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

**Technical Progress Report
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ABSTRACT

This quarterly report consists of two parts. The first part is a selective review of our project work on the effects of a dispersed molybdenum sulfide catalyst and solvents on the liquefaction reactions and structural changes of three low-rank coals. The second part is a report on the synergistic effect between water and a dispersed molybdenum sulfide catalyst for conversion of Wyodak subbituminous coal.

From an extensive experimental study on three low-rank (DECS-1, DECS-9, DECS-11) coals, the following conclusions can be drawn. 1) The existence of moisture in coals does not appear to affect coal conversions in non-catalytic liquefaction at 400°C for 30 min in the absence of solvent. However, it does affect the production of gases. 2) Using a mixture of H₂O/THF as the impregnation solvent for dispersing ammonium tetrathiomolybdate (catalyst precursor) onto coal is more beneficial in achieving a high conversion. The catalyst impregnation techniques applied here (swelling, incipient wetness and slurring) have a mild influence on coal conversions. 3) The conversion from coal to THF solubles is a fast process while that from THF solubles to oil is a relatively slow one at 400°C. Therefore, in order to achieve the maximum conversion, 30 minutes is enough as reaction time; while to achieve a high oil yield, a longer time is needed. 4) Among the effects of catalyst, solvent, temperature conditions and impregnation methods, the first and the second are the most significant ones, while the later two are much less stronger. 5) Gas yields, including hydrocarbons and CO_x, are influenced mainly by reaction temperature, while the yields of hydrocarbon gases are strongly affected by donor solvents and the catalyst. 6) The study of oil with GC shows that the catalyst and/or the donor solvent are essential in order to "move" aromatic fractions from a coal to oil. 7) Studies of residues with solid-state NMR suggest that the removal of aliphatic carbons from coals can be done simply by raising reaction temperature to a certain level, e. g. 400°C for the DECS-1 coal; however the removal of aromatic carbons highly depends on the nature of coals, reaction temperature, a donor solvent and a catalyst.

We have also observed the strong synergistic effect between water and a dispersed molybdenum sulfide catalyst for promoting low-severity liquefaction of Wyodak subbituminous coal (DECS-8). Briefly, we found that addition of water to the catalytic run (water/coal = 0.46 wt ratio) can double the coal conversion at 350°C for 30 min under 6.9 MPa H₂, from 29-30 to 66-67 wt% (dmmf). This finding may offer new opportunities for developing novel low-severity liquefaction processes. Such a synergistic effect may be incorporated into liquefaction process either in the pretreatment step or in the first-stage of a two- or multi-stage liquefaction process.

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 hydrolyrolysis processes.

TECHNICAL PROGRESS

1. Effects of Catalysts and Reaction Solvents on Liquefaction Conversion and Structural Changes of Low-Rank Coals

INTRODUCTION

The objectives of this part of the project are to study the behavior of low-rank coals in liquefaction in the presence of a catalyst or a solvent, and to correlate the liquefaction results with the structural changes of the coals. Reaction conditions, such as temperature-programmed, temperature-staged and single-staged, are compared.

It has been two-and-one-half years since we started this work and now it is coming to an end. We feel that it is a good time for us to look back and summarize what have been done and what else should be done in the last several months. A flow chart given in Scheme 1 shows our major activities of research. In this study, three low-rank coals are involved. They are DECS-1 (Texas Big Brown subbituminous), DECS-9 (Montana subbituminous) and DECS-11 (North Dakota lignite). In order to establish a general background, the properties of these three coals were first studied. Some disputable issues, such as whether the coals should be dried before reactions, how much time is proper for maximum conversions and whether the catalyst impregnation techniques affect coal conversion, were clarified. The three main branches of this work were the study on temperature condition, solvent effect and catalyst effect. For each reaction, the products were separated and classified as gas, oil, asphaltene and preasphaltene. Gas samples were analyzed using headspace gas chromatograph for their composition and for calculating hydrogen gas consumption. The oil samples were analyzed by capillary gas chromatograph and gas chromatograph/mass spectroscopy for their composition as well as for calculating hydrogen consumption from the donor solvent when a donor solvent was involved. Asphaltene and preasphaltenes were studied by solid state ^{13}C NMR and FTIR. Lastly, the reaction residues were studied by using ^{13}C NMR, pyrolysis gas chromatograph/mass spectroscopy (Py-GC/MS), as well as FTIR in an effort to determine aromaticities of the residues, the net changes in aromatic carbons and aliphatic carbons, and also to compare the changes in functional groups before and after reactions.

Part I. COAL PROPERTIES

Information about these three project coals can be obtained from Penn State Coal Sample Bank and they are listed in Table 1.1. All three coals contain about 75% carbon, 5% hydrogen. The DECS-1 and DECS-9 coals contain about 15% oxygen while the DECS-11 coal contains relatively more oxygen, about 20%. From these data, it is obvious that all these coals have high contents of moisture. Therefore it is pertinent to investigate whether or not the moisture should be removed before reactions. Solid State ^{13}C NMR was used to study the dried coal samples, Figure 1.1. The two major peaks at 130 ppm and 30 ppm indicates aromatic carbons and aliphatic $-\text{CH}_2-$ groups. The two left shoulders of the aromatic peak are due to catechols (143 ppm) and phenols (153 ppm). While the two broad and relatively weak peaks at 183 ppm and 211 ppm are due to carboxyl and carbonyl groups, respectively. Aromaticities of these coals can be calculated by integrating the area covered by aromatic carbons and the one covered by all carbons. From the calculated aromaticities it is important to notice that the DECS-1 coal contains the most long chain aliphatic carbons followed by the DECS-9 and DECS-11 coals, though from the early data, all three coals have very close carbon contents. FTIR spectra in Figure 1.2 and py-GC/MS chromatograms, Figure 1.3, suggest the same conclusion that the DECS-1 coal contains more long-chain aliphatic carbons and the DECS-11 coal contains the least. These findings will later be used to explain some different behaviors of these three coals during liquefaction reactions.

In addition, it should be noted that the aromaticity of the DECS-9 coal sample used in the present work (0.53) is lower than that measured for a different batch of DECS-9 coal sample in an earlier work on NMR analysis of raw (0.63) and THF-extracted DECS-9 coal (0.64), as described in the third quarterly report (TPR-3 for this project, August 1992). The comparison of pyrolysis-GC-MS profiles revealed the same trend that the DECS-9 sample used in the present work has lower aromaticity than the DECS-9 sample used in our earlier work (TPR-3 for this project, August 1992).

Part II. PREPARATION KNOWLEDGE

In this part, experiments were done in an effort to clarify some disputes. It will be determined whether we should dry the coals before any reaction, what is the proper reaction time for low-rank coals and what is the best catalyst impregnation methods.

Before getting into the discussion of experimental results, it is necessary to illustrate the product separation procedure and define the termination often used in later discussions. In Figure 2.1, the flow diagram shows that the reactor was first vented and the gas sample was collected. The solid and liquid samples were extracted by hexane, toluene and THF sequentially. The extracts are named as oil, asphaltene and preasphaltene respectively. The THF-insolubles are called residues. Conversions are calculated based on the THF-insolubles.

2.1 Moisture Effect

Liquefaction experiments on raw and dried coals for all these samples were done in order to determine moisture effect on coal conversions. For keeping this summary in a reasonable length, only one of the three coals was used as an example in this and later sections, unless the three coals behave differently. Figure 2.2 presents the comparison of the liquefaction of the raw and dried coals of DECS-11 at 400°C with no solvent and no catalyst. It suggests that at this temperature, moisture does not have a significant influence on conversion with no solvent no catalyst, comparing the 29.9% for the raw coal and 30.8% for the dried coal. However, moisture seems to have effect on the gas and oil yields. The liquefaction of the raw coal tends to give higher yield of gas while lower yield of oil than the liquefaction of the dried coal. Therefore, we decided to dry the coals before any reaction in later work.

2.2 Reaction Time

Low-rank coals contains large amount of heteroatoms such as oxygen, nitrogen and sulfur. Their structures are characterized by small aromatic rings connected by long chain aliphatics. This kind of structure feature tends to be broken down easily and quickly at low temperatures. Hence it is important to determine the proper reaction time and reaction temperature. In this section, reaction time will be studied and reaction temperatures will be targeted in later sections. Figure 2.3 shows the reaction of the DECS-1 coal at 400°C with ATTm as the catalyst precursor and with no solvent. Reaction times were 10 minutes, 30 minutes and 60 minutes. The total conversion and the oil yield increased slightly as reaction time increased from 10 minutes to 30 minutes but dropped about 10% units while the reaction time further increased to 60 minutes. The only increase when the reaction time was extended to 60 minutes was the gas yield. While in the presence of tetralin, in Figure 2.4, 10 minutes seem to be not enough to reach the maximum conversion the maximum oil yield. Furthermore, different from that without the presence of

tetralin, the extension of reaction time to 60 minutes actually benefits the total conversion and oil yield. This indicates the differences of using and not using a donor solvent. Firstly, in the presence of a solvent, a time period must be allowed to let the H_2 gas to penetrate and reach reaction sites. Secondly, in the presence of a donor solvent, recombination of small molecules to larger ones in a long reaction time can be prevented, and actually, when time goes on, asphaltenes and preasphaltenes will be further cracked down to oil which is the desired product. Comparing to the case without a solvent, the gas yield in this situation is lower. The conclusion of this set of experiments is that the proper reaction time is 30 minutes compromising reactions with and without a solvent.

2.3 Catalyst Impregnation Techniques

2.3.1 Study on Catalyst Impregnation Solvents

H_2O and a mixture of H_2O/THF were used to dissolve the catalyst precursor, ATTM, and it is found that the H_2O/THF mixture is more beneficial in achieving high conversion in both temperature-programmed (TPL) and single-staged (SSL) reactions, Figure 2.5.

2.3.2 Study on Catalyst Impregnation Methods

Three impregnation methods were investigated. They are swelling, incipient wetness and slurrying.

In temperature-programmed liquefaction, there is no significant difference in conversion caused by the three methods, Figure 2.6. There are two possibilities:

- 1) During the low-temperature pretreatment, the catalyst (precursor) particles mobilized on the coal surface and formed a uniform distribution. Therefore, even there was difference in dispersion initially, the difference would be eliminated during reaction.
- 2) TPL is an excellent reaction condition and it plays a much more significant role in improving conversion than catalyst dispersion. So any difference in dispersion caused by different impregnation methods will be "covered" under this condition.

Therefore we decided to lower the reaction severity to make the difference in dispersion more obvious, that is to carry out the reaction under single-staged reaction conditions. However,

even in single-staged liquefaction, Figure 2.7, the impregnation methods applied here do not play a significant role in improving conversion. This may be because:

1) The three methods do not lead to any differences in dispersion, and even they do initially, the catalyst precursor particles and coal surface (both internal and external) are loosely bonded, and these weak bonds can be easily broken during drying. Therefore, those catalyst precursor particles initially deposited inside pored would be "dragged" out and the final dispersion (after drying) is the same.

2) The difference in dispersion caused by the three methods are so trivial and furthermore they have such small influence on conversion under the reaction conditions applied that they can just be neglected.

3) There are differences in dispersion by using three methods, but during liquefaction reactions, the catalyst or catalyst precursor particles mobilize on the coal surface thus eliminate the differences.

After performing this set of experiments, a conclusion can be drawn that the catalyst impregnation techniques applied here do not play a significant role. Considering the time and labor required for each technique, we decide to use the most simple and convenient method, that is the solvent slurring in our later work.

Part III. STUDY ON TEMPERATURE CONDITIONS

The so-called temperature conditions refer to the temperature-programmed liquefaction (TPL), temperature-staged liquefaction (TSL) and single-staged liquefaction (SSL). In Figure 3.1, these three conditions are demonstrated. In a single-stage reaction, the reactants are directly heated to a desired temperature, such as 400°C in many cases, in a very short time, usually in three minutes, and kept at that temperature for 30 minutes followed by rapid cooling. In a temperature-programmed and a temperature-staged reaction, there are two temperature stages. The lower one is usually at 200°C and the higher one is at 400°C. Some other temperatures were also tested but not shown here. The time period at the lower stage is 15 minutes and that at the higher stage is 30 minutes. The difference between the two conditions is that in temperature-programmed reaction, there is a slow heating period which lasts about 30 minutes. The reason to conduct reactions under temperature-programmed and temperature-staged condition is to slow down the rate of cracking, or in other words, the rate of free radical formation, and to match the rate of hydrogenation of those free radicals.

In Figure 3.2, the three reaction conditions are compared using the DECS-9 coal. With the presence of ATTM and WIMD (Wilsonville middle distillate), the temperature-programmed and staged conditions have slight beneficial effect in gaining high conversions and oil yields. An other comparison was done with the DECS-1 coal in Figure 3.3. The first group indicates reactions with no solvent and no catalyst at 400°C, and the second group indicates reactions with no solvent but with ATTM. In both cases, the temperature conditions do not play a significant role, comparing to which the catalyst is much more important for high conversions and oil yields. Therefore our conclusion is that the temperature conditions have impact on conversions but compared to the impact of the catalyst or the solvent, they are not significant.

Part IV. EFFECTS OF CATALYST AND SOLVENT

The catalysts or catalyst precursor employed here are nickel acetate, ammonium tetrathiomolybdate (ATTM) and molybdenum naphthanate. In this summary, the effect of ATTM will be emphasized. In the study of solvent effect, four kind situations were considered. The first is the reactions without using any solvent. The second is to use a hydrogen non-donor or poor donor solvent, such as decalin and 1-methylnaphthalene. The third is to use a donor solvent, such as tetralin. The last one is to use a liquefaction process solvent, such as Wilsonville middle distillate (WIMD).

Figure 4.1 shows the effect of solvent on liquefaction of the DECS-1 coal without the presence of any catalyst. The first group are the single-staged reactions at 350°C. The data suggest that even at this temperature, the effect of solvent is significant. For instance, by using the donor solvent, tetralin, the total conversion was increased more than 15% units. The second group are the 200°C/400°C temperature-programmed reactions. Under this conditions, the effect of solvent is more significant. Using the non-donor solvent can increase the conversion by more than 10% units, while using the liquefaction process solvent and the donor solvent can have additional 20% to 30% units increase comparing with those of using a non-donor solvent. Therefore it is obvious that without the presence of a catalyst, the use of a solvent and the type of the solvent is very important, especially at high temperatures.

In Figure 4.2, the effects of solvent on the DECS-1 coal with and without the presence of ATTM are compared. In the presence of the catalyst, the effect of solvent was diminished under temperature-programmed condition. To further test this observation, experiments on the DECS-9 coal were also done at 400°C under single-stage condition with and without the catalyst using

different solvents. Again, we see that without the catalyst, the order of conversion is tetralin>WIMD>1-MN>no solvent, suggesting the necessity of using a good solvent. However, in the presence of the catalyst, the advantages of using a donor solvent are not as manifest as those in the non-catalytic reactions. The catalytic reactions all have conversions in upper 80% or low 90%.

In the next two sets of experiments, liquefaction reactions were carried out at temperatures from 250°C to 450°C with different solvents in the presence and absence of the catalyst. The results of liquefaction without catalyst are shown in Figure 4.4. 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. As the temperature increases to 300°C, the solvents start showing their advantage by providing slightly higher conversions than the reaction without solvent. At 350°C, there is a remarkable increase in oil, asphaltene and preasphaltene yields when a solvent is used. This indicates that in this temperature range, the solvents play a role which enhances the conversion, but since there is no difference between the reaction with tetralin and the reaction with 1-MN, this role may not relate to hydrogen donation. In the temperature range from 350°C to 400°C, there is a drastic increase in conversion no matter whether a solvent is applied or not, suggesting that at this temperature range, thermal energy is enough to break down the coal macromolecular matrix. At 400°C, tetralin made a tremendous difference from 1-MN and no solvent. The conversion reaches 82.0%, composed of gas, 9.5%; oil, 36.7%; asphaltene, 16.6%; and preasphaltene, 19.2%. With 1-MN or without solvent, the conversions are much less, 55.5% and 45.0% respectively. The differences of conversion and product distribution imply that tetralin is active in donating hydrogen at temperatures higher than 350°C. 1-MN, on the other hand, shows a very slight advantage over no solvent in gaining higher conversion and oil yield, but as temperature increases to 450°C, this advantage almost disappears.

The results of catalytic liquefaction are presented in Figure 4.5. In the presence of ATTM, the conversion of all experiments increase drastically as the temperature increases from 250°C to 400°C. Comparing the reactions with no solvent, tetralin or 1-MN with the corresponding non-catalytic reactions, the catalyst increased the conversion, especially at temperatures higher than 300°C, suggesting that ATTM was converted to an active catalyst at temperature between 300°C and 350°C. Furthermore, the product distribution shows that the increasing conversion is accompanied by an increasing yield of light materials, such as oil, when the catalyst is added. The other comparison is among the 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 higher oil yield). In this temperature range, the catalyst has a stronger effect than the solvents; thus any difference caused by the solvents is

diminished. However, at 450°C, tetralin gave a slightly higher conversion while both 1-MN and no solvent actually gave a much lower conversion (almost 20 percentage units lower) relative to those at 400°C. In the case of 1-MN at 450°C, the yields of gas, asphaltene and preasphaltene are still very similar to those in tetralin, while the conversion is much lower. The sole cause of this conversion difference is the decrease of the oil yield. With tetralin at 450°C, yields of asphaltene and preasphaltene dropped by 9 percentage units and 17 percentage units respectively, while the yield of oil increased by 22 percentage units compared with that at 400°C. This suggests that at this temperature (450°C), in the presence of both catalyst and a H-donor solvent, the conversion from preasphaltene and asphaltene to oil, or from heavy products to light products, is favorable. With the presence of the catalyst but absence of a donor solvent (meaning with no solvent or a non-donor solvent), the conversion drops as well as all of the product yields, except gas, suggesting that retrogressive reactions take place and form heavier and more stable materials.

The conclusion of this section is that both the catalyst and the solvent have strong influence on the conversion and they are compatible. However, the effects of the catalyst and the solvent are not synergetic. At temperature 400°C or lower, using one of them is sufficient to achieve a high conversion, while at temperature higher than that, a donor solvent is crucial to prevent retrogressive reactions.

Part V. STUDIES ON LIQUEFACTION PRODUCTS

5.1 Gas Analysis

The total gas yields of the DECS-1 coal under six different reaction conditions are presented in Figure 5.1. Regardless the use of a solvent or a catalyst, the gas yield is a function of temperature. Furthermore, compositions of the gases can be analyzed by using gas chromatograph. Figure 5.2 shows the hydrocarbon gases produced in the liquefaction of the DECS-9 coal. Besides the fact that we have already seen in the early figure that the gas yields increase with temperature, some solvent and catalytic effects can be observed in this figure. Comparing the reactions with and without the catalyst, the ones with the catalyst always produce higher amounts of hydrocarbons. While comparing the reactions with different solvents, we see that the reactions with the donor solvent, tetralin, always produce more hydrocarbons than those with 1-MN or with no solvent. The CO₂ and CO yields were also analyzed and presented in Figure 5.3 and Figure 5.4. As temperature increases, the yields of CO₂ increases which is a sign of retrogressive reactions. It can be seen that the only way to reduce the CO₂ yield at 450°C is to

use the donor solvent in the reaction. The CO yields appear to be quite different from those of CO₂ especially at 450°C. With the presence of the catalyst, the CO yields drastically dropped, indicating that Fisher-Tropic reactions took place under the influence of the catalyst.

Hydrogen consumptions from the gas-phase H₂ and the donor solvent were demonstrated in Figure 5.5-5.7. In Figure 5.5, the H₂ consumption from six types of reactions involving different solvent, with or without the catalyst. It suggests that only at 450°C, significant amounts of H₂ were consumed in the non-catalytic cases. While with the presence of the catalyst, hydrogenation reactions by H₂ were promoted even at temperatures as low as 300°C, strongly suggesting that the ATTM-derived catalyst is an effective hydrogenation catalyst. A comparison of the consumptions from H₂ and that from tetralin without the catalyst is made in Figure 5.6. At all temperatures, they appear to be very close, which explains that in the reactions with tetralin, there is actually twice as much hydrogen consumed by the coal and this is why that the non-catalytic reactions with tetralin yield much higher conversions than those with no solvent or with 1-MN. However, in the presence of the catalyst, it is quite different. The consumption from the H₂ is much more significant than that from tetralin at temperature of 400°C and lower. This explains what we see in Figure 4.5 that the solvent does not play a key role in achieving a high conversion in catalytic reactions. While at 450°C, the consumption from H₂ drops while that from tetralin increases. The result is that the hydrogen consumption from tetralin can no longer be neglected compared to that from H₂. Actually, the "extra" hydrogen from tetralin is the key factor to prevent retrogressive reactions at this temperature.

5.2 Oil Analysis

The oils were analyzed by gas chromatography, identified by gas chromatography/mass spectrometry. Figure 5.8 represents the oils from the DECS-9 coal without the catalyst or the donor solvent, *a*; with the catalyst but not the donor solvent, *b*; and with both the catalyst and the donor solvent, *c*. In Figure 5.8*a*, the oil contains a high proportion of long-chain alkanes, i. e. from n-C₁₂ to n-C₃₃. At retention time of about 6.0 minutes, there is a very strong peak identified as toluene. In low-rank coals such as DECS-9, small aromatic clusters dominate, and they are connected by aliphatic crosslinks. Once the crosslinks break, these small aromatic clusters will be released. In the DECS-9, one-ring structural units are abundant and thus when liquefying the coal, toluene (instead of benzene) will be a major product, because the benzylic C-C bond has a much lower dissociation energy than the phenyl C-C bond. Relative to those of aliphatics, the amounts of aromatic compounds in the oil (with retention times from 15 minutes to 30 minutes) are much smaller (Figure 5.8*a*), indicating that this reaction condition suppresses the production of aromatic

compounds in the oil. Comparing with the case without the catalyst or the donor solvent, adding ATTM into the reaction system appears to favor the yields of aromatic compounds. As shown in Figure 5.8b, the alkylbenzenes, phenol and alkylphenols are the major components in the oil. This observation agrees with our earlier finding that the catalyst is particularly beneficial in converting the aromatic carbons from the coal to THF solubles rather than converting the aliphatic carbons. Furthermore, when we use tetralin in addition to the catalyst, the yields of phenolic compounds remain very high, Figure 5c; the one-ring aromatics seem to be in a lower proportion; and the yields of two-ring aromatics, such as indane, alkylindanes and alkylnaphthalenes have increased. The large peaks at retention times about 24.5 minutes and 27.0 minutes are due to tetralin and naphthalene, the solvent and the dehydrogenated solvent. It is likely that the increased yields of alkylindanes and alkylnaphthalenes are due, at least in part, to the use of tetralin. In the GC study, three- or four-ring compounds appear to be in small amounts and not affected by either the catalyst nor the solvent. This may be because they are less abundant than the one- or two-rings in the coal, or because their solubilities in hexane are smaller and therefore it is hard to detect the differences at different cases.

5.3 Studies on Reaction Residues by Solid State ^{13}C NMR

Reaction residues were characterized by ^{13}C NMR using CPMAS technique. Sample spectra of the residues from the DECS-1 coals without a solvent or a catalyst are shown in Figure 5.9. The spectra were curve-fitted using LabCalc program and the area of each peak was integrated. In order to determine the influence of the catalyst on the aromaticities, all the data are plotted versus conversion in Figure 5.10. A general trend is that the aromaticities of residues increase with conversion, but the data fall into two separate sets: those from reactions with and without the catalyst, regardless of the solvent used. Generally, f_a of the residue from a catalytic reaction is lower than that from a non-catalytic reaction, and the difference between the two increases with increasing conversion. At the most severe conditions, 450°C with the catalyst, the aromaticities deviate from the line of catalytic reaction. The higher aromaticities are caused by more aromatic carbon, which indicates the retrogressive reactions at this temperature. In non-catalytic reactions, the use of tetralin at 400°C and 450°C results in lower aromaticities, suggesting that tetralin helps to convert aromatic carbons from coal to THF solubles.

To achieve a general idea on what kinds of structure have been converted to THF solubles, or what kinds of reactions are actually catalyzed by the catalyst during the liquefaction, the percentages of aliphatic and aromatic carbon that have been reacted are calculated from the

amounts of dry, mineral-matter-free coal charged, aromaticity of the dried coal, the conversions, and the aromaticities of the residues.

In Figure 5.11, the extent of reacted aliphatic carbon is shown as a function of temperature. At each temperature, the lowest point always corresponds to the reactions with no solvent and no catalyst. As expected, these reactions with the worst liquefaction conditions result in the lowest conversion of aliphatic carbon. Comparing the effects of the solvents, the catalyst and temperature, the latter is shown to be the most significant by the fact that highest conversion of aliphatic carbon at one temperature is always lower than the lowest conversion at the next temperature (except that between 400°C and 450°C). Roughly speaking, all the points stay on one curve, regardless of the use of solvent or catalyst. The amount of reacted aliphatic carbon increases nearly linearly when the temperature increases, up to 400°C. At 400°C, about 90% of the aliphatic carbon has been converted to THF solubles. When 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 mainly of temperature, neither solvent nor catalyst has any influence on it.

In Figure 5.12a and 5.12b, the amount of aromatic carbon converted to THF solubles is plotted versus the temperature. Unlike those in Figure 11, the data are much more scattered in Figure 5.12a and b. In non-catalytic liquefaction reactions, tetralin made a remarkable difference from 1-MN and no solvent. When the temperature was 350°C or higher, much more of the aromatic carbon reacted in the presence of tetralin. At 450°C, the conversion of aromatics reached 86% with tetralin, while it only reached 15% and 10% with 1-MN and without solvent respectively. In catalytic liquefaction reactions, the difference caused by the solvents is diminished when the temperature increases to 400°C, indicating that the catalyst is sufficiently active in converting the aromatics into THF solubles and that solvent is no longer a major determining factor. However, when the temperature increased to 450°C, with the presence of the catalyst, reactions with 1-MN or without a solvent have a large decrease from 77% to 36% and from 93% to 42% respectively, while that with tetralin increased from 87% to 92%. At temperature as high as 450°C, the thermal cracking of the coal matrix is very fast, and the hydrogenation from the gaseous H₂ catalyzed by the added catalyst is no longer able to catch up. Therefore at 450°C in the presence of the catalyst, tetralin is no longer a minor factor. In fact, the only way to prevent the retrogressive reaction is to have a donor solvent, such as tetralin.

The study of reacted aliphatic and aromatic carbon helps to explain why a non-catalytic reaction always produces residues with higher aromaticity than a catalytic reaction even though the conversion can be the same. In the former case, the conversion is achieved by having more aliphatic carbon reacted and in the latter case, it is achieved by having a greater proportion of aromatic carbon reacted.

Figure 5.13 and 5.14 present the effect of the catalyst and tetralin on the removals of aliphatic and aromatic carbons on the three coals. In these figures, it is apparent that converting aliphatic carbons from the coal networks to THF solubles is much easier than converting aromatic carbons. At 400°C, even without catalyst or solvent, over 50% of aliphatic carbons are converted for all three coals. Adding the catalyst can increase the aliphatic conversions to greater extents. Furthermore, if tetralin is used in addition to the catalyst, slight increases in the aliphatic carbon conversions of DECS-9 and DECS-11 are observed, while that of DECS-1 shows almost no change, which is expected because even only with the catalyst, the conversion approaches 100%. Comparing these three coals, the aliphatic carbons in DECS-1 are the easiest to be converted; those in DECS-11 are the least. In Figure 5.14, the aromatic carbons appear to be more difficult to be removed from the coal networks, and they are affected more strongly by the catalyst or the donor solvent than the aliphatic carbons. Without the presence of the catalyst or the donor solvent, less than 20% can be converted. For the DECS-9 coal, the conversion is negative, meaning that there are more aromatic carbons than we start with. This indicates the occurrence of retrogressive reactions. Therefore, to convert the aromatic carbons, it is crucial to use the catalyst, the donor solvent or both. For the DECS-1 coal, the catalyst is sufficient to achieve over 95% aromatic conversion; for the DECS-9 coal, with both the catalyst and the donor solvent, 98% can be obtained; while for the DECS-11 coal, the least convertible coal in terms of conversion, even with both the catalyst and the donor solvent, only about 70% aromatic conversion can be achieved.

CONCLUSIONS

- 1). The existence of moisture in coals does not appear to affect coal conversions in non-catalytic liquefaction at 400°C for 30 min in the absence of solvent. However, it does affect the production of gases.
- 2). Using a mixture of H₂O/THF as the impregnation solvent is more beneficial in achieving a high conversion. The catalyst impregnation techniques applied here (swelling, incipient wetness and slurring) have a mild influence on coal conversions.

- 3). The conversion from coal to THF solubles is a fast process while that from THF solubles to oil is a relatively slow one. Therefore, in order to achieve the maximum conversion, 30 minutes is enough as reaction time; while to achieve a high oil yield, a longer time is needed.
- 4). Among the effects of catalyst, solvent, temperature conditions and impregnation methods, the first and the second are the most significant ones, while the later two are much less stronger, as can be seen from Figure 5.15.
- 5). Gas yields, including hydrocarbons and CO_x , are influenced only by reaction temperature, while the yields of hydrocarbon gases are strongly affected by donor solvents and the catalyst.
- 6). The study of oil with GC shows that the catalyst and/or the donor solvent are essential in order to "move" aromatic fractions from a coal to oil.
- 7). Studies of residues with solid-state NMR suggest that the removal of aliphatic carbons from coals can be done simply by raising reaction temperature to a certain level, e. g. 400°C for the DECS-1 coal; however the removal of aromatic carbons highly depends on the nature of coals, reaction temperature, a donor solvent and a catalyst.

2. Strong Synergistic Effect between Dispersed Mo Catalyst and H_2O for Low-Severity Coal Hydroliquefaction

Introduction

For coal hydroliquefaction using dispersed catalysts, drying after impregnation of catalyst or precursor salt has been a common procedure since 1950s [Weller and Pelipetz, 1951; Nomura et al., 1982; Derbyshire et al., 1986a, 1986b; Song et al., 1986, 1991; Garcia and Schobert, 1989; Huang et al., 1992, 1993; Artok et al., 1993; Burgess and Schobert, 1993; Serio et al., 1993; Weller, 1994]. The historical development and advantages of dispersed catalysts for direct coal liquefaction have been reviewed by Weller [1982, 1994], and by Derbyshire [1988, 1990]. It is well known that water or steam deactivates hydrotreating catalysts, such as Mo-based catalysts, under conventional process conditions, and several groups have reported on the negative impacts of water on catalytic hydroliquefaction [Bockrath et al., 1986; Ruether et al., 1987; Kamiya et al., 1988]. The motivation of our study comes from several interesting findings in our recent

work on the influence of drying and oxidation of Wyodak subbituminous coal on its low-severity catalytic liquefaction at 350°C [Song et al., 1994].

In this section, we will report on the strong synergistic effect between water and a dispersed molybdenum sulfide catalyst for promoting low-severity liquefaction of Wyodak subbituminous coal. Briefly, we found that addition of water to the catalytic run (water/coal = 0.46 wt ratio) can double the coal conversion at 350°C for 30 min under 6.9 MPa H₂, from 29-30 to 66-67 wt% (dmmf). This finding may offer new opportunities for developing novel low-severity liquefaction processes. Such a low-severity reaction can be incorporated into liquefaction process either as a pretreatment step or as the first-stage of a two- or multi-stage liquefaction process.

Experimental

A Wyodak subbituminous coal from DOE/Penn State Coal Sample Bank (DECS-8) was used. Detailed properties of the coal have been described elsewhere [Song et al., 1994]. Ammonium tetrathiomolybdate (ATTM) was dispersed as a catalyst precursor [Derbyshire et al., 1986b; Garcia and Schobert, 1989; Artok et al., 1993] on to coal (1 wt% Mo on dmmf basis) by incipient wetness impregnation from its aqueous solution. The impregnated or the raw coal samples were dried in a vacuum oven at 100 °C for 2 h before use. For the experiments with added water, the weight ratio of water to dmmf coal was kept at 0.46. Liquefaction was carried out in 25 mL tubing bomb reactors at 350 or 400°C for 30 min under an initial H₂ pressure of 6.9 MPa. All the reactions were carried out without any organic solvents. The products were separated into gases, oil, asphaltene, and preasphaltene. The gaseous products were analyzed by GC. More experimental details may be found elsewhere [Song et al., 1993, 1994].

Results and Discussion

Figure 6.1 shows the effect of water addition on the liquefaction at 350°C. Relative to the non-catalytic run of the dried coal, the addition of water improved coal conversion from 14.5 to 22.5 wt% (dmmf). The use of ATTM increased the coal conversion from 14.5 to 29.8 wt%. On a percentage basis, the use of ATTM and the addition of water improved coal conversion by 106% $[(29.8-14.5)/14.5=1.06]$ and 55%, respectively. When a small amount of water was added to the catalytic reaction at 350°C, coal conversion increased dramatically to 66.5 wt%. This represents a 123% increase from the catalytic run without water, and 359% increase from the non-catalytic

run without water. We have confirmed these trends by several sets of experiments. These interesting findings reveal that dispersed molybdenum sulfide catalyst and added water can act in concert to promote coal liquefaction at relatively low temperature, 350°C.

Figure 6.2 indicates that the addition of water caused substantial increase in gas yields. This is manifested primarily by the increased CO₂ yield. CO yield decreased upon water addition, indicating the occurrence of water-gas-shift (WGS) reaction (eq. 1). According to the WGS reaction, the increased amount of CO₂ is 1.57 times the decreased amount of CO (MW ratio: 44/28 = 1.57). However, when water was added to the non-catalytic reaction of vacuum-dried coal, CO₂ yield increased from 4.5 to 8.3 wt% on a dmmf basis, whereas the CO yield decreased from 0.24 to 0.12 wt% (dmmf). Apparently, the enhanced CO₂ formation is due primarily to the addition of water, but not the well-known WGS reaction. A similar trend was observed in catalytic runs at 350°C (Figure 6.2). Probably the majority of increased CO₂ yield is due to chemical reactions between the water and the species in coal or coal products, such as the reaction between water and carbonyl (as shown by eq. 2) and carboxyl groups. Eq. 2 also appears to be consistent with Lewan's observation on CO₂ formation in hydrous pyrolysis [Lewan, 1992]. It is possible that part of the CO₂ is due to enhanced decarboxylation in the presence of H₂O, without causing retrogressive cross-linking [Saini et al., 1993; Serio et al., 1993]. This could partially rationalize the enhanced CO₂ formation together with increased coal conversion upon water addition.

Two-dimensional HPLC revealed that the oils from liquefaction with added water contain more phenolic compounds [Song and Saini, 1994], suggesting that water participates in the reaction leading to phenols (eq. 3). Supporting evidence for eq. 3. can also be found in the results of Townsend and Klein [1985] and Siskin et al. [1991] on hydrothermal reactions of dibenzylether with water at 374°C [Townsend and Klein, 1985] and diarylether with water at 315°C [Siskin et al., 1991b].

Figure 6.3 shows the effect of water on the thermal and catalytic liquefaction at 400°C. Compared to the runs at 350°C, the positive effect of water addition to the non-catalytic run becomes much less, but the positive impact of using ATTM becomes much more remarkable. The use of ATTM for reaction at 400°C afforded a high coal conversion, 85.4 wt% (dmmf), and a high oil yield, 45.8 wt%. However, addition of water to the catalytic run decreased coal conversion (to 62.1 wt%) and oil yield (to 28.2 wt%). This is in distinct contrast to the trends for corresponding runs at 350°C. We have performed several sets of experiments using different coal samples and confirmed this trend. An important implication from Figure 3 is that the presence of water in the catalytic run at 400°C decreased the catalytic activity level that can be achieved without water. In other words, water tends to passivate the dispersed catalyst at higher reaction temperatures (400, 30 min).

The most interesting finding from this work is the strong synergistic effect between water and dispersed Mo sulfide catalyst at 350°C under certain conditions. This finding is important both from fundamental and practical viewpoints. Bockrath et al. [1986] showed that using water as vehicle in the catalytic liquefaction of Illinois No.6 coal (water/coal = 2, wt ratio) at 350°C for 60 min gives much lower conversions than the runs using organic solvents. Ruether et al. [1987] examined the effect of water addition in catalytic liquefaction of Illinois No.6 coal (water/coal = 0.33-1.5, wt ratio) at 427°C for 1 h. In the runs using 0.1% dispersed Mo catalyst at 427 °C for 60 min, highest coal conversions were obtained without added water. They concluded that at fixed total pressure, the most reactive environment contains no added water, so that H₂ partial pressure is as high as possible. Mikita et al. [1988] reported on using water and non-donor vehicles for liquefaction of Illinois No.6 coal at 385°C for 30 min. Coal conversion in a non-catalytic run with SRC II solvent and a small amount of water (water/coal=1.7 g/4 g) was similar to a catalytic run with 0.1 wt% Mo and a larger amount of water (water/coal=3.4 g/4 g) (86-88 wt% vs 86-90 wt%). From these results they concluded that in the presence of Mo catalyst and water, it is not necessary to use hydrogen donor solvent. Kamiya et al. [1988] have observed that addition of water deactivates the iron catalyst for liquefaction of a brown coal at 400°C for 30 min and for upgrading of SRC from Wandoan coal (water/SRC = 0.1-0.2 wt ratio) at 450°C for 60 min. The negative influence of water was thought to arise from re-oxidation of the active iron sulfide catalyst.

While the origin of the above-mentioned strong synergism has not been clarified, the promoting effect of water on catalytic liquefaction at 350°C could be partially understood based on literature information on non-catalytic reactions. For non-catalytic coal conversion such as pyrolysis, liquefaction and co-processing, hydrothermal pretreatments of coal has been reported

to be beneficial in terms of increased conversion, or oil yield [Graff and Brandes, 1987; Bienkowski et al., 1987; Ross, 1992a, 1992b; Pollack et al., 1991; Serio et al., 1992a, 1992b; Tse et al., 1991]. Lewan [1992] suggested that water could act as a source of hydrogen and oxygen in petroleum formation by hydrous pyrolysis. Siskin et al. [1991] have suggested that the presence of water during coal pretreatment will facilitate depolymerization of the macromolecular structure to give an increased proportion of liquids by cleaving important thermally stable covalent cross-links in the coal structure. On the other hand, Tse et al. [1991] suggested that the pretreatments of low rank coals in the presence of water should minimize retrogressive reactions such as crosslink formation from phenolics and lead to higher conversion or a better quality product. Serio et al. [1993] indicated that the presence of water may mitigate retrogressive reactions caused by the cations present in the raw coal. Fundamental questions concerning the role of water in catalytic reaction and the reaction mechanisms involving water remain to be answered. Further work is now in progress.

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PLAN FOR FUTURE WORK

Since the project duration is three years and it is scheduled to terminate September 17, 1994, the remaining project time (July 1-September 17, 1994) will be devoted mainly to the summary of results, comprehensive evaluation of catalytic pretreatments, and the preparation of the final report.

Table 1.1 The Three Project Coal Samples

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

Scheme 1.

Figure 1.1 NMR spectra of dried coal samples

Figure 1.2 FTIR Spectra of Dried Coals

Figure 1.3

Pyrolysis GC/MS Chromatogram of Dried Coal Samples

Figure 2.1

**Figure 2.2 Effect of Moisture on Liquefaction of the DECS-11 Coal
(400°C, no Solvent, no catalyst)**

Figure 2.3 Effect of Reaction Time on DECS-1 (400°C, ATTM, no Solvent)

Figure 2.4 Effect of Reaction Time on DECS-1 Coal (400°C, ATTM, Tetr.)

Figure 2.5 Effect of Impregnation Solvent in SSL of DECS-9 (400°C)

Figure 2.6 Effect of Impregnation Methods on TPL(200/400°C) of DECS-11 with WIMD

Figure 2.7 Effect of Impregnation Methods on the DECS-1 Coal with 1-MN

Figure 3.1

Single-Staged Liquefaction

Temperature-Staged Liquefaction

Temperature-Programmed Liquefaction

**Figure 3.2 A Comparison of Liquefaction Conditions
(200/400°C, DECS-9, w/ ATTM, WIMD)**

Figure 3.3

A Comparison of Liquefaction Conditions (DECS-1, w/o solvent)

Figure 4.1 Solvent Effect on the DECS-1 Coal in SSL and TPL (w/o ATM)

Figure 4.2 Solvent Effect in TPL with or without the presence of ATT

Figure 4.3 Solvent Effect on the DECS-9 Coal (400°C, SSL)

Figure 4.4 Conversion of DECS-1 without ATTM

Figure 4.5 Conversions of DECS-1 with ATTM

Figure 5.1

Gas Yield of All Experiments of the DECS-1 Coal

Figure 5.2

Hydrocarbon Gases of DECS-9 Produced in Liquefaction

Figure 5.3

CO₂ Yields of DECS-9

Figure 5.4
CO Yields of DECS-9

Figure 5.5

Hydrogen Consumption from H₂

Figure 5.6

Hydrogen Consumption from H₂ and Tetralin-no ATTM

Figure 5.7

Hydrogen Consumption from H₂ & Tetr. - ATTM

Figure 5.9
NMR Spectra of DECS-1 Coal & Residues without Solven or Catalyst

Figure 5.10
Aromaticity of Residues from All Runs

Figure 5.11
Reacted Aliphatic Carbon in All DECS-1 Runs

Figure 5.12a
Reacted Aromatic Carbon with ATTM (DECS-1)

Figure 5.12b

Reacted Aromatic Carbon in non-Catalytic Runs (DECS-1)

Figure 5.13
Effects of ATTM and Tetralin on the Removal of Aliphatic Carbons

Figure 5.14

Effects of ATTM and Tetralin on the Removal of Aromatic Carbons

Figure 5.15

Effect of Catalyst, Solvent, temperature condition and impregnation methods

Figure 6.1. Effect of water on catalytic liquefaction of Wyodak coal at 350°C for 30 min.

Figure 6.2. Effect of water on gas formation in liquefaction of Wyodak coal at 350°C for 30 min.

Figure 6.3. Effect of water on catalytic liquefaction of Wyodak coal at 400°C for 30 min.

Appendix

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

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