

Influence of Drying and Oxidation of Coal on Its Catalytic and Thermal Liquefaction. 2. Characterization of Dried and Oxidized Coal and Residues.

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INTRODUCTION

Because of the high moisture content of the low rank coals it is desirable to dry coal before liquefaction. It has been recognized that drying of coal could adversely affect the reactivity of subbituminous coal for liquefaction (1,2). This study has been carried out with a view to understand the effect of low temperature oxidative and non-oxidative drying on coal structure and liquefaction residues. In the preceding paper the impacts of coal drying on the liquefaction have been discussed (3).

Several papers have been devoted to understanding the oxidation of coal (4-10) but very little has been reported on the effect of oxidation on the structures of liquefaction residues which could lead to an insight of the oxidative effect on liquefaction. In the present work we have analyzed the residues from thermal as well as catalytic liquefactions of the raw and dried coal under vacuum and in air. The analysis of the residues reveal that although there is a significant decrease in the aliphatics upon oxidative drying of coal compared to the vacuum dried coal the residues from the air-dried coal are more aliphatic rich, and as the oxidation proceeds more longer-chain aliphatics are lost during liquefaction. The raw coal shows an enhanced loss of carbonyls during liquefaction, which may be the cause of its higher conversion.

EXPERIMENTAL

The coal used was Wyodak subbituminous obtained from the Penn State Sample Bank (DECS-8). The characteristics of coal are given elsewhere (11). For the raw coal liquefaction it was used as received. For the drying experiments the coal was dried under vacuum at 100 °C for 2 h and in air at 100 °C for 2, 20 and 100 h. At 150 °C coal was dried for 20 h. The air-drying of coal was done in a preheated oven at desired temperature with the door slightly open to ensure the sufficient air supply. The thermal and catalytic liquefactions of coal were carried out at 350 °C under 6.9 MPa (cold) H₂ pressure for 30 minutes. Ammonium tetrathiomolybdate (ATTM) was used as catalyst. It was loaded on to coal by incipient wetness impregnation method from aqueous solution, with 1 wt % Mo on dmmf coal. After the reaction, the liquid and solid products were separated by sequential extraction with hexane, toluene and THF. After the extraction the THF-insoluble residues were washed first with acetone and then pentane in order to remove all the THF, followed by drying at 110 °C for 6 h under vacuum. The coal and residues were analyzed by Py-GC-MS, solid state CPMAS ¹³C NMR and FTIR techniques discribed elsewhere (12, 13).

RESULTS AND DISCUSSION

Characterization of the Raw and Dried Coal

CPMAS ¹³C NMR

Figure 1 compares between the CPMAS ¹³C NMR spectra of the raw coal and the vacuum and air-dried coal. The raw coal and the dried coal show similar NMR features. The region between 0-80 ppm consists of aliphatic carbons which may include methoxy carbons and the second region between 90 to 170 ppm is due to the aromatic carbons including two shoulders due to catechol-like and phenolic carbons (11). The carboxylic band appears at 170-190 ppm and carbonyl group between 190-230 ppm. Upon drying coal under vacuum there was no noticeable difference in the NMR spectrum as compared to that of the raw coal. When the coal was dried in air a slight difference seems to be apparent but not very significant until the coal was dried at 100 °C for 100 h or at 150 °C for 20 h. It appears that as the coal was dried under oxidative conditions there was a decrease in the intensity of the catechol shoulder. The other change seems to be the broadening in the carboxyl and carbonyl bands. These changes in the coal structure becomes apparent when the coal was dried in air under severe conditions. After drying coal at 150 °C for 20 h the CPMAS ¹³C NMR shows a complete disappearance of the catechol peak and the

carboxyl and carbonyl peaks also show significant broadening, seems to be merging into the aromatic band. The oxidation of coal significantly decreases the aliphatics from the coal. From NMR the decrease in aliphatics is not apparent when coal is dried at 100 °C, but after drying at 150 °C the aliphatic band shows a significant decrease.

FTIR

Obvious difference in the FTIR spectrum of the dried coal compared to that of the raw coal is the decrease in the broad water band between 3000-3600 cm^{-1} which is apparent from the direct comparison of the spectra. The drying of coal in air is known to oxidize the coal causing increase in the ketone, carboxyl and ester type functionalities and decrease in the aliphatic groups. Such changes in the functionalities of the coal upon oxidation at 100 °C were not apparent from direct comparison of the spectra. The difference FTIR technique was utilized to detect the minute spectroscopic changes in the coal structure. Vacuum-dried coal was used as a reference for the difference spectra. The differences in coal structure arising due to oxidative drying of coal apparent from the difference FTIR spectra are consistent with the literature (4-10). The difference spectra show a prominent peak at 1720 cm^{-1} due to carbonyl which increases in intensity with the severity of drying. There is another shoulder on the high energy side of the 1720 cm^{-1} band near 1770 cm^{-1} which also increases with the severity of drying. This band could be assigned to the ester groups. The band at 1640 cm^{-1} in the difference spectra can be assigned to the highly conjugated carbonyls formed by the oxidation of the methylene bridges linking aromatic units (Ar-CH₂-Ar) which are highly susceptible to autooxidation forming Ar-CO-Ar groups. As the oxidative drying at 100 °C proceeds the band at 1720 cm^{-1} due to carboxyl carbonyls seem to be increasing at a faster rate than 1640 cm^{-1} band. This band may also contain carbonyls in unconjugated ketones. After drying coal at 150 °C for 20 h in air the 1720 cm^{-1} band becomes more intense relative to the 1640 cm^{-1} band. A broad band between 1500 and 1590 cm^{-1} also becomes apparent in the difference spectra of the dried coal. This band is assigned to the carboxylate (COO-) groups which increase upon oxidative drying of coal. After drying coal at 150 °C the broad band at 1550 cm^{-1} in the difference spectrum due to the carboxylate carbonyls (-COO-) which is just a broad shoulder in the case when coal was dried at 100 °C, becomes an independent peak. The increase in the intensity of the 1550 cm^{-1} band could be related to the increase in the carboxylic functional groups upon oxidation followed by exchange with cations present in the coal to give COO. The region between the range 1000 and 1300 cm^{-1} consists of the bands due to C-O type of linkages in ethers, esters and phenols. Upon oxidative drying at 100 °C there is a slight increase in the intensity of the ether region.

Pyrolysis-GC-MS

The major aromatic components of wyodak subbituminous coal obtained upon pyrolysis have been reported previously (3). Low rank coals are known to have higher oxygen functionalities. The major oxygen compounds are phenol, methylphenol, ethylphenol, C₂-phenols and catechol and these are the most abundant components in the pyrogram of the raw coal. Among the alkylbenzenes the most abundant compounds identified are toluene, xylenes and C₃-benzenes. The other aromatic compounds such as naphthalene and alkyl-naphthalenes are also found but in a very low concentrations. There are many other peaks appearing over the whole pyrogram of the raw coal. These peaks have been identified as alkanes and alkenes ranging from C₄-C₃₁. The most abundant of these are C₄-C₆ alkanes and alkenes which appear in the early part of the pyrogram and are not very well resolved.

Upon drying coal under vacuum or in air the pyrogram is similar to that of the raw coal from which one can find identical peaks. The only difference is in the relative intensities of the peaks. Table 1 shows the ratios between the total area of the major phenolic and the alkylbenzene compounds in the pyrograms of the raw and the dried coal samples. The vacuum drying of coal did not change the phenolics to alkylbenzene ratio but oxidative drying of coal seems to have a significant effect on these ratios. For first two hours of drying coal in air at 100 °C the change is not very significant but as the extent of drying increases the ratio seems to be decreasing as if the phenolic structures are being consumed from the coal as the air-drying proceeds. After drying coal at 150 °C for 20 h the phenolic to alkylbenzene ratio decreases remarkably.

Using the selective ion chromatogram (SIC) technique for the 71 m/z ion the pattern of the abundances of the alkanes and alkenes can be recognized in the pyrogram of the coal. The SIC for the raw and the vacuum-dried coal using 71 m/z ion show a similar pattern. The most abundant are the C₄-C₆ alkanes and alkenes. Upon air-drying, coal shows a decrease in the intensities of the short chain aliphatic compounds. The extent of air-drying did not change overall pattern of the aliphatics, the SIC of aliphatics for all the air-dried samples looked similar.

Characterization of the Liquefaction Residues

FTIR

To investigate the differences in the structure of the residues from the raw and air-dried coal and to understand the liquefaction behavior of the coal dried under different conditions, the residues from the vacuum dried coal were used as reference for the FTIR difference spectra. The vacuum dried coal residues were subtracted from that of the raw and the air-dried coal. The subtraction factors were calculated on the basis of the amount of organic matters left in the residues after liquefactions and calculated by the ratio of the amount of dmmf coal per mg of the pellet keeping the diameter of the pellet constant. Before discussing the differences in coal structure using difference technique, it should be noted that the frequencies of the bands in the difference spectra are not well defined and also the apparent frequencies of different bands can often be affected by the degree of subtraction and residual band overlap (8).

The difference spectra of the residues from the thermal runs show a significant differences in the coal structure as a consequence of air-drying (Figure 2). The major differences are in the carbonyl region (1500-1800 cm^{-1}). The raw coal shows a negative band at 1740 cm^{-1} which could be assigned to the ester and ketone groups. This band is negative, also in the case when tetralin or 1-methylnaphthalene was used as solvent suggesting that during liquefaction the raw coal losses more of carbonyl structures compared to the vacuum-dried coal. The enhanced loss of carbonyls from the raw coal can also be accounted by the relative increase in the CO_2 and CO gas yields compared to the vacuum-dried coal. The residues from the air-dried coal also show a significantly higher loss of ester groups as indicated by the negative dip in the ester region of the difference spectra. But, there is also a positive band at 1700 cm^{-1} which could be assigned to the carboxylic groups. The carboxylic band increases with the extent of oxidation. The increase in the carboxylic functionalities in the residues could also be noticed by the broad band centered at 1590 cm^{-1} . This band is assigned to the carboxylate (COO^-) groups. The increase in these functionalities is the consequence of increase in the carboxylic groups upon oxidation of coal. This band may also have slight contribution from the aromatic $\text{C}=\text{C}$ stretching which appears at 1610 cm^{-1} .

In the aliphatic region between 2700-2950 cm^{-1} the raw coal shows no significant change in the band (Figure 2). But, relative to the vacuum-dried coal the residues from the air-dried coal show a significantly higher aliphatic content shown by the positive aliphatic bands. This is only true when coal was dried in air at 100 °C but for the coal dried at 150 °C for 20 h the aliphatic region shows a negative change. The increase in the aliphatics in the residues from air-drying at 100 °C is interesting because the unreacted air-dried coal show a decrease in the aliphatics because of the oxidation of some of the aliphatic groups. It appears that during liquefaction, the air-dried coal at 100 °C has retained more of the aliphatic components of the network as compared to that of the vacuum-dried coal. The negative aliphatic band in the case of the coal dried at 150 °C could be due to the extensive loss of these groups initially during air-drying. In the presence of tetralin or 1-MN also the air-dried coal showed an increase in the aliphatics.

Same criteria was adopted, as for the thermal runs, to obtain the FTIR difference spectra for the residues from the catalytic runs. Compared to the thermal runs, the difference spectra for the catalytic runs did not show any significant differences. Similar to the thermal runs, the residues from the air-dried coal at 100 °C were found to be more aliphatic and carbonyl rich compared to the vacuum dried coal. The residues from the tetralin and 1-MN runs also showed similar difference spectra except that the raw coal seemed to be aliphatic richer in the catalytic runs.

More significant differences in the thermal and catalytic runs were observed when the difference spectra were obtained between the residues from thermal and catalytic runs (Figure 3). The FTIR spectra of the catalytic runs were subtracted from that of the thermal runs. The negative mineral matter bands (1010 and 1035 cm^{-1}) in the difference spectra of the thermal and catalytic runs are the signs for more conversion of coal during catalytic runs. In the case of the raw coal the mineral matter bands are negative only in the solvent free runs may be because in the presence of solvents the raw coal did not show any significant difference in conversions between thermal and catalytic runs. The negative aliphatic bands in the difference spectra of the solvent-free runs clearly showed that during thermal runs more aliphatic compounds were lost in all the cases except when coal was oxidized at 150 °C. The differences in the aliphatic contents in the solvent runs were not very clear probably due to the differences in the addition of solvents during liquefaction. In the carbonyl region positive bands near 1700 and 1550 cm^{-1} were observed in the solvent-free as well as solvent runs. The first band could be due to ketone and carboxylic groups and the second band could be assigned to the carboxylate ions. It suggests that the residues from the thermal runs are

richer in such functionalities. The ether region between 1100-1300 cm^{-1} also showed significantly intense positive bands which clearly suggests that more of ether type bonds are broken during catalytic liquefaction compared to that of the thermal runs. At the high oxidation level the ether region did not show any noticeable difference in the ether contents of the thermal and catalytic residues. The most significant difference was observed in the coal dried at 100 °C.

Pyrolysis-GC-MS

Compared to the raw coal the residues from the thermal solvent-free liquefactions show similar pyrolysis compounds, that is one can identify the same compounds in the raw coal as well as in residues. The differences in the pyrograms appear to be in the relative abundances of the compounds. Table 1 gives the ratios between phenolic and alkylbenzene compounds. For these ratios same compounds have been used as for the raw coal mentioned above. These ratios indicate the variations in the chemical composition of the aromatic compounds in the coal network as a consequence of different treatments to coal. After solvent-free thermal liquefaction of the raw coal the phenolic to alkylbenzene ratio decreases remarkably compared to that of the unreacted coal. Similar decrease is observed for the air-dried coal at 100 °C for 2 h and the vacuum-dried coal. For the coal dried at 100 °C for 20 and 100 h and dried at 150 °C there is no significant change in this ratio. From the catalytic solvent-free liquefaction the phenolic to alkylbenzene ratios of the residues are slightly higher than that of the corresponding residue from the thermal run but it is still lower than that of the unreacted coal. It appears that as the oxidative drying proceeds the difference in the phenolic to alkylbenzene ratio between the unreacted coal and the liquefaction residue decreases. Eventually at extensive oxidation of coal this ratio becomes same for the unreacted coal and its liquefaction residue.

Figure 4 compares of the pattern of the aliphatics present in the pyrogram of the residues from solvent-free thermal runs. Noticeable differences can be seen in the relative intensities of the aliphatics compared to that of the corresponding unreacted coal. In the residues from the raw and vacuum dried coal there is an appreciable decrease in the intensities of the shorter chain relative to the longer chain aliphatics, which has been noticed before with different coals too. For the air-dried unreacted coal, as mentioned before the pattern of the aliphatics in the pyrogram remains similar with the extent of drying, but for the residues the pattern is quite different. By comparing the residues from the air-dried coal at different extent of oxidation it appears that as the extent of oxidation increases more and more of longer chain aliphatics are lost during thermal liquefaction (Figure 4). It seems that for the air-dried coal the shorter chain aliphatics are strongly retained upon liquefaction. This phenomena was not observed for the catalytic runs.

All the pyrolysis compounds found in the pyrogram of the raw coal can also be identified in the pyrogram of the residues from the liquefactions in presence of solvents. Besides, there are several new bands which are known to have come from the adduction of solvent used during liquefaction (11). Some of these compounds are in most abundances. From the liquefaction runs in presence of tetralin the peaks due to the solvent are tetralin, dihydronaphthalene, naphthalene and 1 and 2-methylnaphthalenes. C2-naphthalenes may also be due to tetralin but are in a very low abundances. From the runs with 1-methylnaphthalene two solvent adduction bands are observed, naphthalene and 1-methylnaphthalene. In our previous work (11) we reported that the adduction of solvents could be either due to the formation of chemical bond between the solvent molecules and coal network or the solvent molecules could be physically entrapped in the micropores. From Figure 5 the adduction of solvent is apparent by the presence of tetralin, dihydronaphthalene, naphthalene and 1 and 2-methylnaphthalene peaks. It is clear that the extent of adduction of the solvents is remarkably effected by the extent of initial oxidation of the coal. Apparently, as the oxidation proceeds the relative intensities of the adducted compounds increases. Similar trend was observed in the case when 1-MN was used as solvent. The residues from the catalytic runs also show a similar trends in the adduction of solvents with the drying of coal but during catalytic runs the adduction seems to be lower as compared to the thermal run.

Not much difference is observed between the pyrograms qualitatively in Figure 5. All the pyrograms for the raw and dried coal under different conditions have the same compounds but there relative intensities are significantly different. Table 1 gives the phenolic to alkylbenzene ratios. These ratios have increased significantly for residues from the raw coal and for the coal dried in air at 100 °C for 2 h and under vacuum, compared to that of the solvent-free runs. But, for the 1-MN runs these ratios seems to be similar to that of the thermal runs. It seems that during solvent-free runs or in the presence of 1-MN more phenolic type units which produce phenolic compounds upon pyrolysis are lost. This phenomena seems to be true for raw, vacuum-dried coal and for the coal dried in air at 100 °C for 2 h. At the higher oxidative drying of coal the change in the ratios of the phenolic to alkylbenzene is not significant.

CONCLUSIONS

The characterization of the liquefaction residues reveal that the residues from the air-dried coal are more aliphatic and carbonyl rich compared to the vacuum-dried coal. The increase in the carbonyls is due to the oxidation of the coal upon air-drying. It appears that upon oxidation of coal at 100 °C more shorter chain aliphatics are retained in the coal network as compared to the vacuum-dried coal. The enhanced conversion of the unoxidized raw coal may be due to the enhanced loss of carbonyls upon reacting with water. The enhanced loss of carbonyls with water can make coal less refractory for liquefaction. The Py-GC-MS analysis of the residues suggests that the extent of oxidation can enhance the solvent adduction during liquefaction.

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Table 1. Ratios of the amounts of the phenolic compounds to the alkylbenzenes.

Drying Conditions	Unreacted Coal	Residues	
		Thermal	Catalytic
Solvent-Free			
Raw			
Air-dried, 2h, 100	3.8	1.9	2.8
Air-dried, 20h, 100°C	3.5	2.0	2.8
Air-dried, 20h, 100°C	2.5	2.4	2.6
Air-dried, 100h, 100°C	2.3	2.0	2.2
Air-dried, 20h, 150°C	1.1	1.2	1.6
Vacuum-dried	3.6	2.2	2.4
Tetralin			
Raw		2.5	2.9
Air-dried, 2h, 100		3.3	3.7
Air-dried, 20h, 100°C		2.8	3.3
Air-dried, 100h, 100°C		2.2	2.6
Air-dried, 20h, 150°C		1.4	1.5
Vacuum-dried		3.1	3.1
1-Methylnaphthalene			
Raw		2.2	2.0
Air-dried, 2h, 100		2.4	2.7
Air-dried, 20h, 100°C		2.4	2.8
Air-dried, 100h, 100°C		1.5	2.3
Air-dried, 20h, 150°C		1.3	1.1
Vacuum-dried		1.8	2.3

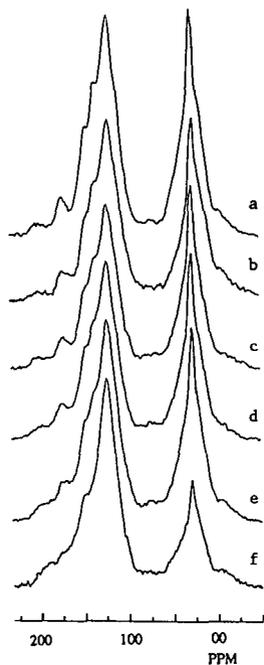


Figure 1. CPMAS ^{13}C NMR spectra of the coal a) raw, b) vacuum-dried at 100°C , dried in air at 100°C for c) 2 h, d) 20 h, e) 100 h, and f) dried at 150°C for 20 h.

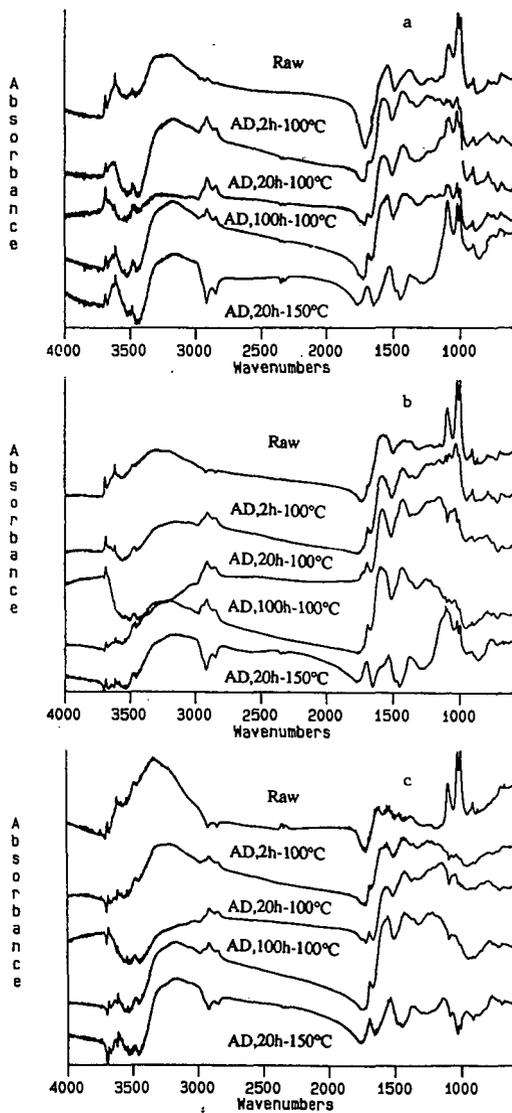


Figure 2. FTIR difference spectra for the residues from thermal liquefactions in a) solvent-free, b) tetralin, and c) 1-methylnaphthalene runs for the raw and air-dried (AD) coal.

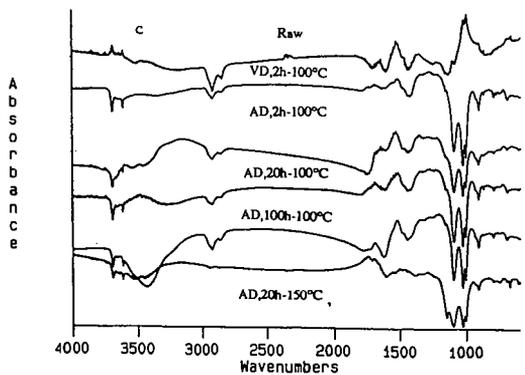
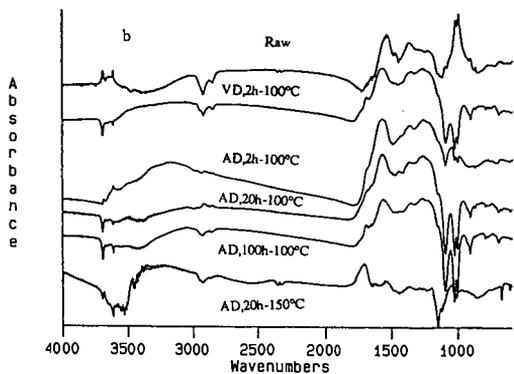
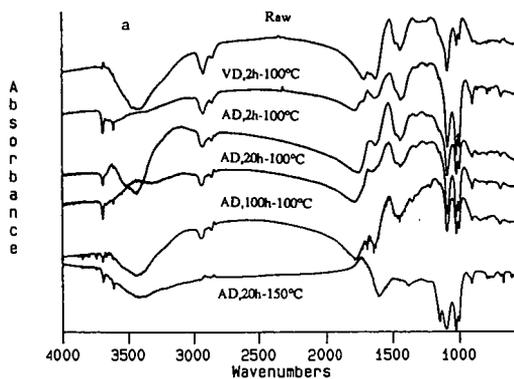


Figure 3. FTIR difference spectra between the residues from the thermal and catalytic a) solvent-free, b) tetralin and 1-methylnaphthalene runs for the raw, vacuum-dried (VD) and air-dried (AD) coal.

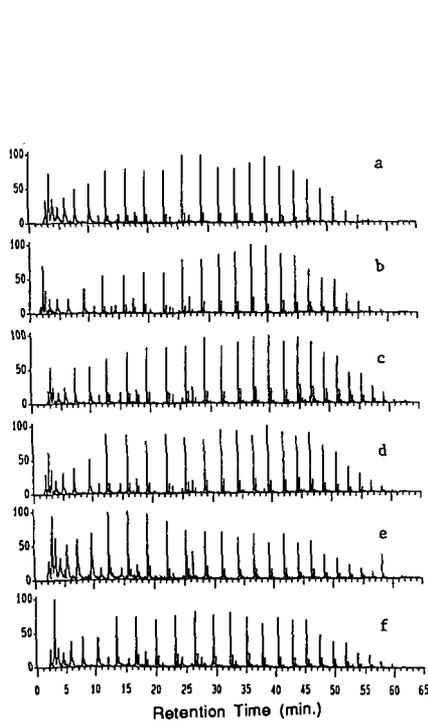


Figure 4. Selective ion monitoring of paraffins at m/z 71 from Py-GC-MS profiles of residues from thermal liquefactions of the coal a) raw, b) vacuum-dried at 100°C , dried in air at 100°C for c) 2 h, d) 20 h, e) 100 h, and f) dried at 150°C for 20 h.

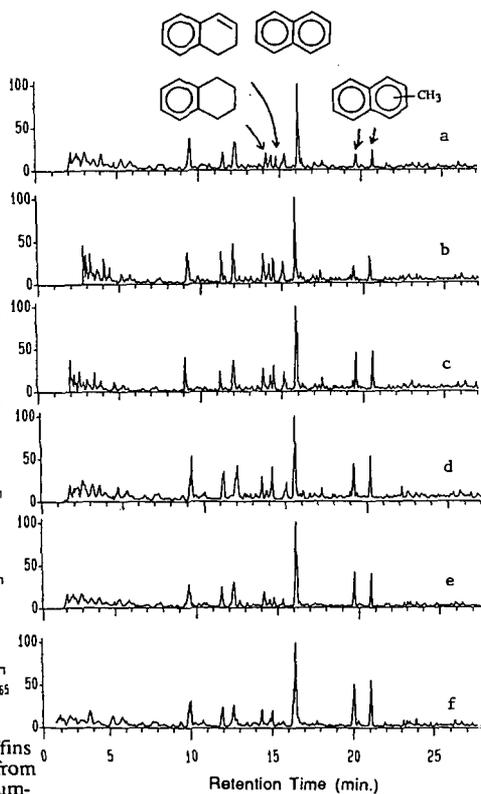


Figure 5. Py-GC-MS profiles of the residues from the thermal liquefactions in presence of tetralin of the coal a) raw, b) vacuum-dried at 100°C , dried in air at 100°C for c) 2 h, d) 20 h, e) 100 h, and f) dried at 150°C for 20 h.