on the influence of drying in liquefaction. This is presumably because water was thought to be inert in coal liquefaction. We also examined the effect of water addition.^{25, 39} Table III shows the effect of adding water in the thermal runs of vacuum-dried coal without solvent and with tetralin solvent. Adding a small amount of water equivalent to the original moisture content (28.4 wt%) back to the vacuum-dried coal increased coal conversion from 9.2 to 22.3 wt% in the solvent-free runs,

and from 25.9 to 39.9 wt% in the runs with tetralin solvent. In fact, adding water back to the vacuum-dried coal restored over 90 % of the oil yield and conversion of those with the fresh raw coal in non-catalytic runs at 350 °C both with and without a solvent, as can be seen from Table III.

The above facts strongly suggest that the decrease in conversion upon drying is due primarily to the removal of water, and the changes caused by drying at 100 °C (except oxidation) are largely reversible upon addition of water. Although the presence of water has significant physical effect (see below), it may also have some impact on the chemical reaction at 350 °C. It has been reported that hydrothermal pretreatment of coal in presence of water is beneficial for improved conversion and better product quality in pyrolysis, liquefaction and coprocessing.^{17,40-44} An increase in the CO₂ yield upon addition of water to vacuum-dried coal is also observed both in thermal and catalytic runs.²⁵ This is probably due to the interaction of water with carbonyl functional groups, as suggested by Petit.³¹ The decrease in CO yield upon water addition indicates that the water gas shift reaction (equation 1) did occur but this reaction only contributes to a small part of the increased CO₂ yield, as can be seen by comparing the CO and CO₂ yields in Table III on a molar basis. From their model compound studies, Tse et al.⁴⁴ suggested water can suppress the retrogressive crosslinking reactions such as those of polyhydroxy groups. From our data in Tables I and III and the results of Petit,³¹ it seems that the added water or the original moisture participated in the reaction and acted also as a hydrogen source through some chemical reactions such as that shown in equation 2.

This rationalizes the enhanced coal conversion together with increased CO₂ formation upon water addition. Since low-rank coals have high propensity towards retrogressive reactions due to their high oxygen functionalities, the removal of oxygen functional groups in the presence of water at 350 °C can make the coal network less refractory for dissolution and hence higher conversion is achieved.²⁵ On the other hand, according to Siskin et al.,^{45,46} the presence of water during the preconversion step can facilitate

depolymerization of the macromolecular structure to give a higher conversion yield by cleavage of ether type crosslinkages.

The second effect, physical change such as pore collapse and shrinkage caused by drying, has been discussed quantitatively in a recent paper by Suuberg et al.¹⁸ Their work has demonstrated that water is a good swelling agent for coals ranging from lignites up to high-volatile bituminous coal, and the coals shrink when dried from the as-mined state. They found that shrinkage upon drying (vacuum drying) is correlated by equation 3:

$$\text{Volumetric shrinkage (\%)} = 0.863 \times (\text{moisture content, wt\%}) - 0.162 \quad (3)$$

Applying this relationship would give a 24.3 % volumetric shrinkage of Wyodak subbituminous coal upon drying. However, drying in vacuum and drying in air may have different impacts on the pore collapse, and the effect of such a difference, if any, needs to be clarified.

One of our hypotheses in designing the experiments with different solvents was the following: if drying affects the rate of solvent diffusion into the coal pores or the rate of uptake of solvents by the coal, then the reaction with an H-donor solvent should be more sensitive to the drying conditions than the one with a non-donor solvent. As can be seen from Table I, for thermal runs in the presence of tetralin solvent, considerably higher conversion (35.1 wt%) and higher oil yield (11.7 wt%) were obtained with the air-dried coal (100 °C for 2 h) than with the vacuum-dried coal (25.9 wt% conversion, 4.1 wt% oil yield), and this trend was confirmed by duplicate tests. However, using 1-MN in the thermal runs gave only slightly higher conversion and oil yield for the air-dried coal (100 °C for 2 h) than for the vacuum-dried coal. These facts can not be rationalized by oxidation induced by drying in air. We believe that for thermal runs in the presence of an H-donor solvent, the advantage with air-dried coal (dried at 100 °C for 2 h) relative to vacuum-dried coal is due to the differences in the physical changes caused by drying under different conditions.

Surface chemical considerations have been briefly discussed in our preliminary communication.³⁹ If drying in different atmosphere or under different conditions affects the surface characteristics of coal, then the

dispersion of the catalyst precursor molecules on coal surface may change with drying. It has been shown that removal of the original moisture by drying contributes to increasing the hydrophobicity of coal surface,^{47, 48} but mild oxidation can convert some hydrophobic sites on coal surface into hydrophilic sites.^{49, 50} Relative to vacuum-drying, the beneficial effect of predrying in air at 100°C for 2 h in catalytic runs (Table II) may be attributed to the mild oxidation-induced increase in surface oxygen functionality and hence increased hydrophilicity, which could contribute to increasing ATTM dispersion in the impregnation process. As Weller⁵¹ pointed out ten years ago, the degree of dispersion is very important when unsupported Mo catalysts are used for coal liquefaction.

The hydrophobicity is a function of coal rank and maceral composition,⁵² but is decreased by prewetting of dried coals.⁴⁸ We also performed several tests to see whether prewetting affects the catalyst impregnation, and the results are given in Table IV. The vacuum-dried coal was prewetted with a small amount of water which is equivalent to the original moisture (28.4 wt%). The prewetted coal was then impregnated with aqueous ATTM solution either immediately after prewetting or after 24 h storage of the prewetted sample. The results in Table IV show that prewetting the vacuum-dried coal before impregnating ATTM from its aqueous solution has increased coal conversion and enhanced oil formation. The advantage of prewetting the vacuum-dried coal becomes more apparent when tetralin solvent was used for catalytic liquefaction at 350°C, where coal conversion and oil yield increased from 36.4 to 44.6 wt%, and from 10.2 to 18.4 wt%, respectively. Prewetting coal with water decreases the hydrophobicity of the surface on the one hand, and causes volume expansion due to coal swelling on the other hand. Both these two effects are desirable for better dispersion of ATTM during incipient wetness impregnation. Gorbaty¹⁹ has shown that drying a Wyodak subbituminous coal in vacuum can decrease the amount of a metal salt (nickel sulfate) adsorbed onto coal from its aqueous solution. He attributed the drying-induced changes primarily to pore collapse and secondarily to the replacement of water by gas, namely, the volume once occupied by water becomes occupied by the gas present during and after drying. However, combination of our results and with those of Gorbaty¹⁹ and Wei et al.⁴⁸ suggest that non-oxidative predrying also increases the

surface hydrophobicity and reduces the adsorption of metal salt onto the surface of low-rank coals, although water is used to dissolve the metal salt. Prewetting the coal prior to the contact with metal solution, however, decreases the surface hydrophobicity and swells the coal, leading to improved the adsorption and dispersion of metal salt from its aqueous solution (onto more hydrophilic surface).

In this context, relative to vacuum drying, the advantage of predrying coal in air (mild oxidation at 100 °C for 2 h) before ATTM impregnation for the solvent-mediated catalytic runs (Table II) should be considered in view of the fact that mild oxidation converts some hydrophobic sites into hydrophilic sites, which contributes to improved dispersion of the ATTM precursor during its impregnation. This may be a case where a negative effect of drying is offset by the positive effect of mild oxidation-induced increase in surface functionality contributing to better ATTM dispersion. In fact, when a solvent was used, the catalytic reactions using ATTM loaded onto the coals predried in air at 100 °C for 2 h afforded similar or slightly higher conversions and oil yields than the run with ATTM loaded onto the raw coal.

It should be mentioned that, relative to vacuum drying, the advantage of air drying completely diminishes upon increasing the drying severity to 150°C for 20 h. In other words, high-severity air drying or oxidation has unambiguously negative impact on catalytic (Table II) as well as non-catalytic liquefaction (Table I) of the coal. Such a clearly negative impact of severe oxidation on coal liquefaction is considered to arise from significantly increased oxygen functionality, which enhances the cross-link formation in the early stage of coal liquefaction.

SUMMARY AND CONCLUSIONS

Drying of Wyodak subbituminous coal, either under vacuum or in air at 100 °C, significantly affects its conversion in non-catalytic and catalytic liquefaction at 350 °C.

For thermal runs, fresh raw coal gave higher conversion and higher oil yield than both the vacuum-dried and air-dried coals, regardless of the solvent. Compared to the vacuum-dried coal, the coal dried in air at 100 °C for 2 h gave a better conversion in the presence of either tetralin or 1-MN

solvent.

For solvent-free catalytic runs using in-situ generated molybdenum sulfide from impregnated ammonium tetrathiomolybdate (ATTM) precursor, the runs using ATTM loaded on the raw coal gave higher conversion and higher oil yield than loading ATTM on vacuum- or air-dried coals. In the presence of either tetralin or 1-MN, however, the runs using ATTM loaded on air-dried coal afford better conversions and oil yields as compared to the runs using vacuum-dried coal. This may be due to the moderate increase in surface functionality contributing to improved dispersion of the ATTM precursor. In fact, loading ATTM on air-dried coal gave similar or slightly better conversions when a solvent was used, as compared to the case using raw coal. This may be a case where negative effect of drying is offset by the positive effect of mild oxidation-induced increase in surface functionality contributing to better ATTM dispersion.

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

Predrying also affects the hydrogen consumption. Overall, in the solvent-free catalytic runs the predrying (in vacuum or air at 100 °C) seems to decrease the hydrogen consumption significantly. In the presence of 1-MN or tetralin solvent the effect of predrying on H₂ consumption is not apparent. There is another external source of hydrogen in the presence of H-donor solvent. The runs of highly oxidatively dried coal samples increased the net hydrogen transfer from tetralin, but using the catalyst significantly decreased the net H-transfer from tetralin.

The effect of predrying on coal conversion in thermal liquefaction is due primarily to the removal of water and secondarily to the physicochemical changes of coal induced by drying. Adding water back to the vacuum-dried coal can restore over 90 % of the conversion of the fresh raw coal in the runs without solvent and with H-donor solvent. For catalytic runs using impregnated ATTM, the effect of predrying is mainly caused by the drying-induced physicochemical changes such as those in

pore volume and surface hydrophobicity.

The important implications from this work are as follows. Overall, predrying Wyodak coal for thermal runs is not desirable in terms of lower conversion or lower oil yield. If drying has occurred (during storage or transportation) prior to use, adding water back to the dried coal can restore most of the reactivity and conversion of the raw coal for non-catalytic liquefaction. For catalytic liquefaction using dispersed ATTM precursor salt, it is better to use raw coal for catalyst impregnation. If the coal is dried, then air drying is better than vacuum drying at 100 °C for 2 h. In practice, one would not consider vacuum drying on an industrial scale. If the coal has been dried under essentially non-oxidative conditions, prewetting the dried coal with water before impregnation of the metal salt from its aqueous solution can help to improve the performance of resulting catalyst. Practical application of the incipient wetness impregnation method for loading of catalyst precursor from its aqueous solution in a larger scale is possible by means of a spray.

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2. EFFECTS OF SOLVENT AND CATALYST ON LIQUEFACTION CONVERSION AND STRUCTURAL CHANGES OF A TEXAS SUBBITUMINOUS COAL

INTRODUCTION

Coal liquefaction involves an initial stage of coal macromolecular break-up driven by thermal energy.^{1,2} The result of this break-up is the formation of free radicals. If these free radicals are stabilized by hydrogenation, light products, e.g. oil, are formed and the goal of liquefaction is achieved. On the contrary, if the radicals recombine with one another and form more stable and heavier product, the liquefaction has essentially failed. Therefore, hydrogenation is a key in coal liquefaction. There are several ways often used to accelerate the rate of hydrogenation: to use a high pressure of H₂ (ref. 3), to use a hydrogen-donor solvent,⁴ and to use a catalyst.

In the work reported here, a Big Brown Texas subbituminous (DECS-1) coal was used for liquefaction. A low-rank coal like this is characterized by low aromaticity, small ring clusters, abundant aliphatic and hydroaromatic carbon and high oxygen content.⁵ These diverse structural features cause the thermal break-up of the coal to occur over a wide temperature range,⁶⁻⁸ and thus hydrogenation should be feasible over the same range. The purpose of the present work is to investigate the liquefaction of DECS-1 in the temperature range from 250°C to 450°C. Two kinds of solvent, a hydrogen-donor solvent (tetralin) and a non-donor solvent (1-MN) were used to compare with the reactions without solvent.

An ammonium tetrathiomolybdate derived catalyst was used. Liquefaction results are presented to determine the solvent effect and the catalyst effect. The residues from THF extraction were studied by CPMA¹³C NMR to obtain their aromaticities. Furthermore, the conversion and aromaticity data were combined to calculate the amounts of aliphatic and aromatic carbon reacted and removed from the coal during liquefaction.

EXPERIMENTAL

1. Materials and Liquefaction Reactions

The coal sample was a Big Brown Texas subbituminous (DECS-1) obtained from Penn State Coal Sample Bank. Its compositional data are summarized as the following on a dry and mineral matter free base: 76.13% carbon, 5.54% hydrogen, 1.50% nitrogen, 1.05% organic sulfur and 15.78% oxygen (by difference). The reaction solvents were tetralin (Aldrich, 99%), and 1-MN (Aldrich, 98%). The catalyst precursor ATTM (Aldrich, 99.97%). All the chemicals were used without further purification.

The catalyst loading was 1 wt% of Mo based on the dmmf coal. A THF/H₂O (1:1) mixture was used to make the solution of the catalyst precursor, because this binary mixture was superior to H₂O for catalyst impregnation in terms of providing higher conversion and oil yield.⁹ The catalyst precursor was first added to just enough water to dissolve the desired amount of the precursor. The same volume of THF was then added to the H₂O solution. After being stirred to achieve a homogeneous solution, the THF/H₂O/ATTM mixture was added to the dried coal to make a slurry. After 20 minutes of magnetic stirring at room temperature and under N₂ atmosphere, the excess water and THF were removed in a rotary evaporator. The "wet" sample (i.e., still containing residual H₂O and THF) was then dried in a vacuum oven at room temperature for 20 hours, at 45°C for 5 hours and at 95°C for 4 hours, sequentially.

Liquefaction experiments were conducted in 25 mL tubing bombs in a fluidized sandbath. For each reaction, 4 grams of the coal sample and 4 grams of a solvent, if a solvent was used, were loaded into a tubing bomb. The reactor was purged three times with hydrogen and then pressurized to a final pressure of 1000 psi (7 MPa) at room temperature. For every

reaction, the sandbath was preheated and kept at a desired temperature, from 250°C to 450°C. The tubing bomb was then plunged into the sandbath and agitated at a rate of 200 cycles per minute. The total time in which a tubing bomb was kept in the sandbath was 33 minutes, with 3 minutes being the time for rapid heat-up. Finally, after reaction, the tubing bomb was taken out of the sandbath and rapidly quenched by dipping into cold water.

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

2. Product Analysis

The gaseous product was analyzed by gas chromatography. CO and CO₂ were determined using a Carbosieve column with a thermal conductivity detector (TCD) while hydrocarbon gases (C₁–C₆) were determined using a Chemipack C18 column with a flame ionization detector (FID) on a Perkin Elmer auto-system gas chromatograph. Hydrogen consumption from the gas phase was calculated by the difference between the amount of the H₂ initially charged into the reactor and that remaining in the gas recovered, which was determined by gas chromatography.

The hexane solubles were also studied by gas chromatography. Besides the determination of the composition, the other major purpose was to obtain data on hydrogen consumption from liquid phase (i.e. tetralin) by determining the amount of tetralin and the amount of naphthalene in the mixture.

The THF insolubles were analyzed by ¹³C solid state NMR using the cross polarization magic angle spinning (CPMAS) technique. All CPMAS spectra were obtained on a Chemagnetics NMR Model M100s. The ¹³C frequency was 25.15 MHz. The pulse delay was 1 second and the contact time was 1 ms.

RESULTS AND DISCUSSION

1) Solvent Effect

The results of thermal liquefaction (without catalyst) are listed in Table V. Conversions are in a large range, from 11.7% to 92.2%. At 250°C, the solvents do not show any significant effect on conversion or product distribution. As the temperature increases to 300°C, the solvents start showing their advantage in providing higher conversions than those reactions without solvent, though the differences between the solvents are not obvious. At 350°C, there is a remarkable increase in oil, asphaltene and preasphaltene yields when a solvent is used. This indicates that, in this temperature range, the solvents play a role which enhances the conversion, but since there is no difference between the reaction with tetralin and the reaction with 1-MN, this role may not have anything to do with hydrogen donation. As the temperature changes from 350°C to 400°C, there is a drastic increase in conversion regardless of whether a solvent is applied or not, suggesting that in this temperature range, the thermal energy is the enough to crack the coal macromolecular matrix. At 400°C, tetralin made a tremendous difference from 1-MN and reaction without solvent. The conversion reaches 82.0%, made up of gas 9.5%, oil 36.7%, asphaltene 16.6% and preasphaltene 19.2%. With 1-MN or without solvent, the conversions are much less, 55.5% and 45.0% respectively. The differences of conversion and product distribution imply that tetralin is active in donating hydrogen at temperatures higher than 350°C. 1-MN, on the other hand, shows a very slight advantage over no solvent in gaining higher conversion and oil yield, but as temperature increases to 450°C, this advantage almost disappears.

2) Catalyst Effect

The results of catalytic liquefaction are presented in Table VI. At the presence of ATTM, the conversion achieved in all experiments increases drastically as the temperature increases from 250°C to 400°C. Comparing these three kinds of reactions (no solvent, tetralin or 1-MN) with the corresponding thermal reactions, the catalyst added apparently increased the conversion, especially at temperatures higher than 300°C, suggesting

that the catalyst precursor was activated at a temperature between 300°C and 350°C. Furthermore, the product distributions show that the increasing conversion is accompanied by an increasing yield of light materials, such as oil, when the catalyst is added. The other comparison is among the three kinds of catalytic reactions. At temperatures between 250°C and 400°C, there is no significant difference in conversion and product distribution (though, at 400°C, the reaction without solvent seems to have a higher oil yield). This means that, in this temperature range, the catalyst has a stronger effect than the solvents; thus any differences caused by the solvents are diminished. However, at 450°C, tetralin gave a slightly higher conversion than at 400°, while both 1-MN and no solvent actually gave a much lower conversions (almost 20% unit lower) relative to those at 400°C. In the case of 1-MN at 450°C, the yields of gas, asphaltene and preasphaltene are still very similar to those obtained in tetralin, while the conversion was much lower. The sole cause of this conversion difference is the decrease of the oil yield. With tetralin at 450°C, yields of asphaltene and preasphaltene dropped by 9 percentage units and 17 percentage units respectively, while the yield of oil increased by 22 percentage units compared with that at 400°C. This suggests that at this temperature (450°C), with the presence of both catalyst and a H-donor solvent, the conversion of preasphaltene and asphaltene to oil, or from heavy products to light products, is favorable. With the presence of the catalyst and the absence of a donor solvent, meaning with no solvent at all or a non-donor solvent, the conversion drops as well as do all of the product yields, except gas make, suggesting that retrogressive reactions take place and form heavier and more stable materials.

In coal liquefaction, once the free radicals are formed, the net reactions that they will undergo are a result of a competition between the radical stabilization by hydrogenation to form light product and the recombination of the radicals to form heavy products. Since the free radical formation is a pyrolytic break-up of the coal matrix, it is a thermally driven reaction.¹ At temperatures up to 400°C, the rate of radical formation is so slow that hydrogenation can match it regardless of whether the hydrogen radicals are obtained from the donor solvent or from gaseous H₂. However, at 450°C, the radical formation is very fast, and the H• radical formation from catalytic dissociation of gaseous H₂ may not

be fast enough to match the rate of coal radical formation, and therefore the radical recombination takes place. Since tetralin has intimate contact with these radicals and is able to donate H, hydrogenation take place to form light products.

The gas yields from all liquefaction experiments are plotted versus temperature in Figure 2. All the yields are in the range from 0% to 20%. Regardless of the solvents and the catalyst used in the reactions, the data all fall onto one line. Therefore, the amount of gas produced in the reactions is a function only of temperature, and neither solvent nor catalyst has any effect, suggesting that gas formation is a reaction driven by thermal energy.

3) CPMAS ^{13}C NMR Study of Liquefaction Residues

Examples of the spectra of CPMAS ^{13}C MNR of residues are shown in Figure 3. The spectra were curve-fitted using LabCal program and the area of each peak was integrated. The reason for using twice the area of the left spinning side band (SSB), rather than adding both left SSB and right SSB to aromatic area, is because the latter overlaps with the aliphatic carbon peaks. It is observed that the right SSB usually is different from the left SSB and we believe that this is caused by the overlap.

As a base line, the aromaticities of the raw coal and the dried coal were first calculated; both were 0.48. This shows that before any reaction, the aromaticity is not affected by vacuum drying at 95°C . The aromaticities of THF-insoluble residues from all runs are summarized in Table 4. It is observed that as temperature increases, the aromaticity increases, from the lowest, 0.50, to the highest, 0.94. There are two possible explanations of this increase: one is that as reaction temperature increases, more and more aliphatic carbons are cracked off the macromolecular structure of the coal while the aromatic carbon may not react as much as the aliphatic carbon; the other is that dehydrogenation and condensation reactions take place during the reaction which increase the amount of aromatics in the coal. More of this will be discussed in a later paragraph. Comparing the aromaticities of the residues from the thermal reactions, it is found that the solvents do not have a remarkable effect. Furthermore, in the case of catalytic reactions, the solvents have no

significant effect either. In order to determine the influence of the catalyst on the aromaticities, all the data are plotted versus conversion in Figure 4. A general trend is that the aromaticities of residues increase with conversion, but the data fall into two separate sets: those from reactions with and without the catalyst, regardless of the solvent used. For any level of conversion, f_a of the residue from a catalytic reaction is lower than that from a non-catalytic reaction, and the difference between the two increases with increasing conversion.

To achieve a general ideal of what kind of structures have been converted to THF solubles, or what kind of reactions are actually catalyzed by the catalyst during the liquefaction, the percentages of aliphatic and aromatic carbon that have been reacted are calculated using the existing data: the amounts of dry mineral matter free coal charged into the tubing bombs, aromaticity of the dried coal, the conversions, and the aromaticities of the residues. In Figure 5, the reacted aliphatic carbon, based on the initial amount in the coal, is plotted versus temperatures. Roughly speaking, all the points fall on one curve, regardless of the use of solvent or any catalyst. The amount of reacted aliphatic carbon increases drastically when the temperature increases to 400°C. At 400°C, about 90% of the aliphatics carbon has been converted to THF solubles. When the reaction temperature was further increased to 450°C, the increase of the reacted aliphatic carbon became insignificant, from 90% to about 95%. This study suggests that, like the yields of the gases, the conversion of aliphatic carbon from coal to THF solubles is a function of temperature; neither solvent nor catalyst has any influence. In Figure 6, the amount of aromatic carbon converted to THF solubles is plotted versus the temperature. Unlike Figure 5, the data are much more scattered in Figure 6. In thermal liquefaction reactions, tetralin made a remarkable difference from 1-MN and no solvent. When the temperature is 350°C or higher, much more aromatic carbon reacted in the presence of tetralin. At 450°C, the conversion of aromatic carbon reached 86% with tetralin, while it only reached 15% and 10% with 1-MN and without solvent, respectively. In catalytic reactions, the difference caused by the solvents is diminished at temperatures to 400°C, indicating that the catalyst is so active in converting the aromatic carbon into THF solubles that solvent is not a determining factor. However, when the temperature was increased to

450°C, with the presence of the catalyst, reactions with 1-MN or without solvent have a large drop, from 77% to 36% and from 93% to 42% respectively, while that with tetralin further increased, from 87% to 92%. At temperature as high as 450°C, the thermal cracking of the coal matrix is very fast, hydrogenation from gaseous H₂ catalyzed by the added catalyst is no longer able to match the rate of coal radical generation because of the lack of intimate contact between the catalyst and the reaction sites. However, tetralin, which has good contact with the coal, shows its advantage in hydrogen donation to prevent the recombination of free radicals and thus convert the aromatic carbon into THF solubles.

The study of reacted aliphatic and aromatic carbons explained why a thermal reaction always produces residues with higher aromaticity than a catalytic reaction, even though the conversion is the same. In the former case, the conversion is achieved by having more aliphatic carbon reacted and, in the latter case, it is achieved by having more aromatic carbon reacted. For example, in experiment no. 331, the conversion is 44.0% and there is -8% aromatic carbon and 79% aliphatic carbon reacted; while in experiment no. 327, the conversion is almost identical (45%) but there is 23% aromatic and 63% aliphatic carbon reacted.

SUMMARY

Liquefaction of a Big Brown Texas subbituminous coal was studied in the temperature range from 250°C to 450°C. Tetralin and 1-MN were used as reaction solvents to compare with the reactions without any solvent. Ammonium tetrathiomolybdate was used as the catalyst precursor. In thermal experiments, tetralin, an H-donor solvent, was beneficial not only in providing high conversion but, most importantly, also in gaining a high yield of oil at temperatures higher than 350°C. In catalytic experiments, conversions are very similar regardless of solvent used at temperatures up to 400°C, and tetralin does not have any advantage. However, at 450°C, conversions with 1-MN or without solvent dropped, while that with tetralin increased, as well as did the oil yield. The gas yields appear to be independent of solvent and catalyst but dependent on temperature.

Cross polarization magic angle spinning ¹³C NMR was performed to

obtain aromaticities of reaction residues. It is found that, in the plot of aromaticity versus conversion, the data fall into two sets: the thermal reactions and the catalytic reactions. At the same conversion, a residue from a catalytic reaction always has lower aromaticity. This is because in a catalytic reaction, more aromatic carbon has been reacted. The study of the amount of aliphatic carbon converted from the coal to THF solubles shows that neither the catalyst nor the solvents have influence, but it is a function of temperature. In the case of conversion of aromatic carbon from coal to THF solubles, both the catalyst and solvents have strong effects. For thermal reactions, tetralin gave much higher conversions of aromatic carbon than 1-MN or no solvent. For catalytic reactions, there is no difference among the solvents, or no solvent, at temperatures up to 400°C. At temperatures higher than that, tetralin again gave a much higher conversion than the other two cases, indicating that the solvent donation of hydrogen played a significant role. As for 1-MN and no solvent, compared with the results obtained at 400°C, the conversion of aromatic carbon at 450°C did not increase, and in fact decreased drastically, suggesting that retrogressive reactions occur in these situations.

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Table I. Results of Non-Catalytic Liquefactions of Raw and Dried Wyodak Coal at 350 °C for 30 min with 6.9 MPa H₂

Drying conditions	Reaction solvent	CO	CO ₂	C ₁ -C ₄	Oil	Asphal.	Preasp.	Total Liquids ^a	Conversion dmmf wt%
Fresh raw coal	none	0.4	8.9	0.2	5.4	2.8	9.1	17.3	25.0
Vacuum-dried, 100°C, 2 h	none	0.2	4.5	0.2	2.1	2.6	4.5	9.2	12.5
Air-dried, 100°C, 2 h	none	0.3	5.9	0.1	3.3	0.7	5.8	9.8	14.8
Air-dried, 100°C, 20 h	none	0.4	6.7	0.2	6.0	0.6	3.2	9.8	15.5
Air-dried, 100°C, 100 h	none	0.7	11.2	0.2	1.2	0.7	3.3	5.2	12.7
Air-dried, 150 °C, 20 h	none	0.8	12.3	0.1	0.6	0.2	0.4	1.1	10.9
Fresh raw coal	Tetralin	0.1	7.4	0.2	15.8	9.3	12.4	37.5	43.3
Vacuum-dried, 100°C, 2 h	Tetralin	0.2	4.1	0.2	4.1	7.6	10.0	21.7	25.9
Air-dried, 100°C, 2 h	Tetralin	0.2	5.9	0.2	11.7	7.4	10.6	29.7	35.1
Air-dried, 100°C, 20 h	Tetralin	0.3	7.5	0.3	11.1	6.5	8.9	26.5	32.4
Air-dried, 100°C, 100 h	Tetralin	0.5	10.9	0.2	6.1	6.3	9.7	22.1	30.8
Air-dried, 150 °C, 20 h	Tetralin	0.6	15.9	0.1	2.1	2.8	3.2	8.1	19.9
Fresh raw coal	1-MN	0.1	7.0	0.2	15.9	6.6	11.4	34.0	39.9
Vacuum-dried, 100°C, 2 h	1-MN	0.2	4.3	0.2	1.1	5.8	7.4	14.3	18.3
Air-dried, 100°C, 2 h	1-MN	0.3	6.2	0.2	4.2	4.0	9.4	17.6	22.7
Air-dried, 100°C, 20 h	1-MN	0.3	7.0	0.2	8.0	5.6	4.7	18.3	24.5
Air-dried, 100°C, 100 h	1-MN	0.5	11.9	0.2	1.7	4.1	6.3	12.1	21.1
Air-dried, 150 °C, 20 h	1-MN	0.7	15.7	0.1	1.8	2.2	2.5	6.6	18.0

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

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

Drying conditions	Solvent	CO	CO ₂	C ₁ -C ₄	Oil		Asphal.	Preasp.	Total	
					dmmf wt%	Liquids ^a			dmmf wt%	Conversion
Fresh raw coal ^b	none	0.3	4.1	0.5	16.9	9.2	14.9	41.1	43.3	
Vacuum-dried, 100°C, 2 h	none	0.2	2.3	0.3	10.0	5.4	11.4	26.8	29.8	
Air-dried, 100°C, 2 h	none	0.4	5.2	0.6	12.6	3.2	10.1	25.9	29.2	
Air-dried, 100°C, 20 h	none	0.4	5.7	0.7	14.6	3.1	8.7	26.4	31.2	
Air-dried, 100°C, 100 h	none	0.7	8.0	0.6	13.3	2.4	5.1	20.8	28.4	
Air-dried, 150 °C, 20 h	none	0.9	9.8	0.5	5.1	0.5	1.7	7.3	18.5	
Fresh raw coal ^b	Tetralin	0.1	4.5	0.4	16.0	11.5	11.9	39.4	42.2	
Vacuum-dried, 100°C, 2 h	Tetralin	0.1	2.6	0.3	10.2	12.9	10.6	33.4	36.4	
Air-dried, 100°C, 2 h	Tetralin	0.2	4.8	0.4	15.7	11.1	14.9	41.7	45.6	
Air-dried, 100°C, 20 h	Tetralin	0.2	6.9	0.4	18.6	8.6	10.7	37.9	43.5	
Air-dried, 100°C, 100 h	Tetralin	0.4	8.8	0.5	16.5	10.8	11.0	38.3	45.0	
Air-dried, 150 °C, 20 h	Tetralin	0.4	12.4	0.4	9.6	2.3	5.7	17.6	29.4	
Fresh raw coal ^b	1-MN	0.1	4.5	0.3	10.4	10.4	11.9	32.7	35.9	
Vacuum-dried, 100°C, 2 h	1-MN	0.1	3.4	0.3	6.1	10.1	12.3	28.5	31.1	
Air-dried, 100°C, 2 h	1-MN	0.2	5.2	0.4	10.3	8.1	16.0	34.4	37.4	
Air-dried, 100°C, 20 h	1-MN	0.2	9.3	0.5	14.1	8.7	10.5	33.3	39.7	
Air-dried, 100°C, 100 h	1-MN	0.3	9.5	0.4	14.4	8.7	11.1	34.2	39.4	
Air-dried, 150 °C, 20 h	1-MN	0.3	12.4	0.3	5.3	2.8	4.3	12.4	24.5	

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

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

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

Coal samples	H ₂ O addition	Reaction solvent	CO	CO ₂	C ₁ -C ₄	Oil	Asphal.	Preasp.	Conversion
	after drying				dnmf	wt%			dnmf wt%
Vacuum-dried, 100°C, 2 h	no	none	0.2	4.5	0.2	2.1	2.6	4.5	12.5
Vacuum-dried, 100°C, 2 h	yes	none	0.1	8.2	0.3	5.4	1.9	7.7	22.3
Fresh raw coal	Orig. Moist.	none	0.4	8.9	0.2	5.4	2.8	9.1	25.0
Vacuum-dried, 100°C, 2 h	no	Tetralin	0.2	4.1	0.2	4.1	7.6	10.0	25.9
Vacuum-dried, 100°C, 2 h	yes	Tetralin	0.1	6.9	0.2	14.5	9.2	10.2	39.9
Fresh raw coal	Orig. Moist.	Tetralin	0.1	7.4	0.2	15.8	9.3	12.4	43.3

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

Coal samples	Prewetting with H ₂ O	Reaction solvent	CO	CO ₂	C ₁ -C ₄	Oil	Asphal.	Preasp.	Conversion
					dmnf wt%				dmnf wt%
Vacuum-dried, 100°C, 2 h	no	none	0.2	2.3	0.3	10.0	5.4	11.4	29.8
Vacuum-dried, 100°C, 2 h	yes ^a	none	0.4	5.6	0.5	16.7	4.2	9.0	34.1
Vacuum-dried, 100°C, 2 h	yes ^b	none	0.3	4.7	0.4	14.0	7.9	8.7	35.0
Fresh raw coal	Orig. Moist.	none	0.3	4.1	0.5	16.9	9.2	14.9	43.3
Vacuum-dried, 100°C, 2 h	no	Tetralin	0.1	2.6	0.4	10.2	12.9	10.6	36.4
Vacuum-dried, 100°C, 2 h	yes ^a	Tetralin	0.1	4.3	0.3	18.4	11.5	11.5	44.6
Fresh raw coal	Orig. Moist.	Tetralin	0.1	4.5	0.4	16.0	11.5	11.9	42.2

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

Table V. Conversion and yield of non-catalytic reactions

Expt.#	Description	Conv.	Gas	Oil	Asph.	Preasph.
317	250C, NC, NS	11.7	1.9	8.2	0.8	0.8
318	250C, NC, TE	13.3	0.6	6.0	3.7	3.1
319	250C, NC, MN	11.9	2.8	5.6	2.4	1.2
335	300C, NC, NS	16.2	3.5	7.9	0.9	3.9
336	300C, NC, TE	17.5	3.5	9.8	3.5	4.0
337	300C, NC, MN	22.2	3.5	10.2	2.0	6.5
320	350C, NC, NS	19.1	6.5	7.4	1.2	4.1
307	350C, NC, TE	38.2	4.4	18.2	8.3	7.4
309	350C, NC, MN	33.8	5.0	14.8	7.4	6.7
331	400C, NC, NS	45.0	11.6	19.8	3.4	10.2
332	400C, NC, TE	82.0	9.5	36.7	16.6	19.2
334	400C, NC, MN	55.5	9.7	24.4	10.4	11.0
349	450C, NC, NS	51.5	17.6	28.8	0.9	4.2
350	450C, NC, TE	92.2	19.2	49.0	8.4	15.6
351	450C, NC, MN	57.0	16.3	31.8	4.3	4.6

Table VI. Conversion and yield of catalytic reactions

Expt. #	Description	Conv.	Gas	Oil	Asph.	Preasph.
322	250C, ATTM, NS	5.0	0.9	0.0	3.1	3.8
323	250C, ATTM, TE	3.8	0.9	0.0	2.3	1.7
324	250C, ATTM, MN	3.6	0.6	6.0	2.3	2.5
338	300C, ATTM, NS	17.2	2.5	9.3	1.8	3.6
339	300C, ATTM, TE	22.0	0.9	12.4	5.5	3.2
340	300C, ATTM, MN	22.9	2.4	10.2	6.0	4.3
325	350C, ATTM, NS	39.4	4.0	23.2	6.2	6.0
326	350C, ATTM, TE	46.6	3.7	23.9	11.4	7.6
327	350C, ATTM, MN	44.0	3.4	18.5	9.9	12.2
328	400C, ATTM, NS	95.5	7.4	58.9	24.0	5.2
329	400C, ATTM, TE	92.0	6.8	44.3	19.3	21.6
330	400C, ATTM, MN	84.8	8.1	41.6	16.4	18.7
352	450C, ATTM, NS	69.4	18.0	44.6	5.2	1.6
353	450C, ATTM, TE	95.8	14.2	66.1	10.4	5.1
354	450C, ATTM, MN	67.2	16.1	37.4	8.4	5.3

Figure 1. Effects of predrying Wyodak subbituminous coal on consumption of gas-phase H₂ and on net hydrogen transfer from tetralin during its liquefaction at 350 °C with 6.9 MPa H₂ (cold).

Figure 2. Gas yield of all liquefaction experiments

Figure 3. NMR spectra of residues from non-catalytic reactions with tetralin

Figure 4: Aromaticity of residues from all experiments as a function of conversion a, b, c, aromaticities of catalytic reaction at 450°C with 1-MN, no solvent and tetralin respectively; d, e, aromaticities of residue from non-catalytic reactions with tetralin at 400°C and 450°C.

Figure 5. Reacted aliphatic carbon as a function of temperature

Figure 6 Reacted aromatic carbon as a function of temperature

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