

# PROMOTING COAL HYDROLIQUEFACTION THROUGH CO-USE OF WATER AND DISPERSED MOLYBDENUM SULFIDE CATALYST

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## INTRODUCTION

Work in our laboratory has demonstrated a remarkable synergism between water and a dispersed molybdenum sulfide catalyst for promoting liquefaction of Wyodak subbituminous coal at relatively low temperature (350-375°C). These results appear to be contrary to conventional wisdom regarding the detrimental effects of water during the catalytic hydroliquefaction of coal [1-4]. Our findings, to date, indicate that both reaction temperature range and water/coal ratio are key factors in determining the net influence of water upon the catalytic liquefaction of this particular coal [5-9]. Significantly, we have observed the same promotional trends arising from the co-use of water and dispersed molybdenum sulfide catalyst both in solvent-free experiments, and in liquefaction experiments performed in the presence of either a non-donor (1-methylnaphthalene), or a H-donor (tetralin) [6,9]. In contrast, however, for catalytic runs at higher temperature (400-450°C), using ATTM without added water always gives the highest conversion, either with or without an organic solvent [6,9]. These interesting results have demonstrated unequivocally that within a specific temperature window, and in the correct proportion, water can have a dramatic promoting effect on the catalytic liquefaction of Wyodak subbituminous coal.

Our findings with Wyodak coal have provided the impetus behind an ongoing fundamental and exploratory study on the promotional effects of water on catalytic coal liquefaction. Although the synergistic enhancement in conversion through co-use of water and dispersed Mo sulfide catalyst has been amply demonstrated for Wyodak subbituminous coal, one of our present primary interests is to determine whether this potentially significant phenomenon is observable with other coals, particularly coals of different rank. In this paper preliminary results from recent work using Pittsburgh #8 high-volatile bituminous coal are presented which indicate a similar marked improvement in coal conversion upon addition of a small amount of water in the presence of dispersed molybdenum sulfide catalyst. The overall improvement in conversion observed for the higher-rank coal, however, is somewhat less dramatic than that for Wyodak coal. Reactions performed at two different temperatures (350 and 400°C) are discussed and compared to those for Wyodak coal. Effects of catalyst loading levels are also described.

## EXPERIMENTAL

The coals used were Wyodak subbituminous coal and Pittsburgh #8 high-volatile bituminous coal. These are Department of Energy Coal Samples (DECS-8 and DECS-12, respectively) maintained in the DOE/Penn State Coal Sample Bank, ground to  $\leq 60$  mesh, and stored under argon atmosphere in heat sealed, argon-filled laminated foil bags consisting of three layers. Wyodak subbituminous coal contains 28.4% moisture, 32.4% volatile matter, 29.3% fixed carbon and 9.9% ash, on as-received basis; 75.8% C, 5.2% H, 1.0% N, 0.5% S, and 17.5% O, on dmmf basis. Pittsburgh #8 high-volatile bituminous coal contains 2.4% moisture, 35.2% volatile matter, 52.4% fixed carbon and 10.0% ash, on as-received basis; 84.8% C, 5.7% H, 1.4% N, 0.8% S, and 7.4% O, on dmmf basis. Both fresh raw coals, and coals pre-dried in a vacuum oven (vd) at 100°C for 2h were used. Reagent grade ammonium tetrathiomolybdate (ATTM), obtained from Aldrich with 99.97% purity) was employed as the dispersed catalyst precursor. The water-soluble inorganic salt ATTM is expected to generate molybdenum sulfide particles on the coal surface upon thermal decomposition at  $\geq 325^\circ\text{C}$ . ATTM was dispersed onto either the raw coal or vacuum-dried coal samples by incipient wetness impregnation from its aqueous solution. The metal loading was kept constant at 1 wt% Mo on dmmf coal basis, unless otherwise specified. Following impregnation, the coal samples were dried in a vacuum oven at 100°C for 2h prior to use.

Liquefaction experiments were carried out in 25 ml tubing bomb reactors with around 4g of coal at 350 or 400°C for 30 min (plus an additional 3 min for reactor heat-up time). For both thermal and catalytic experiments with added water, the weight ratio of water to dmmf coal was kept at around 0.46. All reactions described in this paper were performed in the absence of any organic solvent. The reactors were purged several times with H<sub>2</sub> and finally pressurized with 6.9 MPa H<sub>2</sub> (cold). A fluidized sandbath maintained at the desired temperature was used as the heater. After the desired reaction time, the reactors were removed from the sandbath and quenched in a cold water bath to rapidly bring down the temperature  $< 150^\circ\text{C}$ , then were allowed to cool down to ambient temperature in air. The reactors were vented and the mass of product gases (including residual H<sub>2</sub>) determined. Gaseous products were analyzed by GC, with the aid of gas standards for quantitative calibration of GC responses of CO<sub>2</sub>, CO, H<sub>2</sub> and C<sub>1</sub>-C<sub>4</sub> hydrocarbon gases. H<sub>2</sub> consumption was determined by subtracting the mass of residual H<sub>2</sub> found in the product gases (determined by GC) from the mass of H<sub>2</sub> initially charged. The liquid and solid products were carefully recovered from the reactor and transferred to an extraction thimble. The products were subsequently separated by sequential Soxhlet extraction into oil (hexane soluble), asphaltene (toluene soluble but hexane insoluble), preasphaltene (THF soluble but toluene insoluble), and residue (THF insoluble). Further experimental details may be found elsewhere [6-8].

## RESULTS AND DISCUSSION

Experimental results for the catalytic and non-catalytic solvent-free reactions of Pittsburgh #8 coal, performed in both the presence and absence of added water, are illustrated in Figure 1 (350°C) and Figure 2 (400°C). Equivalent data for Wyodak coal is also given in Figure 3 (350°C) and Figure 4 (400°C), respectively. The catalyst loading level employed in these experiments was 1 wt% Mo on dmmf coal basis. The effects of reducing catalyst loading to 0.1 wt% Mo for reactions of Wyodak coal at 350°C are summarized in Figure 5.

**Positive Effect of Added Water in Catalytic Liquefaction at 350°C.** Our earlier findings concerning the strong promotional effects of added water on the catalytic liquefaction of Wyodak subbituminous coal at 350°C are exemplified in Figure 3. These results have been previously discussed in detail elsewhere [7]. In brief, it can be seen that adding water to the non-catalytic run of vacuum dried Wyodak coal increased coal conversion from 14.5 to 22.5 wt% (dmmf). Using only ATTM improved coal conversion to 29.8 wt%. When both water and ATTM are used in combination, however, there is a remarkable increase in coal conversion to 66.5 wt%.

Referring now to Figure 1 for the runs of Pittsburgh #8 coal at 350°C, it can be seen that compared to the non-catalytic run of vacuum-dried coal, adding water increased coal conversion from 21.9 to 33.6 wt% (dmmf). Surprisingly, using ATTM at 350°C had little apparent benefit on conversion for this coal, giving a conversion of only 25.1 wt%. This is in stark contrast to the results for Wyodak subbituminous coal. Adding water to the catalytic run, however, significantly increased conversion of Pittsburgh #8 coal to 48.0 wt%, representing a 91% increase from the catalytic run without water, and a 119% increase from the non-catalytic run without water. Clearly, as previously seen for Wyodak coal, there is an apparent synergistic enhancement in conversion at 350°C for Pittsburgh #8 coal resulting from co-use of water and dispersed Mo sulfide catalyst. These interesting findings reveal that dispersed Mo sulfide catalyst and added water can act in concert to promote coal liquefaction at relatively low temperature. It is noteworthy, however, that the overall improvement in conversion observed for the higher-rank coal Pittsburgh #8 is somewhat less dramatic than that for Wyodak subbituminous coal. Considering product quality, it is apparent from Figure 1 that Pittsburgh #8 high-volatile bituminous coal is converted largely to preasphaltenes (ie. THF-soluble but toluene-insoluble) at 350°C. The enhancement in conversion through co-use of water and catalyst is also manifest primarily as an increase in preasphaltene yields. As one might expect, gas yields from Pittsburgh #8 coal (particularly CO<sub>2</sub>) are significantly lower than from Wyodak subbituminous coal. Interestingly, however, we observed that CO<sub>2</sub> yields are doubled or even tripled for all reactions with added water. Similar observations have also been made for the hydrous experiments with Wyodak coal [7]. This suggests that water is interacting with certain coal functionalities, ultimately resulting in the evolution of CO<sub>2</sub> through oxidative processes and/or enhanced decarboxylation.

Comparing the conversion data for Pittsburgh #8 (Figure 1) at 350°C to that for Wyodak coal (Figure 3), it is interesting to note that for the non-catalytic reactions, the high-volatile bituminous coal is apparently more reactive than the lower-rank subbituminous coal, both in the absence and presence of water (ie. 21.9 wt% vs 14.5 wt% for anhydrous experiments) and (33.6 wt% vs 22.5 wt% for hydrous experiments), respectively. In contrast, however, for the catalytic reactions, Wyodak coal always gives higher conversion than Pittsburgh #8 (ie. 29.8 wt% vs 25.1 wt% for anhydrous experiments) and (66.5 wt% vs 48.0 wt% for hydrous experiments). These results clearly demonstrate that in the presence of an effective dispersed catalyst, lower-rank subbituminous coals are more reactive than first thought [10], and may in fact be more amenable feedstocks for direct liquefaction than bituminous coals (similar trends are also apparent for the reactions of these coals at 400°C).

**Effect of Temperature on Coal Conversion with H<sub>2</sub>O and ATTM.** For Wyodak coal runs at 400°C (Figure 4), using ATTM without water always gave the highest conversions. The use of ATTM alone at 400°C afforded a very high conversion for this coal (85.4 wt% (dmmf)), and a high oil yield (45.8 wt%), illustrating that, at this temperature, dispersed Mo sulfide catalyst is highly effective at promoting the hydroliquefaction of Wyodak subbituminous coal. However, addition of water to the catalytic run decreased coal conversion (to 62.1 wt%) and oil yield (to 28.2 wt%). An important implication from Figure 4 is that the presence of water at 400°C apparently decreased the effectiveness (or activity) of the dispersed catalyst. This is in distinct contrast to the strong promotional trends observed in the corresponding runs at 350°C.

Considering now the runs at 400°C for Pittsburgh #8 high-volatile bituminous coal (Figure 2), it can be seen that the addition of water to the non-catalytic run of vacuum-dried coal resulted in an increase in conversion from 36.3 wt% to 43.5 wt%. The use of ATTM alone resulted in only a modest increase in conversion (to 54.0 wt%). Adding water to the catalytic run gave a similar conversion to that from the use of catalyst alone (54.9 wt%), though interestingly, did not result in a reduction in conversion as was seen for the catalytic run of Wyodak coal at this temperature. Indeed, addition of water to the catalytic run of Pittsburgh #8 appeared to have some benefit, in terms of product quality, in that there was a notable shift from largely preasphaltenes to an increased yield of asphaltenes isolated in the added water reaction. As was the case for Wyodak coal, however, it is apparent that the strong synergistic enhancement in conversion achieved through co-use of water and dispersed catalyst at 350°C, is lost at higher temperature (400°C). As at 350°C, it is interesting to note that in the absence of catalyst at 400°C, Pittsburgh #8 is apparently more reactive than Wyodak coal. In the catalytic reactions, however, Wyodak coal always gives the

highest conversion. The dispersed Mo sulfide catalyst generated from ATTM does not appear to be a very effective catalyst for promoting the hydroliquefaction of the higher-rank coal.

**Effect of Catalyst Loading on Conversion of Wyodak Coal at 350°C.** Figure 5 summarizes conversion data for Wyodak coal at 350°C obtained using a reduced catalyst loading of 0.1 wt% Mo on dmmf coal basis. Compared to the original data obtained at a loading of 1 wt% Mo on dmmf coal basis (Figure 3), it can clearly be seen that this reduction in the catalyst concentration significantly reduces the overall effectiveness of the catalyst for promoting conversion of Wyodak coal, both in the catalytic runs and catalytic runs with added water. For the catalytic runs, conversion fell from 29.8 wt% to 20.5 wt%. In the case of catalytic runs with added water, conversion fell from 66.5 wt% to 40.3 wt%. This latter observation indicates that the magnitude of the promotional effect arising through co-use of water and ATTM is not only sensitive to the water/dmmf coal ratio but is also dependent upon the catalyst concentration employed.

#### SUMMARY

We have found that there are strong synergistic effects between water and a dispersed molybdenum sulfide catalyst (1 wt% Mo on dmmf coal basis) for promoting the low temperature (350°C) liquefaction of both Wyodak subbituminous and Pittsburgh #8 bituminous coals. Relative to the catalytic runs of the dried coal, the co-use of catalyst and water (at water/dmmf coal = 0.46) can more than double the coal conversion at 350°C for 30 min, from 29.8 wt% to 66.5 wt% for Wyodak coal. In the case of Pittsburgh #8 coal, under the same prevailing conditions, the overall improvement in conversion on addition of water to the catalytic run is less dramatic, i.e. from 25.1 to 48.0 wt%. One of the contributing factors to this observation may be that the dispersed Mo sulfide catalyst generated from ATTM is, in general, less effective for promoting the hydroliquefaction of the higher-rank coal. At higher temperature (400°C) the promotional effects of adding water are lost and, in the case of Wyodak coal, actually inhibits catalyst activity resulting in a reduction in conversion. For Pittsburgh #8 coal, adding water to the catalytic run at 400°C results in a similar conversion to that from the use of catalyst alone. There is, however, some apparent benefit in terms of a slight improvement in product quality for the added water reaction. We plan to perform a more thorough study of the effects of reaction temperature (i.e. 325-425°C) on the water-promoted catalytic liquefaction of Pittsburgh #8 coal in order to construct a temperature vs conversion profile, as we have already done for Wyodak coal [5,9]. In this way, we hope to identify the optimum temperature window in which water-dispersed catalyst synergistic interaction is maximized for conversion of Pittsburgh #8 coal.

In the present study, the water/dmmf coal ratio employed was kept constant at around 0.46. This ratio was selected for this preliminary series of reactions with Pittsburgh #8 as it was previously found to be the optimum ratio for Wyodak coal experiments. Clearly, however, it may not necessarily be the most suitable for Pittsburgh #8, we therefore intend to perform a series of catalytic runs at various H<sub>2</sub>O/coal ratios in order to determine the optimum ratio for maximizing conversion of this particular coal.

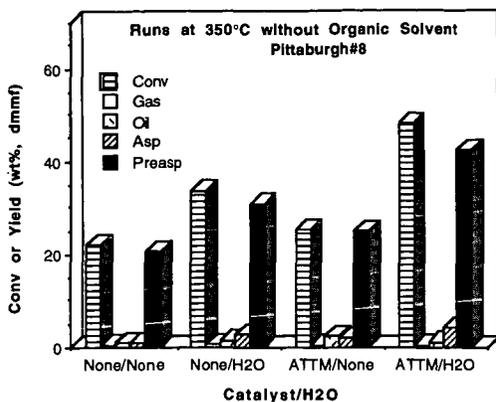
We observed that dropping the catalyst loading, from 1.0 wt% to 0.1 wt% Mo on dmmf coal basis, had an adverse effect on conversion for Wyodak coal at 350°C both for catalytic runs and catalytic runs with added water. The latter finding demonstrates that the magnitude of the promotional effects arising through co-use of ATTM and water is dependent upon the catalyst concentration. We further plan to investigate the effectiveness of a 0.5 wt% Mo catalyst loading.

#### ACKNOWLEDGEMENT

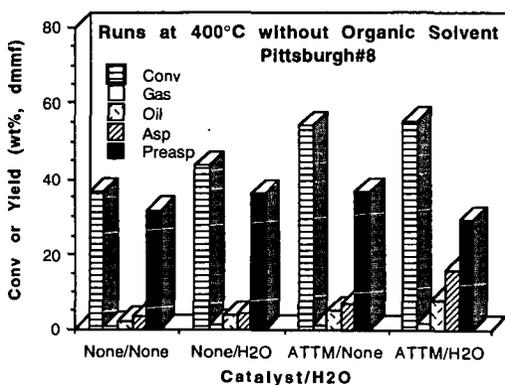
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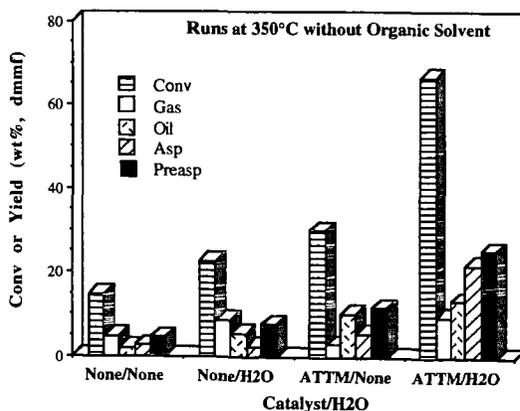
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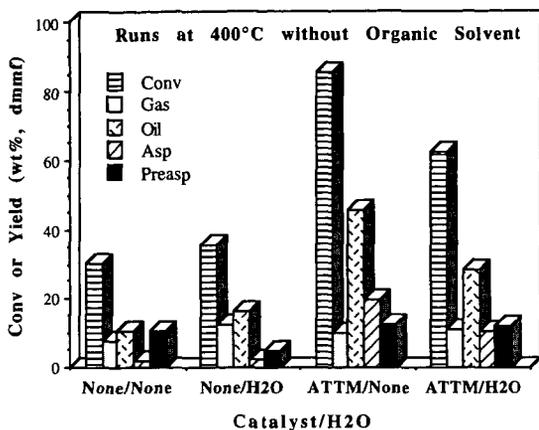
**Figure 1** Effect of water on catalytic liquefaction of Pittsburgh #8 coal at 350°C for 30 min.



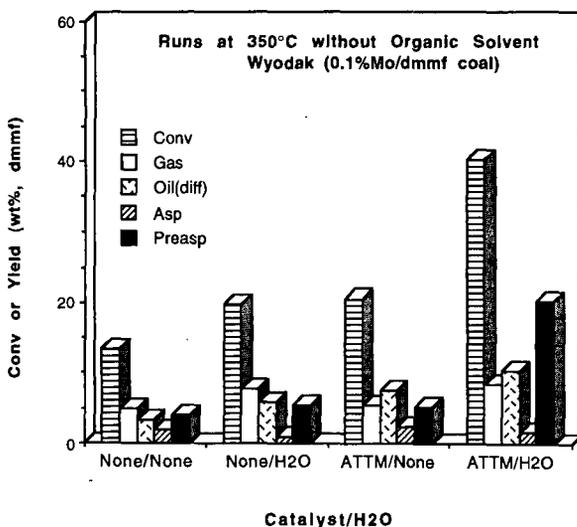
**Figure 2.** Effect of water on catalytic liquefaction of Pittsburgh #8 coal at 400°C for 30 min.



**Figure 3.** Effect of water on catalytic liquefaction of Wyodak coal at 350°C for 30 min.



**Figure 4** Effect of water on catalytic liquefaction of Wyodak coal at 400°C for 30 min.



**Figure 5** Effect of water on catalytic liquefaction of Wyodak coal using catalyst loading of 0.1 wt% Mo to dmmf coal at 350°C for 30 min.