

# USING WATER AND DISPERSED MoS<sub>2</sub> CATALYST FOR COAL CONVERSION INTO FUELS AND CHEMICALS

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## INTRODUCTION

The historical development and advantages of dispersed catalysts for direct coal liquefaction have been reviewed by Weller [1982, 1994], and by Derbyshire [1988, 1990]. Due to their intimate contact with the surface of coal particles, the use of dispersed catalysts facilitates the activation and transfer of hydrogen to coal-derived radicals or reactive fragments in the early stage of coal conversion into soluble products. Recently it has been recognized that coals are more reactive than had been thought previously, especially low-rank coals. Laboratory research has clearly demonstrated that dispersed catalysts can have significant impact on coal liquefaction, even with the solid coal without solvent at temperatures as low as 325-350°C, as reflected by the increase in coal conversion [Bockrath et al., 1986; Derbyshire et al., 1986a, 1986b; Garcia and Schobert, 1989; Burgess and Schobert, 1991; Solomon et al., 1991; Song et al., 1986, 1991, 1993, 1994a; Huang et al., 1992, 1993]. Spectroscopic characterization of residues from liquefaction of Blind Canyon bituminous coal (at 350 or 400°C) using dispersed Mo and Fe catalysts (introduced onto coal by impregnation) has revealed that the metallic species have fully penetrated the coal particle [Anderson et al., 1993; Sommerfield et al., 1992, 1993]. Recent pilot plant tests have also demonstrated that the use of dispersed catalyst can be superior to supported catalyst for primary liquefaction (dissolution) of coal, particularly subbituminous coals [Vimalchand et al., 1992; Lee et al., 1992; Swanson, 1992a, 1992b]. Coal-derived liquids can be used as sources of aromatic chemicals and polymeric materials as well as transportation fuels [Song and Schobert, 1993; Derbyshire et al., 1994].

This paper reports on an alternative process for converting coal to liquid fuels and useful chemicals through low-severity liquefaction using dispersed MoS<sub>2</sub> catalyst with added water. It is well known that water or steam deactivate hydrotreating catalysts, such as Mo-based catalysts, under conventional process conditions. For coal liquefaction using dispersed catalysts, drying after impregnation of catalyst or precursor salt has been a standard procedure [Weller and Pelipetz, 1951; Derbyshire et al., 1986a, 1986b; Garcia and Schobert, 1989; Artok et al., 1993; Weller, 1994]. It was demonstrated that water removal and the drying conditions after impregnation of catalyst precursor were influential for liquefaction of subbituminous and bituminous coals at 400°C [Derbyshire et al., 1986b]. Several groups have reported on the negative impacts of water addition in catalytic coal liquefaction [Bockrath et al., 1986; Ruether et al., 1987; Kamiya et al., 1988]. In a preliminary work, however, we have observed the synergistic effect between water and dispersed molybdenum sulfide catalyst for promoting coal liquefaction at a temperature (350°C) lower than those used in the previous studies mentioned above [Song et al., 1993]. The motivation of our study comes from several interesting findings in our recent work on the influence of drying (water removal) and oxidation of Wyodak subbituminous coal on its catalytic liquefaction at 350°C [Song et al., 1994a].

## EXPERIMENTAL

The coal used was a Wyodak subbituminous coal, which is one of the Department of Energy Coal Samples (DECS-8) maintained in the DOE/Penn State Sample Bank. Detailed properties of the coal are described elsewhere [Song et al., 1994a]. Ammonium tetrathiomolybdate (ATTM) was dispersed as a catalyst precursor on to coal (1 wt% Mo on dmmf basis) by incipient wetness impregnation from its aqueous solution. ATTM is expected to generate molybdenum sulfide particles on coal surface upon thermal decomposition at  $\geq 325^\circ\text{C}$  [Garcia and Schobert, 1989; Artok et al., 1993]. 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.

The liquefaction was carried out in 25 mL tubing bomb reactors at a given temperature (350, 375, 400, 425°C) for 30 min (plus 3 min heat up) under an initial H<sub>2</sub> pressure of 6.9 MPa. For the experiments with added water, the weight ratio of added water to dmmf coal was kept constant (0.46) for both thermal and catalytic runs. All the liquefaction reactions described here were carried out in the absence of any organic solvents. The yields of gaseous products were determined in two different ways: by weight difference of microreactor (method I) and by GC analysis (method II). More experimental details have been given elsewhere [Song et al., 1993].

The oils were analyzed using a Waters high-performance (high-pressure) liquid chromatography (HPLC) equipped with a photodiode array (PDA) detector and Millennium 2010 Chromatography-Manager software system, which allows continuous two-dimensional scanning analysis over UV/VIS range. The molecular components in oils were identified using gas chromatography combined with mass spectrometry (GC-MS). More analytical details may be found elsewhere on the two-dimensional HPLC [Saini and Song, 1994] and GC-MS [Song et al., 1994b].

## RESULTS AND DISCUSSION

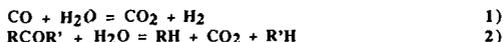
### Liquefaction at 350°C

Figure 1 shows the effect of water addition on the liquefaction of Wyodak subbituminous coal at 350°C for 30 min in the absence of an organic solvent. Relative to the non-catalytic run of vacuum-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, as compared to the non-catalytic run of the vacuum-dried coal. Adding a small amount of water to the catalytic reactions at 350°C dramatically increased coal conversion, 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 duplicate experiments. These interesting findings indicate that dispersed molybdenum sulfide catalyst and added water can act in concert to promote coal liquefaction at relatively low temperature, 350°C.

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Figure 2 indicates that the addition of water caused substantial increase in gas yields. This is manifested primarily by the increased CO<sub>2</sub> 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 CO<sub>2</sub> is 1.57 times the decreased amount of CO (MW ratio: 44/28 = 1.57). However, when water is added to the non-catalytic reaction of vacuum-dried coal, CO<sub>2</sub> 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). A similar trend was observed in catalytic runs at 350°C (Figure 2). Apparently, the enhanced CO<sub>2</sub> formation is due primarily to the addition of water, but not the WGS reaction. Probably the majority of increased CO<sub>2</sub> 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 groups, as shown by eq. 2. This could partially rationalize the enhanced CO<sub>2</sub> formation together with increased coal conversion upon water addition.



#### Effect of Reaction Temperature in the Range of 325-425°C

Figure 3 shows the effect of water on the thermal and catalytic liquefaction at 400°C for 30 min. 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 for 30 min 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 tests and have 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 in the absence of water. In other words, water tends to passivate the dispersed catalyst at higher reaction temperatures (400, 30 min).

It is clear from Figures 1 and 3 that water can affect coal conversion in opposite directions at different temperatures. Therefore, we further examined the effect of reaction temperature in the range of 325-425°C at 25°C interval. Figure 4 shows the coal conversion as a function of reaction temperature for catalytic liquefaction using ATTM precursor with added water. It appears that coal conversion displays a volcano-shape change with increasing temperature from 325°C to 425°C. Coal conversion increased with temperature up to 375°C and decreased with further increase in temperature up to 425°C. At 375°C, maximum coal conversion, nearly 80 wt%, was achieved with added water in solvent-free catalytic runs. This suggests that retrogressive reactions in the coal-H<sub>2</sub>O-catalyst system become considerable at higher temperatures (400-425°C).

#### HPLC and GC-MS Analysis of Oils

We have reported on the characterization of oils using two-dimensional HPLC and GC-MS techniques in a companion paper [Saini and Song, 1994]. In the present work we also applied these techniques. Figures 5 and 6 show the three-dimensional HPLC chromatograms of oils from water-assisted liquefaction at 350°C with and without the catalyst, respectively. In these 3-D chromatograms, peak intensity is plotted against UV wavelength range (250-400 nm) and retention time (0-120 min). The peaks between 2-30 min are due to 1-, 2-, 3- and 4-ring aromatics, and the two peaks between 50 and 60 min are due to phenolic compounds. Comparison of Figure 6 with Figure 5 indicates that the oils from liquefaction with added water contain more phenolic compounds. We also confirmed this trend by GC-MS analysis. It should be noted that the phenolic compounds as well as alkylaromatics in the oils may be industrially useful chemical feedstocks [Song and Schobert, 1993].

#### Role of Water in Thermal and Catalytic Reactions

Our results show that, at constant water/coal ratio (0.46, wt ratio), water can have either a strong promoting effect or an inhibiting effect on coal conversion in catalytic liquefaction, depending on the reaction conditions. The most interesting finding from our work is the strong synergistic effects between water and dispersed molybdenum sulfide catalyst under certain conditions. This finding is important both from fundamental and practical viewpoints. Little has been reported in the literature on the positive effect of water addition on catalytic liquefaction under H<sub>2</sub> pressure. The results of Bockrath et al. [1986] showed that using water (water/coal = 2, wt ratio) as solvent in the catalytic liquefaction of Illinois No.6 coal at 350°C for 60 min gives much lower conversions than the runs using organic solvents. In an earlier work, Ruether et al. [1987] examined the effect of water addition in catalytic liquefaction of Illinois No.6 coal at 427°C for 1 h (water/coal = 0.33-1.5, wt ratio). They concluded that "at fixed total pressure, the most reactive environment contains no added water, so that H<sub>2</sub> partial pressure is as high as possible". In the runs using 0.1% dispersed Mo catalyst at 427°C for 60 min, highest coal conversions were obtained without added water. They reported that "the absence of any positive effect of water in catalyzed reaction systems could be explained on the basis of a very strong catalytic effect of molybdenum in promoting hydrocracking and hydrogenation reactions." 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 reoxidation of the active iron sulfide catalyst. Consequently, addition of sulfur can resist reoxidation of iron catalyst by water under coal liquefaction conditions [Kamiya et al., 1988]. 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. Their work was directed toward replacing or reducing the amount of organic recycle vehicle. They observed that coal conversion in water is greater than with dry hydrogenation under otherwise comparable conditions. 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. As discussed above, we have not found any published literature that reports on strong synergistic effect between water and dispersed catalyst for coal liquefaction.

The strong promoting effect of water on catalytic liquefaction at 325-375°C observed in our work may be partially understood by the literature information from non-catalytic reactions. The origin of the above-mentioned strong synergism, however, has not been clarified. For non-catalytic coal conversion such as pyrolysis, liquefaction and coprocessing, 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 and Hirschon, 1990; Pollack et al., 1991; Serio et al., 1991, 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.

#### SUMMARY

We have found that there are strong synergistic effects between water and a dispersed molybdenum sulfide catalyst for promoting low-severity liquefaction of Wyodak subbituminous coal. There is substantial improvement in coal conversion upon addition of water to the reaction using dispersed Mo catalyst at relatively low temperatures, 325-375°C. Relative to the non-catalytic run of the dried coal, the co-use of the catalyst and water (at water/dmmf coal = 0.46) can double the coal conversion at 350°C for 30 min, from 29-30 to 66-67 wt%. On the other hand, water tends to passivate the dispersed catalyst at higher reaction temperatures (400-425°C, 30 min). HPLC and GC-MS of oils revealed that the oils from liquefaction with added water contain more phenolic compounds. However, some fundamental questions concerning the role of water in catalytic liquefaction and catalytic reaction mechanisms involving water need to be answered by further research.

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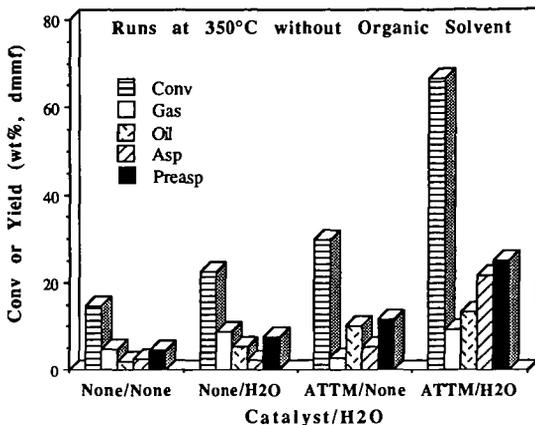


Figure 1. Effect of water on catalytic liquefaction of Wyodak coal at 350°C for 30 min.

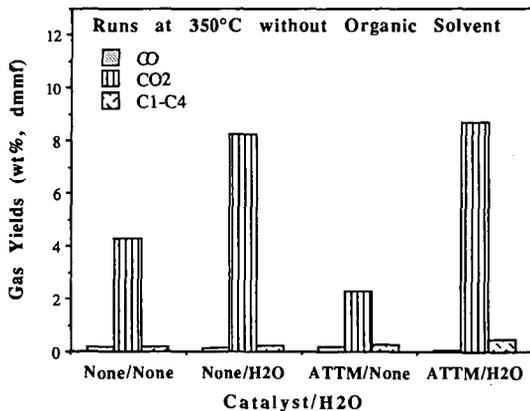


Figure 2. Effect of water on gas formation in catalytic liquefaction at 350°C for 30 min.

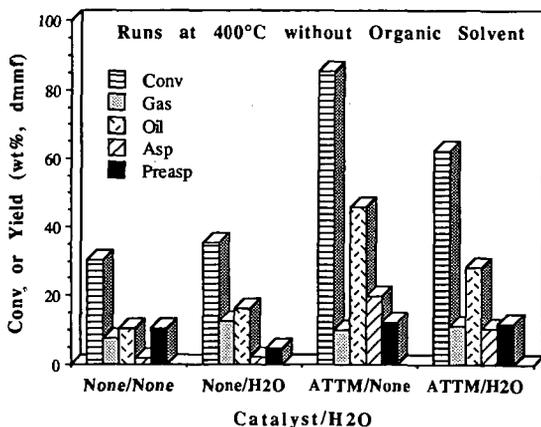


Figure 3. Effect of water on catalytic liquefaction of Wyodak coal at 400°C for 30 min.

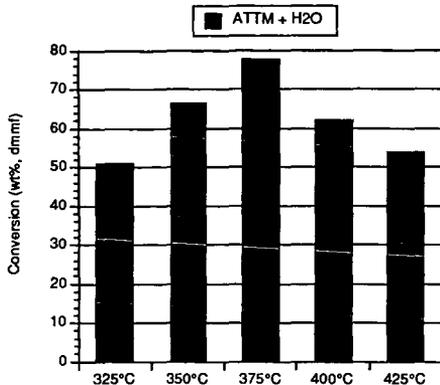


Figure 4. Effect of temperature on conversion of Wyodak coal in the presence of H<sub>2</sub>O without any organic solvent

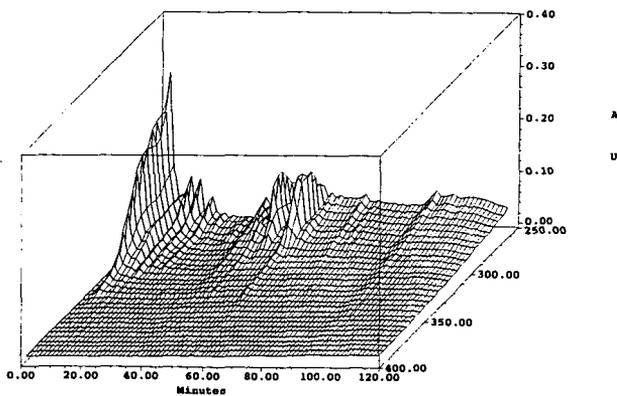


Figure 5. 3-D HPLC chromatogram of oils from non-catalytic liquefaction of Wyodak coal at 350°C for 30 min in the presence of water.

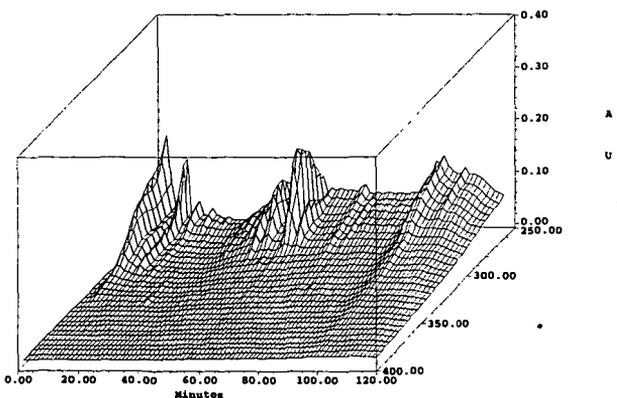


Figure 6. 3-D HPLC chromatogram of oils from catalytic liquefaction of Wyodak coal at 350°C for 30 min with dispersed Mo catalyst in the presence of water.