

Influence of Drying and Oxidation of Coal on its Catalytic and Thermal Liquefaction. 1. Coal Conversion and Products Distribution.

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INTRODUCTION

Most of the subbituminous coals contain more than 25 wt % of moisture and it is considered an economic necessity to dry these coals prior to liquefaction. The drying of coal can have significant effect on the conversion reactivity of coal. Atherton (1) reported that the drying of low rank subbituminous coal in a gas atmosphere did not effect the total conversion except in air. The air-drying gave somewhat lower conversion, which may be a result of the adverse effect of preoxidation. The best conversion was obtained by vacuum and microwave drying. The oxidation of coal has been known to have an adverse effect on the coal conversion. Neavel (2) reported a significant reduction in the yield of benzene soluble products from hvc bituminous coal as a result of oxidation. Cronauer et al. (3) reported that partial drying of subbituminous coal in a mixture of nitrogen and oxygen or even in nitrogen alone reduced the conversion as compared to that of the raw coal. On the other hand, Vorres et al. recently reported that drying improves the oil yield in liquefaction of lignite samples (4)

In the present study we report the influence of drying Wyodak subbituminous coal in air and vacuum on the THF-conversion in thermal and catalytic liquefactions. From our results it appears that the drying of coal in air to some extent, which has been considered to be worse for liquefaction, may give a better conversion with dispersed Mo catalyst compared to the vacuum-dried coal in the presence of a liquefaction solvent. The raw coal was also subjected to liquefaction. Best conversion was obtained from the raw coal in the thermal and catalytic solvent-free run. In presence of solvents during catalytic runs the raw coal did not show any improvement over the thermal runs.

EXPERIMENTAL

The coal used was Wyodak subbituminous coal (DECS-8). This coal contains 32.4 % volatile matters, 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 coal was dried under vacuum for 2 h at 100 °C. The drying of coal in air was done in an oven maintained at 100 and 150 °C with the door partially open. At 100 °C the coal was dried for 2, 20 and 100 hours and at 150 °C it was dried for 20 hours. The liquefaction was carried out at 350 °C for 30 minutes under 7 MPa (cold) H₂ in 25 ml tubing bomb. Ammonium tetrathiomolybdate (ATTM) was used as precursor for molybdenum sulfide catalyst. It was loaded on to coal by incipient wetness impregnation method from aqueous solution with 1 wt % Mo on dmmf basis. The impregnated coal samples were dried in a vacuum oven at 100 °C for 2 h. The experimental details about the liquefaction and the product work up is given elsewhere (5). The total conversion (TC) of the coal into soluble products have been calculated on the basis of the THF-insoluble residues. The analysis of the gases evolved during liquefactions at 350 °C show that the major components of the gases are CO and CO₂. The total yield of the hydrocarbon gases produced is less than 1 wt % dmmf coal, in all the liquefaction runs.

RESULTS AND DISCUSSION

Solvent-free Liquefaction

The products distribution for the solvent-free thermal liquefactions are given in Table 1. As compared to the vacuum-drying the air-drying of coal at 100 °C for up to 100 h did not effect the total conversion on the basis of THF-insoluble residue. But the total gas yield increased with the drying time in air. This increase is mainly due to the increase in the CO and CO₂ yields (Table 3) at the expense of other products which is undesirable. The drying in air, oxidizes the coal, increasing the carboxylic and carbonyl functionalities which upon thermolysis produce CO₂ and CO gases. Upon excessive oxidation at 150 °C for 20 h the coal conversion slightly decreased but the gas yield increased considerably, which was accompanied by the decrease in the oil, asphaltene and preasphaltene yields. Since the main constituent of the gas is CO₂ which is associated with air-oxidation, it would be more appropriate to see the effect of drying on the desirable products. Figure 1 shows the distributions of the liquid and solid products in the

solvent-free thermal liquefaction experiments. It is clear that compared to the vacuum-drying, the air-drying of coal at 100 °C for up to 20 h increases the oil yield with no significant effect on the total conversion into THF-soluble products in thermal runs. But oxidative drying for the extended period of time decreases the total conversion as well as the oil yield because of the extensive degradation of the coal.

As with the vacuum-dried coal, the presence of catalyst in the solvent-free runs of the air-dried coal increases the total conversion compared to that of the thermal runs on the basis of THF-insoluble residues (Table 2). Similar to the thermal runs, in catalytic liquefactions the drying of coal in air at 100 °C for up to 100 h does not show any significant effect on the total conversion as compared to that of the vacuum-dried coal. The gas yields in the catalytic runs are lower than in the corresponding thermal runs with the most contribution from CO₂ and also increases with the drying time. If the conversion is calculated excluding the gas yield, the air-dried coal at 100 °C for up to 20 h does not show any effect but for the drying time of 100 h and at 150 °C for 20 h there is a considerable decrease in the conversion compared to that of the vacuum-dried coal (Figure 1). Over all, the increase in total conversion for the air-dried coal in catalytic runs over the thermal runs is similar to that for the vacuum-dried coal (Table 2 and Figure 1).

As-received coal (raw) was also subjected to thermal and catalytic liquefactions. The products distribution is given in Tables 1 and 2. Surprisingly, best values for the total conversions are obtained in the solvent-free thermal (25.0 wt%) and catalytic (43.3 wt%) runs on the basis of THF-insoluble residue compared to the vacuum- (12.5 and 29.8 wt%, respectively) and air-dried coal (14.8 and 29.2 wt%, respectively, for 2 h drying time). Significant increase in the oil yield is also observed from the raw coal compared to the dried coal. There is also a higher gas yield from the raw coal in thermal run compared to the vacuum- and air-dried coal at 100 °C for upto 20 h (Table 3). The increase in the gas yield is mainly due to the remarkable increase in the CO and CO₂ yields. The increase in the CO and CO₂ gases is due to the presence of water in the coal. It has been reported that the presence of water in the oxidized coal may enhance the removal of oxygen-containing groups (6). It appears that the presence of water during liquefaction removes the carbonyl functionalities from the coal network which makes the coal less refractory for liquefaction and hence improved conversion. The total-conversions excluding the gas yield shown in Figure 1, are the best in the case of the raw coal both in the solvent-free thermal and catalytic runs.

Liquefaction in Presence of Tetralin

It is known that the presence of a hydrogen donor solvent during liquefaction, enhances the total conversion of a coal to THF-soluble products as compared to the solvent-free runs. In the presence of tetralin during thermal runs the increase in total conversion of the vacuum-dried and air-dried coal is quite remarkable but, relatively, air-dried coal shows more increase in conversion (Table 1 and 2). The vacuum-dried coal shows an increase of 13.4 % (12.5% excluding gas yield) while the total conversion for the air-dried coal for 2 h at 100 °C increases by 20.3 % (19.9% excluding gas yield). The coal dried in air for 20 and 100 h at 100 °C also show a remarkable increase in conversion in the presence of tetralin but the increase is not as much as for the coal dried for 2 h. The oil yield for the air-dried coal for 2 h at 100 °C increases from 3.3 % to 11.7% with an increase of 8.4% in presence of tetralin, correspondingly, the increase in the oil yield for the vacuum-dried coal is only 2.0%. The oil yield for the coal dried at 100 °C in air for 20 h is also better than that of the vacuum-dried coal. The increase in the asphaltene and preasphaltene yields in presence of tetralin as compared to that of the solvent-free runs for the air-dried for 2 h and vacuum-dried coal are not significantly different. As the coal was dried in air for longer periods of time at 100 °C the increase in the oil production declined. The coal dried in air for 20 h at 150 °C showed only an increase of 1.5%. These results show that in thermal runs with tetralin the air-dried coal at 100 °C for up to 20 h gives better conversion and oil yield compared to the vacuum-dried coal (Figure 2). This suggests that the oxidation of a coal to some extent may enhance the oil yield and the total conversion but excessive oxidation of coal may have a negative effect.

The total conversion for the raw coal is 43.3% (37.5%, excluding gases) in thermal liquefaction in the presence of tetralin (Table 1). This conversion is undoubtedly better than the air-dried or vacuum-dried coal runs. Raw coal liquefaction gives an oil yield of 15.8% with an increase of 10.4% over the solvent-free run. Increasing the oil yields in liquefaction experiments is most desirable. Compared to the air-dried or vacuum-dried coal the oil yield is better in the case of raw coal run (Figure 2).

In the catalytic liquefactions also there is a remarkable increase in the total conversion from that of the solvent-free runs in presence of tetralin. This increase is similar to that in the thermal runs for the air-dried coal at 100 °C and vacuum-dried coal (Tables 1 and 2). In the catalytic runs in presence of tetralin the air-dried coal at 100

°C gives better total conversion compared to the vacuum-dried coal, on the basis of THF-insoluble or the total yields of oil, asphaltene and preasphaltene (Table 2 and Figure 2). It seems that the extent of drying at 100 °C also does not decrease the total conversion. Unexpectedly, the liquefaction of the raw coal in presence of tetralin does not show any significant catalytic improvement in total conversion (Figure 2). In the catalytic liquefaction in presence of tetralin of the raw coal the total conversion is 42.2% (39.4% excluding gas yield) and is 43.3% (37.5% excluding gas yield) in the thermal runs with tetralin. The products distribution of the raw coal experiments are also quite similar. As seen before in the thermal runs the raw coal showed a remarkably higher conversion in presence of tetralin, compared to the air-dried coal (Table 1). In the catalytic runs the raw coal and the air-dried coal showed a very similar conversions (Table 2 and Figure 2). It seems that during liquefaction of the raw coal in presence of tetralin the catalyst is less active. The decrease in the H₂-consumption by the raw coal during catalytic liquefaction in presence of tetralin from that in the solvent-free run is much higher than that for the dried coal (Figure 4).

Liquefaction in the Presence of 1-Methylnaphthalene

It has been seen before that the presence of a non-donor solvent such as 1-methylnaphthalene (1-MN) also enhances the total conversion to some extent compared to that of the solvent-free runs. In the thermal liquefaction of the vacuum-dried coal the total conversion increases from 12.5% in the solvent-free run to 18.3% with 1-MN (Table 1). The difference is significantly high. The liquefaction of the air-dried coal in presence of 1-MN also show a considerable increase as compared to that of the solvent-free runs. Total conversions for the coal dried at 100 °C for 2 and 20 h in air increases from 14.8 and 15.5% to 22.4 and 24.1% respectively, in presence of 1-MN. These conversion figures are better than that of the vacuum-dried coal (Table 1). Even after excluding the gas yields, the conversion is better if the coal was dried at 100 °C for up to 20 h in air. (Figure 3). Upon drying coal for 100 h at 100 °C in air the total conversion decreases and it is worse for the extensively oxidized coal at 150 °C for 20 h.

The total conversion of the raw coal in the thermal liquefaction increases from 25.0% (17.3% excluding gas) in solvent-free run to 39.9% (34.0%, excluding gas) with 1-MN (Table 1). This increase is significantly higher than that of the air- or vacuum-dried coal. In the thermal runs with 1-MN the raw coal gives 19.7% more THF-soluble products excluding gas yield, compared to the vacuum-dried coal, which is remarkably higher than that of the air-dried coal. The most importantly the increase in the total conversion of the raw coal is due to the significant increase in the yield of the most desirable product, oil. The oil yield increases from 1.1% in the vacuum-dried coal to 15.9% in the raw coal.

The catalytic liquefaction of vacuum- or air-dried coal in presence of 1-MN improves the conversion. The best conversion is obtained in the case of air-dried coal at 100 °C. The extent of drying at this temperature does not seem to make any considerable difference in the conversion (Table 2 and Figure 3). The catalytic liquefaction of the raw coal in presence of 1-MN gives a total conversion of 35.9% on the THF-insoluble residue basis. This conversion is rather lower than that of the thermal liquefaction under similar conditions. The unusual decrease in the oil yield for the raw coal in the catalytic run compared to that in the thermal run may be an artifact which needs to be reconfirmed. As in the presence of tetralin, the liquefaction of the raw coal in the presence of 1-MN in the catalytic runs there is no improvement in the total conversion compared to the thermal runs. In the catalytic liquefaction in presence of 1-MN the best conversion obtained is with the coal-dried in air at 100 °C with a significantly higher oil yields compared to the vacuum-dried coal.

Hydrogen Consumption

Figure 4 shows the H₂-consumption profile for the thermal and catalytic liquefactions from H₂-gas and from tetralin.. There is a significant decrease in the H₂-consumption during thermal liquefaction if the coal is pre-dried. In the solvent-free thermal run the H₂-consumption increases with the drying time in air at 100 °C and also the consumption increases as the coal is dried at 150 °C for 20 h. With tetralin and 1-MN there is an initial decrease in the H₂-consumption from 2 h to 20 h drying time and then it increases with the increased oxidative drying of coal. This suggests that the oxidative drying of coal increases the H₂-consumption during liquefaction and the consumption is higher if no solvent is used. In the catalytic runs the oxidative drying of coal at 100 °C for up to 100 h does not seem to have any significant effect on H₂-consumption. When the coal is dried at 150 °C for 20 h a slight decrease in the H₂-consumption in the solvent-free catalytic liquefaction is observed otherwise in presence of a solvent the H₂-consumption is essentially the same. These results suggest that the H₂-consumption increases with the extent of oxidation in thermal liquefaction and in catalytic liquefactions the oxidation does not make any considerable difference.

The vacuum-dried coal shows a similar H₂-consumption value as that of the coal dried in air for 2 h in thermal as well as catalytic runs. But during thermal liquefaction of the raw coal the H₂-consumption is higher than that of the vacuum- and air-dried coal for 2 h. In the catalytic liquefaction of the raw coal in presence of solvents the H₂-consumption is not much different from that of the vacuum- or air-dried coal for 2 h, but in the solvent-free catalytic run the H₂-consumption is remarkably higher. These results may account for the better conversions in the case of raw coal liquefaction compared to that of the vacuum- or air-dried coal.

Hydrogen-transfer from tetralin (Figure 4) increases (in the thermal liquefactions) with the extent of oxidation of coal. Vacuum-dried and the raw coal show a lower H-transfer compared to that of the air-dried coal. In the catalytic runs the H-transfer from tetralin is relatively lower than that in the corresponding thermal run and does not make any noticeable difference as the coal is dried at 100 °C in air up to 100 h. When the coal is dried at 150 °C for 20 h the H-transfer is slightly higher. The vacuum-dried coal shows a lowest value for the H-transfer from tetralin in the catalytic run.

CONCLUSIONS

The air-dried coal at 100 °C for up to 20 h gave similar conversions as the vacuum-dried coal in the solvent-free thermal and catalytic liquefactions. In the presence of solvents, better conversions were obtained from the coal dried in air at 100 °C for 2 h compared to the vacuum-dried coal. The extensive oxidation of coal decreased the coal conversions in thermal as well as catalytic runs. These results suggests that air-drying of coal to some extent may be beneficial for liquefaction. The raw coal gave the best conversions in the solvent-free runs. The improved conversion seems to be due to the presence of water, which enhances the removal of carbonyl functionalities during liquefaction making coal network less refractory for liquefaction.

ACKNOWLEDGEMENTS

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Table 1. Products distributions (dmmf wt %) for the thermal liquefactions of the raw and dried coal at 350 °C with different solvents.

Drying Conditions.	Gas*	Oil	Asphal.	Preasp.	Total Conv.
Solvent-free					
Raw-undried	7.7 (9.5)	5.4	2.8	9.1	25.0
Air-dried,2h,100°C	5.0 (6.3)	3.3	0.7	5.8	14.8
Air-dried,20h,100°C	5.7 (7.3)	6.0	0.6	3.2	15.5
Air-dried,100h,100°C	8.5 (12.0)	1.2	0.7	3.3	12.7
Air-dried,20h,150°C	9.8 (13.2)	0.6	0.2	0.4	10.9
Vac.-dried,2h,100°C	3.3 (5.9)	2.1	2.6	4.5	12.5
Tetralin					
Raw-undried	5.8 (7.7)	15.8	9.3	12.4	43.3
Air-dried,2h,100°C	5.4 (6.3)	11.7	7.4	10.6	35.1
Air-dried,20h,100°C	5.9 (8.7)	11.1	6.5	8.9	32.4
Air-dried,100h,100°C	8.7 (11.6)	6.1	6.3	9.7	30.8
Air-dried,20h,150°C	11.8(16.6)	2.1	2.8	3.2	19.9
Vac.-dried,2h,100°C	4.2 (5.4)	4.1	7.6	10.0	25.9
1-Methylnaphthalene					
Raw-undried	5.9 (8.4)	15.9	6.6	11.4	39.9
Air-dried,2h,100°C	5.1 (7.6)	4.2	4.0	9.4	22.7
Air-dried,20h,100°C	6.2 (7.5)	8.0	5.6	4.7	24.5
Air-dried,100h,100°C	9.0 (12.7)	1.7	4.1	6.3	21.1
Air-dried,20h,150°C	11.4(16.5)	1.8	2.2	2.5	18.0
Vac.-dried,2h,100°C	4.0 (5.7)	1.1	5.8	7.4	18.3

* The figures in parenthesis give the total gas yields calculated from GC analysis.

Table 2. Products distributions (dmmf wt %) for the catalytic liquefactions of the raw and dried coal at 350 °C with different solvents.

Drying Conditions.	Gas*	Oil	Asphal.	Preasp.	Total Conv.
Solvent-free					
Raw-undried	2.2 (4.3)	16.9	9.2	14.9	43.3
Air-dried,2h,100°C	3.3 (6.2)	12.6	3.2	10.1	29.2
Air-dried,20h,100°C	4.8 (6.8)	14.6	3.1	8.7	31.2
Air-dried,100h,100°C	7.6 (9.3)	13.3	2.4	5.1	28.4
Air-dried,20h,150°C	11.2(11.2)	5.1	0.5	1.7	18.5
Vac.-dried,2h,100°C	3.0 (2.9)	10.0	5.4	11.4	29.8
Solvent Tetralin					
Raw-undried	2.8 (4.9)	16.0	11.5	11.9	42.2
Air-dried,2h,100°C	3.9 (5.5)	15.7	11.1	14.9	45.6
Air-dried,20h,100°C	5.6 (7.4)	18.6	8.6	10.7	43.5
Air-dried,100h,100°C	6.7 (9.7)	16.5	10.8	11.0	45.0
Air-dried,20h,150°C	11.8(13.2)	9.6	2.3	5.7	29.4
Vac.-dried,2h,100°C	3.0 (2.9)	10.2	12.9	10.6	36.4
Solvent 1-MN					
Raw-undried	3.2 (5.0)	10.4	10.4	11.9	35.9
Air-dried,2h,100°C	3.0 (5.8)	10.3	8.1	16.0	37.4
Air-dried,20h,100°C	6.4(10.0)	14.1	8.7	10.5	39.7
Air-dried,100h,100°C	5.2(10.3)	14.4	8.7	11.1	39.4
Air-dried,20h,150°C	12.1(13.0)	5.3	2.8	4.3	24.5
Vac.-dried,2h,100°C	2.6 (3.7)	6.1	10.1	12.3	31.1

* The figures in parenthesis give the gas yields calculated from GC analysis.

Table 3. Gas yields (dmmf wt %) for the thermal and catalytic liquefactions.

Drying Conditions.	Thermal				Catalytic			
	CO	CO ₂	C ₁ -C ₄	Total	CO	CO ₂	C ₁ -C ₄	Total
Solvent-free								
Raw-Undried	0.37	8.90	0.25	9.52	0.24	3.52	0.35	4.26
Air-dried,2h,100°C	0.26	5.93	0.14	6.33	0.38	5.18	0.59	6.15
Air-dried,20h,100°C	0.39	6.70	0.16	7.25	0.42	5.67	0.71	6.79
Air-dried,100h,100°C	0.66	11.18	0.17	12.01	0.65	8.01	0.63	9.29
Air-dried,20h,150°C	0.80	12.32	0.09	13.21	0.94	9.76	0.54	11.24
Vac.-dried,2h,100°C	0.24	4.50	0.19	5.93	0.19	2.30	0.29	2.88
Tetralin								
Raw-Undried	0.11	7.41	0.19	7.72	0.14	4.45	0.35	4.94
Air-dried,2h,100°C	0.24	5.91	0.19	6.35	0.21	4.83	0.43	5.47
Air-dried,20h,100°C	0.28	7.18	0.28	8.74	0.17	6.86	0.36	7.39
Air-dried,100h,100°C	0.46	10.95	0.22	11.63	0.36	8.80	0.51	9.67
Air-dried,20h,150°C	0.59	15.87	0.11	16.58	0.41	12.43	0.38	13.20
Vac.-dried,2h,100°C	0.19	4.10	0.15	5.44	0.13	2.58	0.28	2.99
1-Methylnaphthalene								
Raw-Undried	0.14	7.02	0.18	8.45	0.14	4.48	0.34	4.96
Air-dried,2h,100°C	0.25	6.18	0.15	7.59	0.19	5.23	0.37	5.79
Air-dried,20h,100°C	0.28	7.04	0.15	7.48	0.18	9.26	0.51	9.95
Air-dried,100h,100°C	0.50	11.95	0.21	12.67	0.32	9.50	0.44	10.26
Air-dried,20h,150°C	0.65	15.69	0.12	16.47	0.33	12.36	0.32	13.01
Vac.-dried,2h,100°C	0.16	4.34	0.16	5.66	0.11	3.37	0.25	3.73

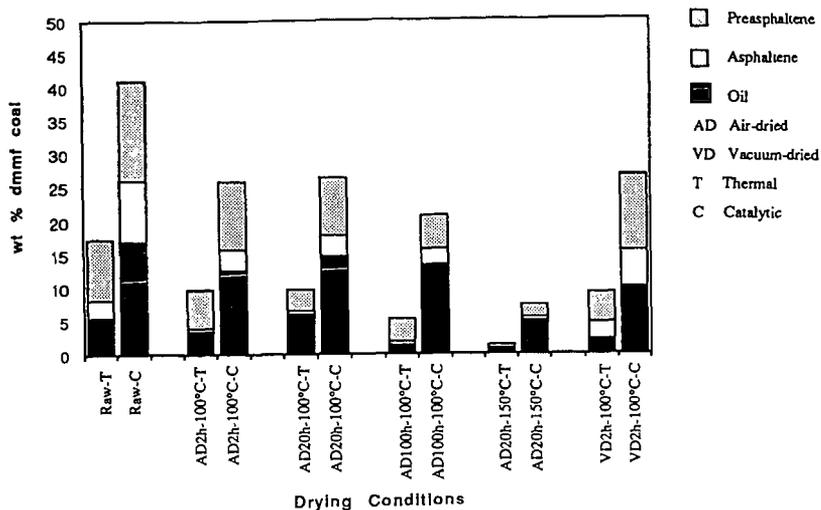


Figure 1. Products distribution from solvent-free thermal and catalytic liquefactions at 350 °C of the raw and coal dried in different conditions.

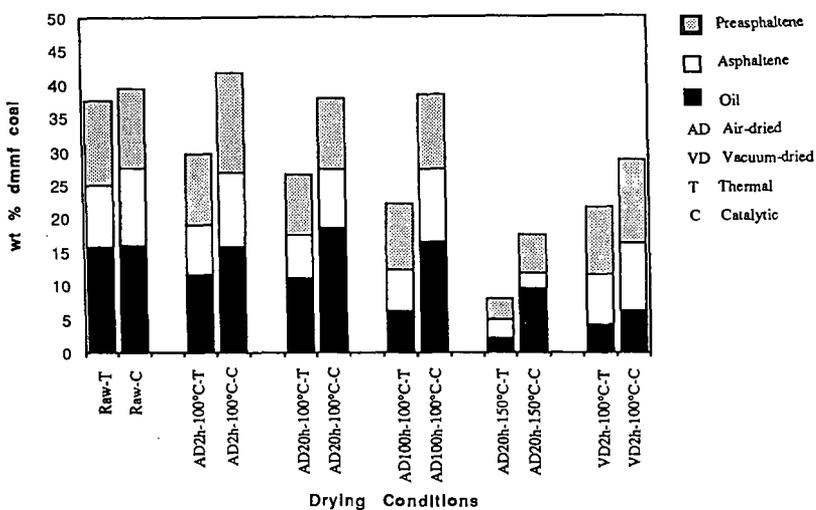


Figure 2. Products distribution from the thermal and catalytic liquefactions in the presence of tetralin at 350 °C of the raw and coal dried in different conditions.

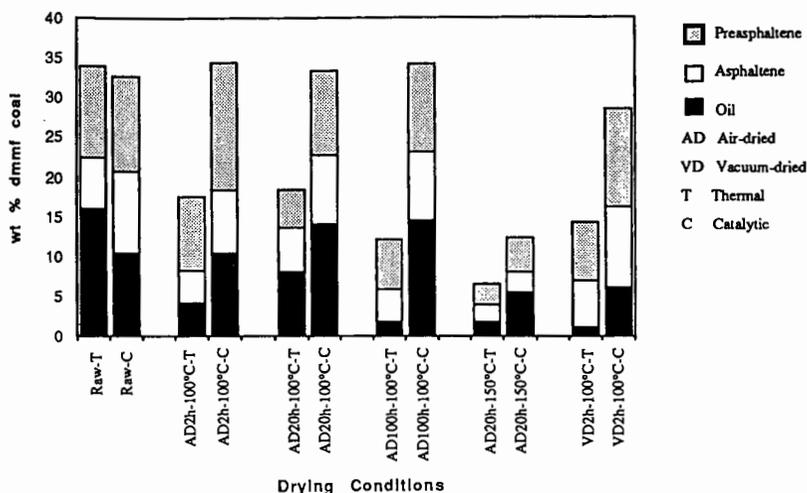


Figure 3. Products distribution from the thermal and catalytic liquefactions in the presence of 1-methylnaphthalene at 350 °C of the raw and coal dried in different conditions.

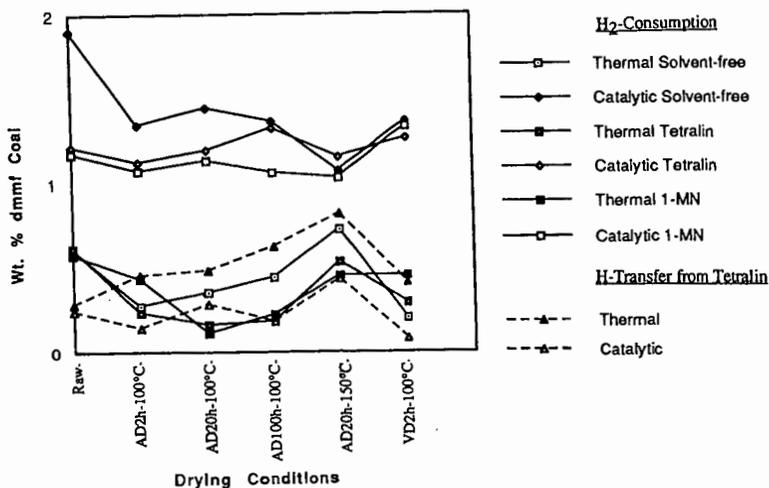


Figure 4. Hydrogen consumption profiles during thermal and catalytic liquefactions from H₂ and tetralin.