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The effect of flame coal oxidation on the solid and soluble products of its extraction

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Abstract: Solid and soluble products of THF and CH_2Cl_2 extraction of flame coal oxidised by four different oxidising agents (peroxyacetic acid (PAA), 5 % HNO_3, O_2/Na_2CO_3, air/125 °C) were studied by elemental analysis and FTIR. The extraction yield with THF was much higher than that with CH_2Cl_2 for all samples. The greatest changes in elemental composition were in the extracts from coal oxidised by nitric acid. The sulphur content was lowest in extracts from coal oxidised with 5 % HNO_3 and PAA. FTIR confirmed that coal treatment with nitric acid incorporates nitrogen into the coal structure.

Keywords: Oxidised coal, extraction with THF, CH_2Cl_2, FTIR

1 Introduction

The great contribution of coal to energy production and recent concern over its sulphur content have prompted the search for effective and economical methods of coal desulphurisation. This requires a detailed understanding of coal structure. One effective method to study the chemical structure and physico-chemical properties of coal is oxidation with different oxidising agents [1-5].

Coal desulphurisation efficacy can be enhanced by extraction with appropriately chosen solvents. The extracts can be important products of coal processing used in many branches of industry, not just chemical. Moreover, after oxidation, solvent extraction is the most common technique for coal structure study [6].

The main factor determining the success of extraction is proper solvent choice. A good

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solvent should show two basic properties: it should cause swelling of raw coal and stabilise the coal extract in the liquid phase. The most commonly used solvents are pyridine [7-9], ethylenediamine [10], anthracene oil [11], dichloromethane [12,13], and tetrahydrofuran [14-19]. Strongly polar solvents such as pyridine [20,21] or tetrahydrofuran are used to enhance the extraction yield.

Beside the solvent, extraction yield depends on the properties and structure of the coal. For the majority of solvents, the extraction yield decreases with increasing degree of coalification. It decreases smoothly for coals containing up to 87 % C, then decreases very rapidly; coals of over 92 % C are practically insoluble [10]. Coal behaviour during extraction depends significantly on petrographic composition. It has been shown that the most soluble is vitrain; durain is less soluble, and fusain does not dissolve significantly [10].

Preliminary treatment of coal with NaOH or KOH and mineral acids (*e.g.* HCl, HF, HNO_3, H_2SO_4) removes the undesirable mineral components, which significantly affects the extraction yield and the extracts' properties [10,22]. Li *et al.* [23], among others, have shown that increasing the treating HCl concentration from 0.01 to 0.1 M leads to a significant increase in ash removal.

Extraction processes are mostly performed at room temperature [14], but the speed and yield of extraction usually increase with increasing temperature. Ouchi *et al.* [21] reported that raising the temperature from 200 to 400 °C caused an increase in yield from 20 to 50 % for enhanced pressure pyridine extraction of coal containing 81.2 % C. Similarly, the quinoline extraction yield of low carbon content coals at 300 °C is 40 %, but when temperature is raised to 350 °C it increases to 90 %.

Pinto *et al.* [15] studied the relation between solvent and extraction yield. They reported that coal treatment with an appropriate solvent can significantly increase its porosity and the yield of products such as oils, asphaltenes and preasphaltenes. Extraction with THF can be used to remove some coal substances selectively. Rodriguez *et al.* [16] applied a 24-hour extraction with THF to remove preasphaltenes. Coal swelling on treatment with THF can increase its internal conversion and change the quality of extraction products by increased accessibility of the agent to the coal's reactive sites. The solvent can transform the internal interactions in the coal lattice by replacing C–C bonds with strong hydrogen bonds between the coal and solvent [17].

Rong *et al.* [13] varyied CH_2Cl_2 extraction times to reduce the amount of organic substances (aliphatics, cyclic hydrocarbons and monocyclic and larger aromatics). They reported that removal of harmful organic compounds is most effective when CH_2Cl_2 extraction is carried out for at least 41 hours. After this time the further removal of undesirable compounds which combustion converts to exhaust gases significantly decreases. Wachowska and Kozłowski [24] studied the CH_2Cl_2 and n-pentane extraction efficiency of reduced and alkylated coals; the extracts were analysed by IR spectroscopy. The CH_2Cl_2 extracts of all coals studied had similar elemental composition. The products of the extraction with n-pentane had molecular masses much lower than those of the extraction with CH_2Cl_2.

Many authors have been interested in extracting coal with different solvents but surprisingly few have studied the effect of oxidation on the yield and properties of the products. In view of the above we undertook a study of the effect of coal oxidation on the sulphur compounds' conversions and the properties of the coal extraction products.

The study is a continuation of earlier work [1]. Its main aim is the determination of the effect of coal oxidation by four different oxidising agents on the extraction yield and the properties of the solid and liquid extraction products. The products were extracted by THF and CH_2Cl_2 from a coal in which the dominant sulphur species was pyrite.

2 Experimental

2.1 Samples

The materials studied were the solid and soluble products obtained by extraction of Siersza colliery Polish flame coal which had been subjected to: demineralisation (designation "dem"); demineralisation and removal of pyrite (designation "dpf"); and oxidation. Most measurements were made on samples demineralised by the Radmacher and Mohrhauer method [25], and on samples with pyrite removed by nitric acid according to the procedure described by Wachowska *et al.* [26]. Oxidation was performed by peroxyacetic acid (designation "PAA"), 5 % nitric acid (designation "5 % HNO_3"), air at 125 °C (designation "air/125"), or oxygen in a water solution of sodium carbonate (designation "O_2/Na_2CO_3"). Sample preparation, detailed oxidation procedures, and characterisation of the initial samples and the insoluble oxidation products were described previously [1,27].

								Types of sulphur species^b			
Coal	V^{daf}	A^d	C^{daf}	H^{daf}	N^{daf}	S^{daf}_{org}	O^{daf^a}	S^d_t	$S^d_{SO_4}$	S^d_p	S_{org}
raw	37.8	11.1	73.8	4.7	1.1	0.5	19.9	2.29	0.37	1.44	0.48
dem	36.0	1.6	76.1	4.5	1.1	1.1	17.2	2.14	0.00	1.05	1.09
dpf	44.7	0.3	62.4	3.9	3.3	0.9	29.5	0.92	0.00	0.00	0.92

^{daf} – dry ash-free;
^{d} – dry matter;
^{a} – by difference;
^{b} – S^d_t,S_{SO_4},S^d_p, S_{org} are total content of sulphur and S in sulphates, pyrite or organic S compounds, respectively.

Table 1 Characteristics of raw, demineralised, and demineralised pyrite-free coal [wt %] [1,27].

2.2 Extraction of oxidised coal samples by tetrahydrofuran [THF] and dichloromethane [CH_2Cl_2]

Prior to extraction the oxidised coal samples were dried for 2 hours at 60 °C and 3 torr.

In order to remove peroxides present in THF, it was first dried with calcium sulphate, then heated to boiling under reflux with lithium aluminium hydride. Finally, it was fractionally distilled in a dry atmosphere.

Dichloromethane used in the extraction was purified by shaking with a 5 % solution of Na_2CO_3, then washing followed by drying with anhydrous $CaCl_2$. Directly prior to extraction it was dried with 3A molecular sieves and distilled in dry air.

Extractions were performed in a Soxhlet apparatus in dry air for 48 hours.

The solid extraction products were dried in vacuum to constant mass. The liquid extract was filtered through a sintered glass funnel into a flask, from which the solvent was then removed in a vacuum evaporator. The precipitate obtained was dried in vacuum to constant mass.

2.3 Analytical procedures

2.3.1 Analysis of the solid product of extraction

Elemental analysis (C,H,N) was performed according to Polish Standards [28,29]. Total sulphur was determined by the micro method using thorin as indicator [30,31] with minor modifications. An 0.05 g portion of coal was placed on filter paper and put in a platinum net mounted on the flask stopper so that a small piece of the paper protruded outside. The flask contained 5 cm^3 of 3 % hydrogen peroxide solution and was filled with oxygen. Then the protruding piece of tissue was ignited and the stopper was quickly placed in the neck of the flask. During the combustion the stopper was lightly pressed into the flask. The flask was set aside and shaken every few minutes so the gases formed would be absorbed. After 40 minutes, the stopper was taken out and rinsed into the flask with 15 cm^3 of isopropyl alcohol. Four drops of thorin and 1 drop of methyl blue were added to the solution obtained, and the mixture was titrated with barium perchlorate to a colour change from green- yellow to pale pink.

2.4 Analysis of the extracts

Elemental analysis (C,H,N,S) of the soluble products was performed on a Perkin Elmer 2400 Series II CHNS elemental analyser. FTIR was performed on a Bruker IFS 113v spectrophotometer, using 2 mg sample with 200 mg KBr.

3 Results and discussion

The coals studied are characterised in Table 1 [1,27]. According to the data in this table, demineralisation leads to a significant decrease in the ash content, which is even more pronounced after pyrite removal. The pyrite removal process also increases the oxygen content (calculated by difference), caused by oxidation at this stage of coal processing. Demineralisation of raw coal causes a total removal of sulphate sulphur and a small removal of pyrite sulphur. The latter sulphur species is removed by pyrite removal and the sulphur remaining in the demineralised pyrite free coal is of organic origin, as follows from the data.

Both demineralised (dem) and demineralised pyrite free (dpf) samples of coal from the Siersza colliery, as well as their oxidation products, were subjected to extraction by tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2). The products were a solid residue and a fraction dissolved by the solvents. The extraction yields are given in Table 2. The extraction yield using THF was always greater than that using CH_2Cl_2.

Extraction yields from samples after pyrite removal (dpf) were higher than before removal (dem), showing that pyrite removal by acid at room temperature partly oxidised the coal. The exceptions were the samples oxidised by nitric acid, for which the CH_2Cl_2 extraction yield of demineralised coal was higher. Comparing extraction yields for oxidized and unoxidized coals, oxidation with O_2/Na_2CO_3 gave the smallest yield increase upon THF extraction, while the smallest yield increase upon CH_2Cl_2 extraction was observed for air/125 °C oxidation. A lower extraction yield of coal samples oxidised with atmospheric oxygen follows from the burn out of the aliphatic structures under these conditions, whereas a lower extraction yield of samples oxidised with O_2/Na_2CO_3 is a consequence of the solubility of the oxidised products [1].

Further analysis of the results shows that the extraction yield of all samples, oxidised under wet or dry conditions, depends on the oxidising agent and the solvent. The highest THF extraction yields were obtained for the samples oxidised with nitric acid or peroxyacetic acid.

	Oxidation				
Coal	Unoxidised	PAA	5 % HNO_3	O_2/Na_2CO_3	air/125
	Extraction with THF				
dem	7.8	16.9	30.2	5.8	8.3
dpf	20.9	31.2	30.4	10.1	10.5
	Extraction with CH_2Cl_2				
dem	1.4	1.8	2.5	3.1	0.8
dpf	2.3	2.0	2.3	3.5	1.2

Table 2 The yields of extraction of the initial and oxidised coal samples with THF and CH_2Cl_2 [%].

3.1 Analysis of the solid extraction residue

Elemental analysis of the solid THF and CH_2Cl_2 extraction residues of the demineralised coal (dem), demineralised pyrite free coal (dpf), and oxidised coal samples are listed in Tables 3 and 4. The least ash in the solid residue from THF extraction was from samples oxidised by peroxyacetic acid, while with CH_2Cl_2 extraction the least ash was in samples oxidised with nitric acid. The greatest amount of carbon was in the extraction residues of samples oxidised by the system O_2/Na_2CO_3, while the smallest was in those oxidised with 5 % HNO_3 (see the second column of Tables 3 and 4). These results suggest that oxidation with nitric acid causes the greatest degradation of the coal structure.

Oxidation with nitric acid also results in the greatest changes in the extracts' hydrogen content, relative to that in the initial coal samples, as is also indicated by the lowest H/C ratio (see Tables 3 and 4).

Analysis of the nitrogen content in the CH_2Cl_2 and THF extraction residues confirmed our earlier results [1] that oxidation with nitric acid leads to incorporation of nitrogen into the coal structure. The results clearly indicate the highest content of nitrogen in the samples oxidised with 5 % HNO_3. Also, extraction residues of oxidised coal samples from which pyrite had been removed by nitric acid show a higher nitrogen content than corrresponding samples from which pyrite had not been removed.

The sulphur content is given in the next column of Tables 3 and 4. It was highest in the extraction residues of samples oxidised by O_2/Na_2CO_3 and air/125 °C. These results (Tables 3 and 4) together with the yields of the extraction processes given in Table 2, confirmed that these oxidising agents were the least effective in sulphur removal from the coal studied, among those used in this study. The least sulphur was found in the extraction residues of samples oxidised with HNO_3 and PAA. These were most effective sulphur removal agents used in this study [1,27,32]. The above conclusions are confirmed by the last columns of Tables 3 and 4, presenting the S/C ratio.

The greatest content of oxygen (calculated by difference and expressed on a dry, ash-free basis) characterised coal oxidised with 5 % HNO_3. The results show that this acid is the most effective agent in introducing oxygen into coal.

Coal	A^{daf}	C^{daf}	H^{daf}	N^{daf}	S^{daf}	O^{daf*}	H/C	O/C	S/C $[10^{-3}]$
dem	2.4	73.7	2.9	1.1	2.0	20.3	0.47	0.21	10.2
PAA	0.8	69.4	2.6	1.3	0.8	25.9	0.45	0.28	4.3
5 % HNO_3	1.7	65.4	1.5	3.7	0.6	28.8	0.27	0.33	3.4
O_2/Na_2CO_3	2.2	73.8	2.1	1.1	1.8	21.2	0.34	0.22	9.2
air/125	2.4	68.8	0.8	1.2	1.9	27.3	0.14	0.30	10.4
dpf	0.2	67.0	1.8	2.0	0.9	28.3	0.32	0.32	5.0
PAA	0.2	66.4	1.2	3.0	0.8	28.6	0.22	0.33	4.5
5 % HNO_3	0.6	65.8	1.1	3.6	0.7	28.8	0.20	0.33	4.0
O_2/Na_2CO_3	1.9	74.0	2.2	0.9	1.8	21.1	0.35	0.21	9.1
air/125	0.2	67.7	2.1	2.9	1.0	26.3	0.37	0.29	5.5

* – by difference

Table 3 Results of the elemental analysis of the solid products of extraction with THF [wt %] and molar ratios of H/C, O/C and S/C.

3.2 Analysis of the extracts

For extracts of wet oxidised coal, oxidation with HNO_3 gave the least carbon in the soluble extraction products (Tables 5 and 6). The greatest carbon contents were found

Coal	A^{daf}	C^{daf}	H^{daf}	N^{daf}	S^{daf}	O^{daf*}	H/C	O/C	S/C $[10^{-3}]$
dem	2.3	72.7	4.5	1.6	2.0	19.2	0.74	0.20	10.3
PAA	3.2	65.6	3.2	1.2	0.7	29.3	0.58	0.34	4.0
5% HNO_3	0.6	63.0	2.6	3.4	0.8	30.2	0.49	0.36	4.4
O_2/Na_2CO_3	1.8	72.5	3.9	1.4	1.9	20.3	0.64	0.21	9.9
air/125	2.1	66.6	3.4	1.1	2.0	26.9	0.61	0.30	11.3
dpf	0.1	62.8	3.7	3.9	0.9	28.7	0.70	0.34	5.4
PAA	0.3	63.7	3.0	1.8	0.7	30.8	0.56	0.36	4.1
5% HNO_3	0.1	61.5	2.8	3.4	0.7	31.6	0.54	0.39	4.3
O_2/Na_2CO_3	1.8	71.0	4.3	1.6	1.9	21.2	0.72	0.22	10.0
air/125	0.2	64.9	3.4	2.6	0.9	28.2	0.62	0.33	5.2

* – by difference

Table 4 Results of the elemental analysis of the solid products of extraction with CH_2Cl_2 [wt %] and molar ratios of H/C, O/C and S/C.

in the extracts of coal samples oxidised by O_2/Na_2CO_3, followed by those using PAA. The carbon content in THF extracts of coal dry oxidised by air at 125 °C (Table 5) was comparable with those oxidised by PAA. Carbon content of CH_2Cl_2 extracts (Table 6) of coal air oxidised at 125 °C was similar to those oxidised with HNO_3. The hydrogen content was lowest in the THF and CH_2Cl_2 extracts of coal samples oxidised with nitric acid.

The extracts obtained from all samples (demineralised and oxidised with HNO_3, demineralised pyrite free, and demineralised pyrite free oxidised with HNO_3) treated with nitric acid are characterised by a significantly enhanced content of nitrogen, which is further evidence confirming that nitrogen is built into the coal structure.

The next column of Tables 5 and 6 presents the results of sulphur determination in the extracts. The least sulphur is found in the soluble products obtained from the coal samples oxidised by PAA. These results confirm that peroxyacetic acid is very effective in sulphur removal from the initial coal. Further analysis of the sulphur content indicates it is highest in extracts obtained from the demineralised coal samples oxidised with HNO_3. It is known that nitric acid is most effective in interactions with inorganic sulphur compounds [33-35]. Earlier study [27] has shown that pyrite is the dominant sulphur species in the coal from Siersza. As follows from the data from Tables 5 and 6, besides removing sulphur in the process of oxidation, nitric acid considerably weakens the sulphur bonds, as manifested by a greater amount of sulphur in the extracts obtained from the coal oxidised with HNO_3. The observations on the efficacy of HNO_3 in sulphur removal are also true for the samples demineralised and demineralized pyrite free (see the data in the last column of Tables 5 and 6).

Among all samples subjected to wet oxidation, the S/C ratio is the highest for those oxidised with 5 % HNO_3. The content of sulphur in extracts of coal oxidised under dry conditions by air at 125 °C is close to that in the samples oxidised by PAA, except for

Coal	C	H	N	S	O*	H/C	O/C	S/C [10^{-3}]
dem	72.5	7.2	0.8	2.1	17.4	1.18	0.18	10.9
PAA	64.4	6.0	0.8	0.5	28.3	1.11	0.33	2.9
5% HNO_3	58.7	5.0	4.2	1.0	31.1	1.01	0.40	6.4
O_2/Na_2CO_3	71.8	7.0	0.7	0.7	19.8	1.16	0.21	3.7
air/125	62.1	5.6	0.8	0.5	31.0	1.07	0.37	3.0
dpf	60.9	5.5	4.0	1.2	28.4	1.08	0.35	7.4
PAA	60.4	5.2	3.5	0.5	30.4	1.03	0.38	3.1
5% HNO_3	59.9	5.0	4.0	0.6	30.5	0.99	0.38	3.8
O_2/Na_2CO_3	71.4	7.4	0.7	0.7	19.8	1.23	0.21	3.7
air/125	61.6	5.1	3.3	0.7	29.3	0.99	0.36	4.3

* – by difference

Table 5 Elemental analysis of THF extracts [wt %] and molar ratios of H/C, O/C and S/C.

Coal	C	H	N	S	O*	H/C	O/C	S/C [10^{-3}]
dem	71.6	7.7	0.7	7.5	12.5	1.28	0.13	39.2
PAA	74.2	10.3	0.1	1.0	14.4	1.65	0.15	5.1
5% HNO_3	66.3	8.7	3.1	2.5	19.4	1.56	0.22	14.1
O_2/Na_2CO_3	77.4	8.6	0.4	2.3	11.3	1.32	0.15	11.1
air/125	64.6	9.8	0.3	1.4	23.9	1.81	0.37	8.1
dpf	65.9	8.4	2.8	5.2	17.7	1.52	0.20	29.6
PAA	69.1	8.7	2.7	0.7	18.8	1.50	0.20	3.8
5% HNO_3	66.3	8.4	3.5	1.6	20.2	1.50	0.23	9.0
O_2/Na_2CO_3	76.9	9.0	0.4	1.5	12.2	1.39	0.12	7.3
air/125	66.3	8.2	2.2	1.6	21.7	1.47	0.25	9.0

* – by difference

Table 6 Elemental analysis of CH_2Cl_2 extracts [wt %] and molar ratios of H/C, O/C and S/C.

the CH_2Cl_2 extract from the demineralised and pyrite free sample.

Considering the oxygen content of wet oxidised samples - it is highest in the extracts of samples oxidised by HNO_3. This result confirms the earlier observation that nitric acid is the most effective in introducing oxygen into the coal structure. The content of oxygen is the lowest in the CH_2Cl_2 and THF extracts from the coal samples oxidised in the system O_2/Na_2CO_3. This is consistent with earlier reports that this system is the weakest oxidant. The oxygen content of extracts from samples oxidised by air at 125 °C is close to that in extracts from coal oxidised with HNO_3. Moreover, extracts from demineralised pyrite free coal have a higher oxygen content than those from the demineralised coal, confirmings that the coal is also partly oxidised during pyrite removal.

3.3 Analysis of FTIR spectra

The solid and soluble products of coal extraction with CH_2Cl_2 and THF were analysed by FTIR spectroscopy. The spectra are presented in Fig. 1−8. All reveal absorption bands at $\sim$ 2916 and 2860 cm^{-1}, assigned to the vibrations of the CH_2 and CH_3 groups in aliphatic and alicyclic structures. The intensity of these peaks are much lower in the spectra of solid (Fig. 1-4) than liquid (Fig. 5-8) products of extraction. The most important changes in the spectra take place in the range 1000−1800 cm^{-1}.

Characteristic changes appear in the bands at about 1700 cm^{-1}, occurring in the spectra of all liquid and solid extraction products using either THF or CH_2Cl_2. The bands are assigned to the carbonyl groups (=C=O). A comparison of the IR spectra of all solid extraction residues (Fig. 1-4), shows that the most intense bands at 1700 cm^{-1} occur in the spectra of the coal samples oxidised with HNO_3 and PAA (Fig. 1d,e; 2d,e; 3d,e; 4d,e). This =C=O band is more intense in the spectra of the extracts (Fig. 5-8) than in those of the solid products (Fig. 1-4). Greater intensity of this band in the spectra of the products obtained from demineralised pyrite free coal (Fig. 3a,4a,7a,8a) than in the spectra of those obtained from demineralised coal (Fig. 1a,2a,5a,6a) indicates partial oxidation of coal in the process of pyrite removal by nitric acid. The lowest intensity of the 1700 cm^{-1} band is in the spectra of the solid and soluble extraction products of coal oxidised by O_2/Na_2CO_3 (Fig. 1c-8c), which confirms that this system is the weakest oxidant.

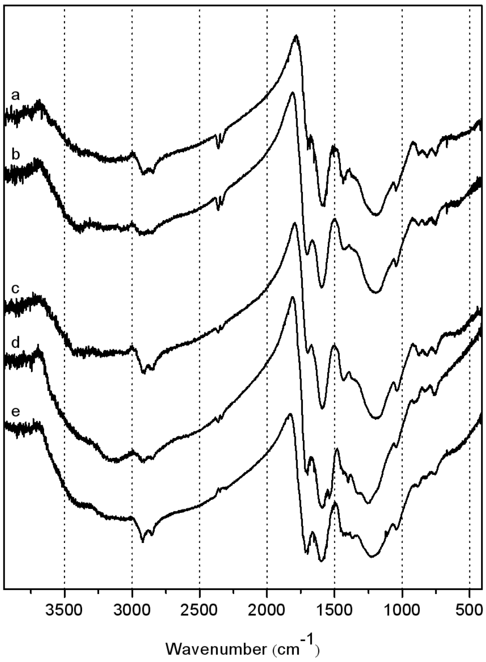

Fig. 1 FTIR spectra of solid products of extraction with THF: (a) dem, (b) $O_2/125$, (c) O_2/Na_2CO_3, (d) 5% HNO_3, (e) PAA.

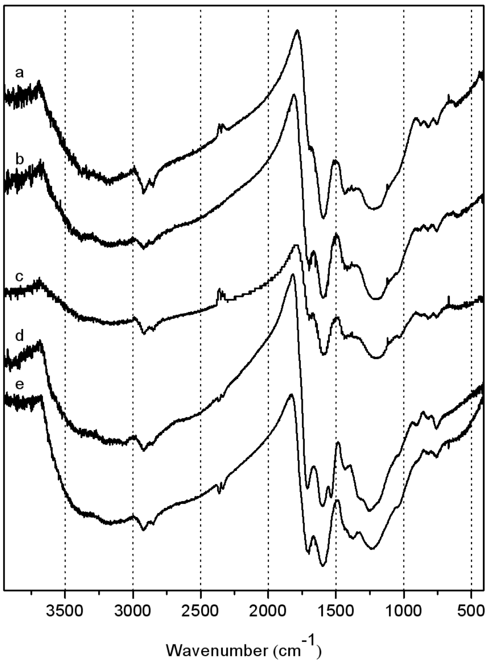

Fig. 2 FTIR spectra of solid products of extraction with CH_2Cl_2: (a) dem, (b) $O_2/125$, (c) O_2/Na_2CO_3, (d) 5% HNO_3, (e) PAA.

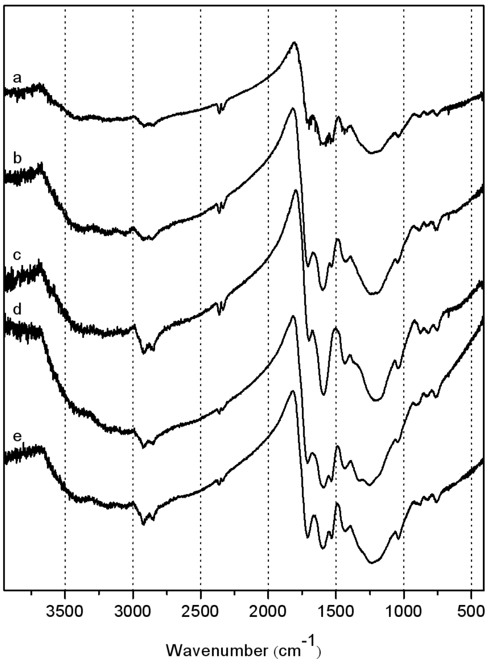

Fig. 3 FTIR spectra of solid products of extraction with THF: (a) dpf, (b) O_2/125, (c) O_2/Na_2CO_3, (d) 5% HNO_3, (e) PAA.

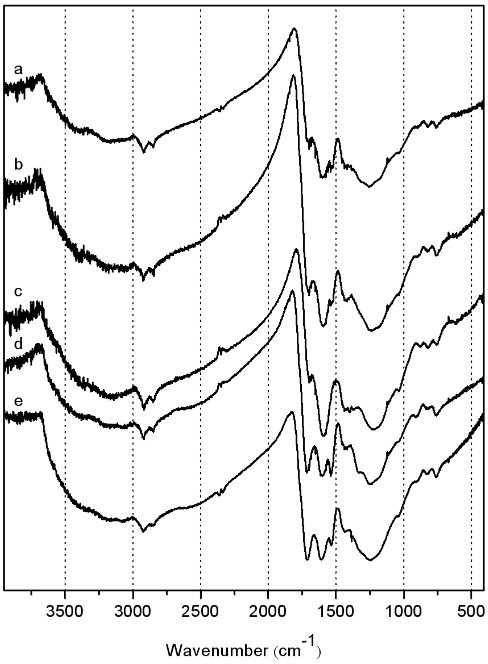

Fig. 4 FTIR spectra of solid products of extraction with CH_2Cl_2: (a) dpf, (b) O_2/125, (c) O_2/Na_2CO_3, (d) 5% HNO_3, (e) PAA.

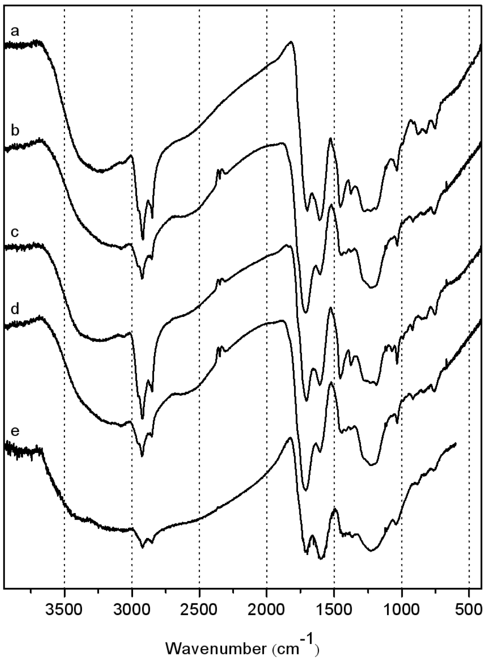

Fig. 5 FTIR spectra of THF extracts: (a) dem, (b) O_2/125, (c) O_2/Na_2CO_3, (d) 5% HNO_3, (e) PAA.

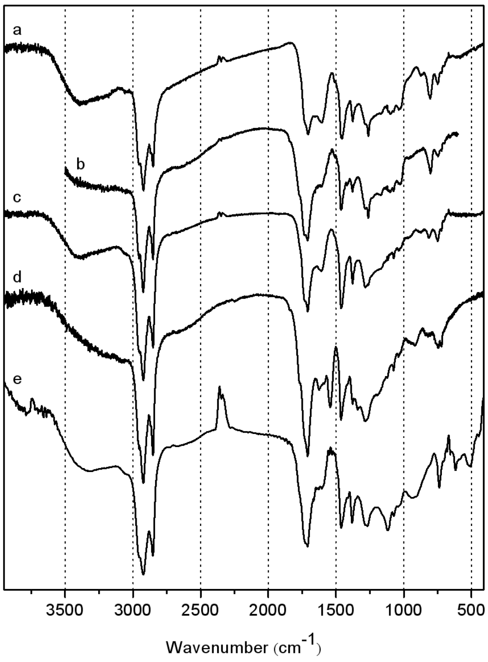

Fig. 6 FTIR spectra of CH_2Cl_2 extracts: (a) dem, (b) O_2/125, (c) O_2/Na_2CO_3, (d) 5 % HNO_3, (e) PAA.

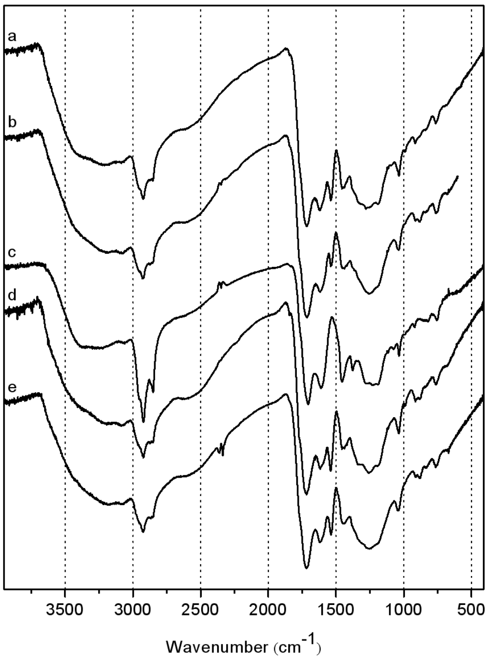

Fig. 7 FTIR spectra of THF extracts: (a) dpf, (b) O_2/125, (c) O_2/Na_2CO_3, (d) 5 % HNO_3, (e) PAA.

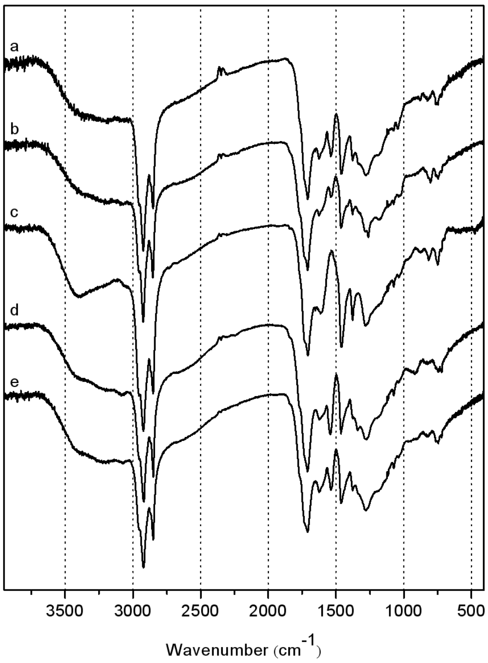

Fig. 8 FTIR spectra of CH_2Cl_2 extracts: (a) dpf, (b) O_2/125, (c) O_2/Na_2CO_3, (d) 5% HNO_3, (e) PAA.

In the spectra of all solid and soluble products of extraction with either THF or CH_2Cl_2 no significant changes are observed in the intensity of the bands at 740−870 cm^{-1} (assigned to aromatic rings of differing degree of substitution).

The spectra of soluble extraction products also show characteristic bands due to oxidised sulphur species (absorption bands in the range 1350 – 1300 cm^{-1} assigned to asymmetric vibrations of $=SO_2$ in sulphones, and 1070-1030 cm^{-1} assigned to stretching of $=S=O$ in sulphoxides [36]). Because of the low sulphur content in the initial coal samples (dem – 2.14 wt %, dpf – 0.92 wt %; Table 1) the intensity of these bands is rather weak. They occur in the spectra of all extraction products (Fig. 5-8) but are most pronounced in the extracts of the demineralised coal obtained with CH_2Cl_2 (Fig. 6) characterised by the highest sulphur content (Table 6).

The spectra of the solid and soluble products of THF and CH_2Cl_2 extraction of coal oxidised with nitric acid (Fig. 1d - 8d) and demineralized pyrite free coal (Fig. 3 ,4, 7, 8), show absorption bands in the range 1520 – 1535 cm^{-1}. On the basis of the literature [37,38] this can be assigned to nitro groups. This is consistent with elemental analysis showing an increased content of nitrogen in the extraction products of these samples.

4 Conclusions

According to the results of our study the coal extraction yield with THF is greater than that with CH_2Cl_2. Using extracts from the initial samples as reference, the greatest changes in elemental composition occur in the products of extraction of the coal samples oxidised by HNO_3, while the smallest changes are detected in those oxidised by O_2/Na_2CO_3. As shown by the sulphur content in the extraction products, the most effective desulphurisation agents are nitric acid and peroxyacetic acid. The FTIR spectra of the extraction products show the characteristic bands of oxidised sulphur species. The IR spectra of the extraction products obtained from the coal treated by HNO_3 (both demineralised pyrite free and oxidised) reveal bands at 1535 cm^{-1} due to the nitro groups ($-NO_2$). This is because nitrogen is incorporated into the coal structure by its reaction with nitric acid.

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