

## Enhancing Low-Severity Catalytic Liquefaction of Low-Rank Coal by Adding Water

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### INTRODUCTION

As a part of an on-going program for investigating the effects of thermal and catalytic pretreatments on coal structure and reactivity in liquefaction, the present study seeks to explore the effects of water in low-severity catalytic liquefaction of low-rank coal. The motivation of the present study comes from our recent work on the influence of mild pretreatments, drying and oxidation, of Wyodak subbituminous coal on its catalytic liquefaction [Saini et al., 1993; Song et al., 1993]. In that work we found that adding a small amount of water equivalent to the original moisture content (28.4 wt%) back to the vacuum-dried or air-dried coal restored over 90 % of the conversion of the fresh raw coal in non-catalytic runs at 350 °C with and without solvents. This fact strongly suggests that the negative impact of drying on thermal (uncatalyzed) liquefaction reactions is largely due to the removal of water. Another fact that puzzled us is that the conversions of fresh raw coal in the non-catalytic runs and catalytic runs with either tetralin or 1-methylnaphthalene (1-MN) solvent are very similar to each other, although the catalytic runs of the vacuum-dried or air-dried coal afforded significantly higher conversions than the corresponding thermal runs. These two facts prompted us to examine the effects of water addition in catalytic coal liquefaction. This paper reports on the dramatic improvement of coal conversion upon addition of a small amount of water in low-severity liquefaction of Wyodak subbituminous coal using a dispersed molybdenum sulfide catalyst at 350 °C for 30 min.

### 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. It was collected in June 1990, ground to  $\leq 60$  mesh, and stored under argon atmosphere in heat-sealed, argon-filled laminated foil bags consisting of three layers. It 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. The as-received fresh sample is designated as raw coal. Vacuum-drying (VD) of the coal was conducted in a vacuum oven at 100 °C for 2 h. Air-drying (AD) was done in an oven maintained at 100 °C for 2-100 h, or at 150 °C for 20 h, with the door partially open. For the loading of dispersed catalyst, ammonium tetrathiomolybdate (ATTM) was used as precursor, which is expected to generate molybdenum sulfide particles on coal surface upon thermal decomposition at  $\geq 325$  °C. ATTM was dispersed on to coal (1 wt% Mo on dmmf basis) by incipient wetness impregnation from its aqueous solution. The impregnated coal samples were dried in a vacuum oven at 100 °C for 2 h.

The liquefaction was carried out at 350 or 400 °C for 30 minutes (plus 3 minutes heat-up time) with an initial (cold) H<sub>2</sub> pressure of 7 MPa (1000 psi) in 25 ml tubing bomb microreactor. We conducted three types of reactions including solvent-free runs, the runs in the presence of a hydrogen donor tetralin solvent, and the runs with a non-donor 1-methylnaphthalene solvent, using 4 g of coal and 4 g of solvent, and optionally, added water. The wt ratio of added water to dmmf coal was kept constant (0.46) for both thermal and catalytic runs with added water. After the reaction, the gaseous products were analyzed by GC, with the aid of gas standards for quantitative calibration of GC responses of CO, CO<sub>2</sub>, and C<sub>1</sub>-C<sub>4</sub> hydrocarbon gases. The liquid and solid products were 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). The conversions of coal into soluble products were determined from the amount of THF-insoluble residues. More experimental details may be found elsewhere [Song and Schobert, 1992; Saini et al., 1993]. In order to obtain highly reliable data, almost all the experiments were duplicated or triplicated. The deviations in conversions and product yields are generally within  $\pm 2$  wt%. Most results reported here are average of two runs.

### RESULTS AND DISCUSSION

Tables 1, 2 and 3 show the results for liquefaction of the coal at 350 °C with and without added water in the absence of any solvent (Table 1) and in the presence of a non-donor 1-methylnaphthalene (1-MN) solvent (Table 2) and a hydrogen-donor tetralin solvent (Table 3). Tables 4 and 5 show the results for thermal (non-catalytic) and catalytic runs, respectively, at

higher temperature (400 °C) with and without added water. The data include coal conversion, total yields of gaseous products by two different methods, yields of CO, CO<sub>2</sub>, and C<sub>1</sub>-C<sub>4</sub> hydrocarbon gases determined by GC, yields of oil, asphaltene, and preasphaltene obtained from Soxhlet extraction, consumption of gas-phase H<sub>2</sub>, and net hydrogen transfer from solvent where appropriate. These results are grouped and discussed below.

#### **Effect of Water Reflected by the Influence of Drying**

For the thermal (non-catalytic) runs, both vacuum-drying and air-drying decreased coal conversion significantly, as compared to the run of the raw coal. Original fresh raw coal contains 28.4 wt% water. To see whether the changes caused by the drying is reversible or irreversible, we added a small amount of water equivalent to the original moisture content, to the dried coal. The liquefaction results showed that adding water back to the vacuum-dried and air-dried coals restored over 90% of the conversion of the fresh raw coal. The coal conversion levels always follow the order of solvent-free < 1-methylnaphthalene < tetralin; the use of the raw coal always give the highest conversion. In the absence of water, there were some differences between the vacuum-dried and air-dried coals, with the latter affording higher conversion when a solvent was used. When water is added back, the differences between the two types of dried coals become much smaller.

These trends reveal that the major effect of drying on thermal liquefaction is associated with the effect of water. Under the conditions of vacuum-drying at 100 °C for 2 h, most of the changes caused by drying are reversible, as can be seen by the over 90% restoration of coal conversion. The other effects of drying and oxidation may include the changes in pore structure (Suuberg et al., 1991; Vorres et al., 1992), surface characteristics (Song et al., 1993), and, if oxidation involved, the change in functionality (Saini et al., 1993). These kinds of changes may be irreversible if high severity conditions were used for drying. However, when water is added back, the differences caused by using different drying methods, largely diminish. In other words, decrease in conversion caused by some undesirable changes during drying is largely compensated by the desirable effect of water addition.

The results for uncatalyzed runs in Tables 1 to 3 demonstrate that the presence of water promotes the conversion of the coal, increases oil yields, and significantly enhances the oxygen removal as CO<sub>2</sub>. Adding water also resulted in small but consistent decrease in the yield of CO. This is considered to be due to water gas shift reaction:  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ . However, the increase in CO<sub>2</sub> yield upon H<sub>2</sub>O addition is much more than the decrease in CO on a molar basis, indicating the occurrence of other reactions between water and species in or from coal, which led to substantial increase in CO<sub>2</sub> formation.

#### **Positive Effect of Added Water in Catalytic Liquefaction at 350 °C**

For all the catalytic runs listed in Tables 1 to 3, regardless how the coal was pre-dried or undried, all the ATTM-loaded coals were dried in vacuum at 100 °C for 2 h before use. In the runs testing the effect of water addition, we added a small amount of water (H<sub>2</sub>O/dmmf coal = 0.46, wt ratio). It is clear from Table 2 that adding water to the catalytic reactions at 350 °C dramatically promoted the coal conversion from 29-30 wt% for the vacuum-dried or air-dried coals to 62-63 wt% in the solvent-free runs, and from 43 to 66 wt% for the fresh raw coal. Therefore, the present results demonstrate that dispersed MoS<sub>2</sub> catalyst and a small amount of water can act in concert to strongly promote coal conversion at 350 °C. In fact, the use of ATTM with added water at 350 °C without solvent (Table 1) or with 1-MN solvent (Table 2) resulted in coal conversion level (63-66 dmmf wt%) that is much higher than that (30-38 wt%) from the non-catalytic runs at much higher temperature, 400 °C (Table 4).

For the solvent-free runs, the increased coal conversion upon water addition is mainly manifested by the significant gain in asphaltene and preasphaltene yields (Table 1). In the presence of either a H-donor tetralin solvent or a non-donor 1-MN solvent, the enhanced conversions are largely due to the increase in the yields of preasphaltene and oil, and this trend was most apparent with 1-MN solvent (Table 2).

With respects to the effect of water associated with influence of drying, it also appears that dispersing ATTM on vacuum-dried coal gives higher conversion upon water addition, as compared to loading ATTM on air-dried coal. The extents of increase in conversion due to water addition are also higher with the former than with the latter. These results show that for water-aided catalytic liquefaction at 350 °C, less oxidation of the coal sample can lead to higher conversion.

The use of catalyst generally decreased the yield of CO<sub>2</sub> in the runs of the dried coals without added water. Similar to the thermal runs, adding water to the catalytic runs also decreased the CO yield and significantly enhanced the formation of CO<sub>2</sub>. The increasing extent in CO<sub>2</sub> yield is much higher than the decrease in CO yield, indicating the contribution of the reactions between water and coal species, other than water gas shift reaction, to the increased CO<sub>2</sub> formation.

#### **Negative Effect of Added Water in Catalytic Liquefaction at 400 °C**

In order to examine the effect of added water in relation to the influence of reaction temperature, we also carried out the liquefaction experiments at 400 °C. In uncatalyzed runs, adding water resulted in moderate increase in oil yields and coal conversion (5-7 wt%) with 1-MN solvent and without solvent, and small increase in coal conversion with tetralin

solvent. The changes in coal conversion with solvents are much larger at 400 °C than at 350 °C, but conversion always increases in the consistent order of none < 1-MN < tetralin.

As can be seen by comparing Table 5 with Table 4, the trends for the water effect in catalytic runs at 400 °C are different from those in non-catalytic runs. In the absence of added water, the solvent-free run of the vacuum-dried and ATTM-impregnated coal afforded highest conversion, 85 wt%, and highest oil yield, 46 wt%. The run with 1-MN solvent gave the lowest conversion, 71 wt%. Relative to the solvent-free run, the use of H-donor tetralin solvent at 400 °C did not display any advantage in terms of coal conversion and oil yields. Given the fact that water acts as a very good promoter for coal conversion at 350 °C (Tables 1-3), it is surprising to note from Table 5 that adding water to the catalytic runs at 400 °C decreased coal conversion substantially in the runs with 1-MN and without solvent. We conducted duplicated runs under the three different conditions at 400 °C, and confirmed a reproducible trend for the negative impact of water on the catalytic reactions at 400 °C. The solvent-free run suffered large decrease in coal conversion from 85 to 62 wt%. The run with tetralin displayed less sensitivity to the water, with slight but consistent decrease in conversion in duplicated runs from about 84 to 80 wt%.

These results show that the catalytic activity is significantly lower in the presence of water at 400 °C, indicating that water is detrimental for liquefaction at higher temperature. The action of water at 400 °C may be inferred through the following comparative examination. The highest oil yield and the highest conversion in the solvent-free run with no added water indicate that dispersed molybdenum catalyst exhibited maximum activity in activating molecular H<sub>2</sub>, namely dissociation of H<sub>2</sub> on catalyst surface, and in transfer of the active H atom to the coal-derived free radicals and other coal species when there is no externally added solvent. Relative to the solvent-free catalytic run, the decrease in conversion and H<sub>2</sub> consumption upon addition of 1-MN may be attributed to the decrease in partial H<sub>2</sub> pressure, additional difficulty in mass transport of H<sub>2</sub> to the catalyst surface in the presence of solvent, and competitive adsorption of aromatic 1-MN molecules on catalyst surface. The same trends also applies to the run using tetralin, but the negative impact of tetralin to mass transport of H<sub>2</sub> gas is largely compensated by hydrogen donation from benzylic hydrogens in tetralin. As a result, oil yield decreased but conversion did not decrease as much as oil yield. Relative to the runs with added 1-MN, the added water initially occupied less space and therefore the partial H<sub>2</sub> pressure should be higher during the water-added but solvent-free run. Such an inference indicates that the presence of water deactivated the catalyst. The conversion decrease due to water addition was also accompanied by significant reduction in gas-phase H<sub>2</sub> consumption, from 2.8 to 1.4 in solvent-free runs, and from 1.8 to 0.7-0.9 in the runs with a solvent (Table 5). It should also be noted that the enhanced formation of CO<sub>2</sub> upon water addition seems to be unaffected at higher temperature, suggesting the enhanced CO<sub>2</sub> formation is caused by thermal reaction between added water and coal species.

#### The Desirable and Undesirable Functions of Water at 350 and 400 °C

Little is reported in literature about the effects of water on the catalytic coal liquefaction using dispersed catalyst. However, 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; Tse et al., 1991). 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 crosslinks 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 by phenolic compounds such as catechol and lead to higher conversion or a better quality product. The present results for thermal runs are consistent with those in literature. However, there is no comparable literature data for the desirable and undesirable effects of water addition in catalytic liquefaction. Ruether et al. (1987) reported that in uncatalyzed systems, a substantial water partial pressure at fixed H<sub>2</sub> partial pressure increases the conversion of Illinois #6 bituminous coal, but in the runs using 0.1% dispersed Mo catalyst at 427 °C for 60 min, highest conversions are obtained without added water. How water affects the catalytic reaction is not clear. The present results suggest that water promotes coal liquefaction with dispersed MoS<sub>2</sub> catalyst at 350 °C (Tables 1 to 3), but has less promoting effect to thermal reaction at 400 °C (Table 4) and can deactivate or passivate the catalyst at 400 °C (Table 5).

#### CONCLUSIONS

Water can be excellent promoter or undesirable inhibitor for coal conversion in catalytic liquefaction, depending on the reaction systems and conditions. For catalytic liquefaction at 350°C, adding a small amount of water has a dramatic promoting effect on coal conversion, but a significant inhibiting effect of water is observed for catalytic runs at 400 °C. It appears that water and dispersed molybdenum sulfide catalyst can act in concert to promote coal conversion and oil production at 350 °C, but water can passivate the catalyst at 400°C. The remarkably high conversion level at low-temperature (350 °C) achieved with the co-use of ATTM and added water may give rise to new opportunities for developing novel low-severity catalytic liquefaction processes with significantly reduced operational costs.

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Table 1. Effects of Water Addition on Solvent-Free Liquefaction of DECS-8 Wyodak Coal at 350 °C for 30 min under 6.9 MPa H<sub>2</sub>

ID No.	51/63/93	7	26/32	90/139	119	54/66/96	10	29/55	116	113	122/142
Coal Sample <sup>a</sup>	Raw	VD-100°C-2 h	AD-100°C-2 h	VD-100°C-2 h	AD-100°C-2 h	Raw	VD-100°C-2 h	AD-100°C-2 h	Raw	VD-100°C-2 h	AD-100°C-2 h
Solvent	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free
Catalyst (ATTM)	-	-	-	-	-	ATTM	ATTM	ATTM	ATTM	ATTM	ATTM
H <sub>2</sub> O Addition	Original H <sub>2</sub> O	-	-	H <sub>2</sub> O added	H <sub>2</sub> O added	-	-	-	H <sub>2</sub> O added	H <sub>2</sub> O added	H <sub>2</sub> O added
Prod. dmmf, wt%											
Conversion	25.0	12.5	14.8	22.5	26.1	43.3	29.8	29.2	66.0	66.5	62.3
Gases	7.7 <sup>b</sup> (9.52) <sup>c</sup>	3.3 (4.93)	5.0 (6.33)	7.4 (8.64)	8.4 (11.49)	2.2 (4.11)	3.0 (2.78)	3.3 (6.20)	6.2 (8.41)	6.5 (9.20)	6.6 (7.50)
CO	0.37	0.24	0.26	0.12	0.17	0.24	0.19	0.38	0.04	0.04	0.03
CO <sub>2</sub>	8.90	4.50	5.93	8.27	11.11	3.52	2.30	5.18	8.18	8.70	7.09
C <sub>1</sub> -C <sub>4</sub>	0.25	0.19	0.14	0.25	0.21	0.35	0.29	0.59	0.44	0.46	0.38
Oil	5.4 (3.1) <sup>d</sup>	2.1	3.3	5.4 (3.1)	8.5	16.9	10.0	12.6	13.0	13.3	13.4
Asphaltene	2.8	2.6	0.7	2.3	2.1	9.2	5.4	3.2	19.9	21.6	19.5
Preasphaltene	9.1	4.5	5.8	7.6	7.1	14.9	11.4	10.1	26.9	25.1	22.9
H <sub>2</sub> content, dmmf, wt%											
H <sub>2</sub> gas	0.72	0.20	0.28	0.44	0.43	1.92	1.35	1.34	1.64	1.70	1.73
H <sub>2</sub> -donor, wt%											

a) Including fresh raw coal (Raw); vacuum-dried at 100°C for 2 h (VD); air-dried at 100°C for 2 h (AD). b) The gas yields determined by weighing the microreactor before reaction and after releasing the gaseous products. c) The figures in parentheses are the gas yields determined by GC and volumetric analyses. d) Yield of physically recovered oil.

Table 2. Effects of Water Addition on Liquefaction of DECS-8 Wyodak Coal at 350 °C for 30 min in 1-Methylnaphthalene under 6.9 MPa H<sub>2</sub>

ID No.	53/65/95	9	28/74	92/141	121	5668/98	12	31/37	118	115	124/144	
Coal Sample <sup>a</sup>	Raw	VD-100°C-2 h	AD-100°C-2 h	VD-100°C-2 h	AD-100°C-2 h	Raw	VD-100°C-2 h	AD-100°C-2 h	Raw	VD-100°C-2 h	AD-100°C-2 h	
Solvent	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN	
Carrier (ATM)	--	--	--	--	ATM	ATM	ATM	ATM	ATM	ATM	ATM	
H <sub>2</sub> O Added	Original H <sub>2</sub> O	--	H <sub>2</sub> O added	H <sub>2</sub> O added	H <sub>2</sub> O added	--	--	--	H <sub>2</sub> O added	H <sub>2</sub> O added	H <sub>2</sub> O added	
Prod. dmmf, wt%												
Conversion	38.4	18.3	22.7	34.8	36.5	35.9	31.1	37.4	60.0	56.0	51.7	
Gas	6.4 <sup>b</sup>	7.34 <sup>c</sup>	5.1 (6.58)	6.4 (7.14)	8.9 (10.93)	3.2 (4.96)	2.6 (3.7)	3.0 (5.8)	5.7 (9.82)	5.8 (10.39)	6.8 (0)	
CO	0.14	0.16	0.25	0.11	0.16	0.14	0.11	0.19	0.04	0.05	0.04	
CO <sub>2</sub>	7.02	4.34	6.18	6.84	10.57	4.48	3.37	5.23	9.46	9.99	8.54	
C <sub>1</sub> -C <sub>4</sub>	0.18	0.16	0.15	0.19	0.20	0.34	0.25	0.37	0.32	0.35	0.28	
Oil	15.9	1.1	4.2	11.2	12.2	10.4	6.1	10.3	25.3	15.4	15.5	
Araphene	6.6	5.8	4.0	7.1	6.9	10.4	10.1	8.1	9.6	13.2	9.5	
Prearaphene	11.4	7.4	9.4	10.1	8.4	11.9	12.3	16.0	19.5	21.6	19.9	
H <sub>2</sub> gas	0.58	0.45	0.43	0.44	0.29	1.17	1.00	1.08	0.99	1.02	0.75	

H content, dmmf wt%

a) Including fresh raw coal (Raw); vacuum-dried at 100°C for 2 h (VD); air-dried at 100°C for 2 h (AD). b) The gas yields determined by weighing the microreactor before reaction and after releasing the gaseous products. c) The figures in parenthesis are the gas yields determined by GC and volumetric analyses.

Table 3. Effects of Water Addition on Liquefaction of DECS-8 Wyodak Coal at 350 °C for 30 min in Tetralin under 6.9 MPa H<sub>2</sub>

ID No.	52/6494	8	27/93/β3a	91/140	120	55/67/97	11	3026	117	114	123/143
Coal Sample <sup>a</sup>	Raw	VD-100°C-2 h	AD-100°C-2 h	VD-100°C-2 h	AD-100°C-2 h	Raw	VD-100°C-2 h	AD-100°C-2 h	Raw	VD-100°C-2 h	AD-100°C-2 h
Solvent	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin
Catalyst (ATM)	-	-	-	-	-	-	-	-	-	-	-
H <sub>2</sub> O Addition	Original H <sub>2</sub> O	-	-	H <sub>2</sub> O added	H <sub>2</sub> O added	-	-	-	H <sub>2</sub> O added	H <sub>2</sub> O added	H <sub>2</sub> O added
Prod. amount, wt%											
Conversion	43.3	25.9	35.1	40.0	40.4	42.2	36.4	45.6	64.1	62.9	60.5
Gas	5.8 (7.7) <sup>c</sup>	4.2 (4.4)	5.4 (6.3)	6.0 (7.31)	7.1 (9.60)	2.8 (4.94)	3.0 (2.9)	3.9 (5.47)	5.9 (9.67)	6.2 (8.96)	5.7 (8.10)
CO	0.11	0.19	0.24	0.10	0.19	0.14	0.13	0.21	0.05	0.04	0.03
CO <sub>2</sub>	7.41	4.10	5.91	7.01	9.20	4.45	2.58	4.83	9.27	8.57	7.79
C <sub>1</sub> -C <sub>4</sub>	0.19	0.15	0.19	0.20	0.21	0.35	0.28	0.43	0.35	0.35	0.28
Oil	15.8	4.1	11.7	14.0	16.6	16.0	10.2	15.7	18.2	20.8	18.1
Asphaltene	9.3	7.6	7.4	10.5	5.9	11.5	12.9	11.1	13.9	13.8	9.3
Preasphaltene	12.4	10.0	10.6	7.9	10.8	11.9	10.6	14.9	26.1	22.0	27.4
H <sub>2</sub> consum, dm <sup>3</sup> /wt%											
H <sub>2</sub> gas	0.67	0.29	0.24	0.48	0.19	1.21	1.35	1.36	1.07	1.37	0.81
H <sub>2</sub> -donor sol	0.28	0.41	0.47	0.36	0.42	0.24	0.08	0.14	0.28	0.22	0.26

a) Including fresh raw coal (Raw); vacuum-dried at 100°C for 2 h (VD); air-dried at 100°C for 2 h (AD). b) The gas yields determined by weighing the microreactor before reaction and after releasing the gaseous products. c) The figures in parenthesis are the gas yields determined by GC and volumetric analyses.

**Table 4. Effect of Water Addition on Thermal Liquefaction of DECS-9 Coal at 400 °C**

ID No.	73	133/162	60	135/164	59/87	134/163
Coal Sample <sup>a</sup>	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h
Solvent	Solvent-free	Solvent-free	1-MN	1-MN	Tetralin	Tetralin
Catalyst (ATTM)	-	-	-	-	-	-
H <sub>2</sub> O Addition	-	H <sub>2</sub> O added	-	H <sub>2</sub> O added	-	H <sub>2</sub> O added
Prod. dmmf wt%						
Conversion <sup>b</sup>	30.3	35.4	38.2	43.1	71.4	73.1
Gas	8.8 <sup>b</sup> (7.6) <sup>c</sup>	12.3 (12.54)	8.5 (9.78)	10.3 (12.45)	8.4 (9.37)	10.3 (12.39)
CO	0.41	0.21	0.25	0.25	0.33	0.25
CO <sub>2</sub>	6.35	11.26	8.56	10.75	7.80	10.55
C <sub>1</sub> -C <sub>4</sub>	0.85	1.07	0.97	1.45	1.24	1.59
Oil	10.4 (5.3) <sup>d</sup>	16.1	13.1	20.7	27.3	32.0
Asphaltene	1.8	2.2	7.4	6.1	16.4	16.3
Preasphaltene	10.5	4.8	9.2	6.0	19.3	14.4

a) Including fresh raw coal (Raw); vacuum-dried at 100°C for 2 h (VD); air-dried at 100°C for 2 h (AD).

b) The gas yields determined by weighing the microreactor before reaction and after releasing the gases.

c) The figures in parenthesis are the gas yields determined by GC and volumetric analyses. d) Recovered oil.

**Table 5. Effect of Water Addition on Catalytic Liquefaction of DECS-9 Coal at 400 °C**

ID No.	148/155	136/165	150/157	138/167	149/156	137/166
Coal Sample <sup>a</sup>	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h
Solvent	Solvent-free	Solvent-free	1-MN	1-MN	Tetralin	Tetralin
Catalyst (ATTM)	ATTM	ATTM	ATTM	ATTM	ATTM	ATTM
H <sub>2</sub> O Addition	-	H <sub>2</sub> O added	-	H <sub>2</sub> O added	-	H <sub>2</sub> O added
Prod. dmmf wt%						
Conversion	85.4	62.1	70.9	61.8	83.6	80.3
Gas	7.5 <sup>b</sup> (10.1) <sup>c</sup>	11.4 (11.23)	7.3 (9.91)	9.7 (12.82)	7.7 (9.74)	9.7 (12.73)
CO	0.10	0.02	0.18	0.02	0.17	0.03
CO <sub>2</sub>	7.39	9.57	7.87	11.31	7.71	11.14
C <sub>1</sub> -C <sub>4</sub>	2.61	1.64	1.86	1.49	1.86	1.56
Oil	45.8	28.2	34.0	28.1	36.4	34.0
Asphaltene	19.7	10.5	12.8	10.7	16.9	14.9
Preasphaltene	12.4	12.0	16.9	13.3	22.6	21.7
H <sub>2</sub> consum. dmmf wt%						
H <sub>2</sub> gas	2.80	1.38	1.81	0.90	1.75	0.72

a) Including fresh raw coal (Raw); vacuum-dried at 100°C for 2 h (VD); air-dried at 100°C for 2 h (AD).

b) The gas yields determined by weighing the microreactor before reaction and after releasing the gases.

c) The figures in parenthesis are the gas yields determined by GC and volumetric analyses.