Role of instrumental techniques in studies on wet oxidation of coal: A review

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Coal being a complex macromolecular solid is insoluble in most organic solvents. For structural studies, coal has to be subjected to chemical degradation to generate smaller fragments, which are more amenable for characterisation. For this, oxidative degradation is commonly used. A large number of wet oxidising agents have been used by researchers. All these oxidising agents have shown different reactivities and mode of attack with respect to coal. However, for structural analysis to be successful the fragments generated by oxidation must be well characterised to generate the maximum information. This review discusses the use of various instrumental techniques used to characterise the oxidation products.

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The major long-standing problem regarding coal is that in spite of quantum advances in the science of characterisation, the exact structure of coal is yet to be determined. This is principally due to the fact that coals, which have a very complex structure, as such are not soluble in most common organic solvents to a great degree. This and the fact that coals swell in solvents and are viscoelastic indicate that coal consists of heterogeneous polyaromatic clusters in a complex array resulting in a highly crosslinked macromolecular gel structure or a highly associated mixture of large macromolecules.

The low solubility of coal in common solvents poses difficulties in obtaining and evaluating structural information of coal. Therefore, to study the chemical structure of coal, it has become a common practice to degrade the macromolecular network of coal by chemical means to generate smaller organic entities, simpler than the original coal matrix so as to enhance the solubility in organic solvents. Among the various available chemical means to degrade/depolymerise coal, aqueous phase oxidation reaction is very often preferred. By oxidative degradation, the organic matter of coal forms low molecular weight substances those are extractable by single organic solvents or their mixtures. Apart from structural studies, oxidation of coal also has been and is increasingly being studied as a means of producing useful chemical products and as a starting material for producing various types of carbon products. Considering that the carbonisation route of producing coal chemicals is proving to be increasingly environmentally hazardous, direct sourcing of chemicals by oxidative degradation of coals is increasingly being considered as a promising route for environmentally acceptable production method of chemicals from coal. However, this inter alia requires better characterization of coal and intermediates and products, which is necessary for better understanding of the chemical reactions involved. New and more sophisticated instrumental techniques are coming up and are subsequently being used in coal science. This review summarises the application of various instrumental techniques, which are used in the study of wet oxidation of coal.

Oxidation by nitric acid

Studies in HNO₃ oxidation of coal may be divided under two categories. The first, which is mainly concerned with the soluble products and the second, which is confined to the water insoluble residue after oxidation, referred to as oxycoal. Hayatsu et al.1,2 studied the oxidation of lignite (C, 66.4% maf), a HV bituminous coal (C, 73.9% maf) and anthracite (C, 91.0% maf) with 15% nitric acid. Little or no oxidation was observed in case of anthracite. In case of the lignite and bituminous coal the oxidation yielded apart from the non oxidised coal, organic acids and humic acid like materials. Gas
Chromatography (GC) analysis (15m × 0.5mm OV-17 SCOT column, He flow with 6 mL/min, temperature programmed from 100 to 250°C at 4°C/min) of the methyl esters of the organic acids revealed that benzene carboxylic acids were the most abundant among the aromatic acids identified. Nitrobenzene di- and tetra carboxylic acids were also identified. Solid probe Time of Flight Mass Spectrometry (TOFMS) and High Resolution Mass Spectrometry (HRMS) showed the presence of nitrobenzene penta carboxylic acids in the form of methyl ester which being low volatile was not detected by Gas Chromatography-Mass Spectrometry (GCMS). Detection of furancarboxylic, thiophene carboxylic and pyridine carboxylic acids in the oxidative degradation products indicated that these entities are indigenous to coals. The major products resulting from nitric acid oxidation are thus benzene carboxylic acids, short chain aliphatic acids and humic acid type of materials, the yields of which depend to a large extent upon the nature of coal and oxidation conditions\(^3\).\(^4\) The generation of relatively small molecules as product of this oxidation tends to negate the theory that coal consists of a complex highly condensed, multi-ring polynuclear aromatic system. On the basis of nitric acid oxidation data, coal can be considered to be a matrix of much smaller aromatic systems\(^3\).

Fourier Transform Infrared (FTIR) spectroscopy has been used mainly to characterize oxycoals generated from oxidation of coals by dilute nitric acid. Since coal structure has aromatic ring systems, nitric acid not only oxidises but also nitrates the coal\(^5\),\(^6\). Pietrzak and Wachowska\(^7\) observed pronounced increases in the intensity of the band (\(-1700 \text{ cm}^{-1}\)) assigned to carbonyl groups and decrease in the intensity of bands assigned to methylene and methyl groups indicated by decrease in bands at \(-2923 \text{ cm}^{-1}\) and at \(-1450 \text{ and } 1370 \text{ cm}^{-1}\). They also observed that except for high sulphur Labin coal, all coals underwent oxidation during pyrite removal step\(^8\) using nitric acid during demineralization. They observed decrease in the aromatic bands at \(-3030 \text{ cm}^{-1}\) and at \(-870\text{-740 cm}^{-1}\). Rubiera \textit{et al.}\(^9\) treated the high volatile bituminous coal with \(25\% \text{ HNO}_3\) as pyrite removing step\(^8\) during demineralisation incorporating \(-\text{NO}_2\) groups as confirmed by FTIR and MS. The FTIR spectra of nitrated coal showed peaks at around \(-1530\) and \(-1330 \text{ cm}^{-1}\), which were assigned to the asymmetric and symmetric stretching vibrations, respectively of aromatic nitro groups. Similar observations were made by Zawadzki\(^10\) and Bodoev \textit{et al.}\(^1\). Subsequent research\(^12\) has shown that thorough treatment with either distilled water or heat treatment can completely remove the absorbed nitro groups. In their Thermo Gravimetric Analyser-Mass Spectrometry (TGA-MS) study and Temperature Programmed Combustion test, Rubiera \textit{et al.}\(^9\) observed that when nitro group was subjected to thermal treatment in the presence of air/argon, decomposition of chemically stable nitro group occurred. Similar results were obtained when Mehandjiev \textit{et al.}\(^13\) who studied nitric acid oxidised samples followed by its thermal treatment using X-Ray Photoelectron Spectroscopy (XPS) and FTIR. Zawadzki\(^10\) observed that the carbonaceous aromatic structure reacting with \(\text{HNO}_3\) forms nitro groups absorbing at \(1530 \text{ cm}^{-1} (\nu_1 \text{ NO}_2)\) and \(1330 \text{ cm}^{-1} (\nu_2 \text{ NO}_2)\). Tamarkina \textit{et al.}\(^14\) used Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy to characterise ‘Structurally Modified Coals’ (SMCs) prepared from oxidation of coal by nitric acid-acetic anhydride system. They concluded that coal aranes were converted to nitroaranes indicated by corresponding bands of stretching around \(1540 \text{ and } 1350 \text{ cm}^{-1}\) and deformation at around \(750 \text{ cm}^{-1}\) and that bands at \(1300-1255 \text{ cm}^{-1}\) and \(1655-1610 \text{ cm}^{-1}\) indicate covalent nitrates \(\text{Ar-O-NO}_2\). According to Ubbelohde\(^15\), the carbon-HNO\(_3\) reaction at room temperature leads to the formation of surface nitrate structure. Surface organic structure \(-\text{O-NO}_2\) forms the absorption band at \(1640 \text{ cm}^{-1} (\nu_1 \text{ NO}_2)\) and the broad band at \(1250 \text{ cm}^{-1} (\nu_2 \text{ NO}_2)\) in the spectrum of oxidized carbonizate. The surface nitrate complexes\(^16\) give the band of \(\text{NO}_3^-\) ion at \(1560 \text{ cm}^{-1} (\nu_3)\) and the band at \(1330 \text{ cm}^{-1} (\nu_4)\) overlaps with the band of nitro groups. The abovementioned structure containing nitro-oxygen bonds causes the intensity increase of the band at \(820 \text{ cm}^{-1}\). The formed surface structures do not decompose during the desorption at room temperature. A partial decomposition of these structures takes place when desorbed at \(200\text{°C}\). Then, the bands at \(1640 \text{ and } 1560 \text{ cm}^{-1}\) decay and the absorption in the range of \(1200-1400 \text{ cm}^{-1}\) and around \(820 \text{ cm}^{-1}\) decreases. These observed spectral changes show that organic nitrates and surface nitrate complexes are relatively less stable. The nitro compounds decompose when desorbed at \(400\text{°C}\) when the bands at \(1520 \text{ and } 1330 \text{ cm}^{-1}\) completely disappear. Alvarez \textit{et al.}\(^17\) using FTIR studied the
variation in the structure of coals treated with nitric acid according to variation in coal rank. They showed how nitrocompound formed bands migrate with time and temperature of reaction. Choudhury et al. have recently studied the solubility of nitric acid oxidised coal (NOC) in aqueous organic solvents. They have suggested that introduction of nitro group in coal brings substantial enhancement in solubilization of coal in aqueous organic solvents through its participation as a strong electron-withdrawing group causing a negative inductive effect in the aromatic system. Thermal treatment of NOC at 150°C caused depletion of non-aromatic carbon and elimination of nitro group in the form of nitric acid molecule leading to re-polymerization and lowering of solubility in the aqueous solvents. They concluded that presence of nitro groups in coal played important role in enhancing the solubilization of coal in aqueous organic solvents. Garcia et al. studied the nature of nitro complexes and characterised them using XPS.

**Oxidation by hydrogen peroxide in acetic acid**

Even though hydrogen peroxide in combination with acetic acid has been used widely for oxidation studies of lignin, this oxidant has been rarely used in case of coal. Hayatsu et al. applied Meneghel's mild conditions (hydrogen peroxide, acetic acid, 40°C, 8 days) to oxidise coal. 2g of solvent extracted coal sample was stirred into 250 mL of glacial acetic acid with isopropyl alcohol at 40 — 60°C. Four 20mL aliquots of 30% aq. H₂O₂ were added dropwise at 24 h intervals. Oxidation was continued for further 96 h (total 8 days). The mass was then filtered and the filtrate was evaporated under vacuum. The resultant solids were taken up in methanol and methylated with diazomethane. The esterified organic acid fraction of the lignite oxidation product was analysed by GCMS (OV-101 SCOT column in GC connected to MS with TOF detector) and HRMS. Phenolic, benzene carboxylic, furan carboxylic and aliphatic dibasic acids were identified. For the bituminous coal, the yield of phenolic acids was half of that from lignite suggesting that the lignite sample contained twice the phenolic content than bituminous coal samples. H₂O₂ has also been found to be effective in isolating thiophene carboxylic acids. In the oxidation of high volatile sulphur rich coal (C 78.9, S ory 4.01) by H₂O₂ in acetic acid, Hayatsu et al. using Gas Chromatography-Microwave Plasma Detector Computer (GCMPD), detected a series of thiophene carboxylic acids.

**Oxidation by hydrogen peroxide in acetic acid-trifluoroacetic acid (Deno oxidation)**

Hydrogen peroxide(30%) and trifluoroacetic acid with and without the addition of 96% H₂SO₄ was first applied to the oxidation of lignite and bituminous coal by Deno et al. This group observed that while all aromatic rings were destroyed during this reaction, most of the aliphatic structures were preserved. The methyl esters of the products were characterised by Proton NMR of the methyl esters in CDCl₃ and by GC. For NMR, malonic acid and 1,2, ethane diol were used as internal standards. DSS was used as reference. Carrying out identical reaction on pure compounds such as toluene, ethylbenzene, n-propylbenzene and isopropylbenzene, Deno et al. obtained acetic, propionic, butyric and isobutyric acids, respectively as major oxidation products. This technique is therefore a good method to study the aliphatic structure of coal.

**Oxidation by dichromate**

Although dichromates are extensively used as an oxidising agent in organic reactions, it has not been applied widely in the case of coal. According to Hayatsu et al. and Vaughan and Swithenbank who have studied this reaction in considerable detail, the yields and nature of the products depend upon experimental conditions like dichromate concentration, oxidation time and temperature, use of buffer, etc. apart from the rank of coal used. Very high rank coals are oxidised sparingly or not oxidized. Organic acids, humic acids and carbon dioxide are the products commonly obtained. Hayatsu et al. oxidised d₃-methylated high volatile bituminous coal and similarly treated lignite with aqueous sodium dichromate and characterised the benzene polycarboxylic acids by GCMS (45m × 0.5mm OV-17 SCOT column, 4 mL/min He flow, temp. programmed from 100-250°C at 4°C/min) and HRMS. Sizeable number of peaks due to methyl esters of polynuclear aromatic carboxylic acids and heteroaromatic carboxylic acids have been identified. The use of aqueous sodium dichromate at elevated temperature results in the oxidation of side chains on polynuclear aromatic rings yielding the corresponding carboxylic acids with minimum degradation of the aromatic systems. However, presence of oxygenated functional groups such as phenolic and oxygen heterocyclics e.g., furans are extensively degraded by aqueous Na dichromate. Stephens et al. studied the aromatic structures present in vitrinite
concentrates from Australian coals of various ranks using aqueous sodium dichromate oxidation followed by analysis of the products by GCMS. After extraction, the organic acid residue was methylated with methanol and boron trifluoride before being analysed by computerised GCMS. GC was done with 30m × 0.2mm (I.D.) silica capillary column wall coated with SE 30. Samples were injected in splitless mode at 10°C (2min) and oven temperature raised to 100°C at 20°C/min. before being programmed to 280°C at 4°C/min with He flow rate of 1mL/min. Only 13 relatively simple aromatic carboxylic acids, principally the di- and triacids of benzene, combined in widely different proportions constituted the oxidation products. The largest compound found was a monoacid of naphthalene. There was no obvious pattern to be observed in the nature of the oxidation products that was consistent with the concept of coal maturation as a process of increasing aromatization.

**Oxidation by sodium hypochlorite**

Chakrabartty et al. have studied the aqueous sodium hypochlorite oxidation of coal and model compounds in detail and have concluded that this oxidation is a highly selective procedure which discriminates between aromatic (sp²) and aliphatic (sp³) carbon and oxidises only the aliphatic carbon. This oxidation process was found to be related to the amount of oxygen in the coal and therefore while low rank coal having higher percentage of oxygen, reacted vigourously with hypochlorite, bituminous coal had to be activated by nitration or acylation to bring about positive reaction. From the hypochlorite oxidation of coals having 76-90% carbon, the estimation of tertiary (sp³) carbon abundance in coal was based on the yield of carbon dioxide and the carboxyl acidity of the product. Major component of the organic acids was benzene polycarboxylic acids while short chain aliphatic acids were present as minor constituents. The molecular weight distribution curves for methyl ester mixture of the benzene polycarboxylic acids was obtained by Gel Permeation Chromatography (GPC) using a blank of 5 styragel columns with polystyrene chain length exclusive values of 800, 800, 100, 70 and 70⁰A. Dual detector comprising UV detector set at 254 nm and differential refractometer in series was used. Tetrahydrofuran (THF) was used as a solvent. The methyl esters of the non volatile products were also characterised by GC using 71/2' × 1/8° OD SS column packed with 3% OV-17 on CHROMOSORB-W (H.P.) using flame ionisation detector. On the basis of this data, after subtracting the contribution of heteroaromatic structures, it was estimated that 55-60% of the total carbon existed as tertiary (sp³) carbon. This led Chakrabartty and Berkowitz to postulate that major part of the molecular skeletal structure of coal was not made up of poly aromatic systems but of bridged tricycloalkane configuration based on adamantane structure as unit. This theory has been severely and successfully challenged by several workers and the concept of polyadamantane structure has now been completely rejected.

**Oxidation by alkaline nitrobenzene**

Pioneering work was done in 1940 by Freudenberg et al. Since then this method has been used extensively for structural studies of lignins, humic substances, marine sediments, and to some extent for coals. In this method, the material under study is heated in 2 N NaOH and nitrobenzene for about 2.5 h. Under the oxidation conditions, nitrobenzene acts as a two-electron acceptor and undergoes stepwise reduction through nitrosobenzene and phenylhydroxylamine to aniline. Secondary reactions between reduction intermediates also occur in alkaline media to produce by-products, which not only interfere with the analysis of the oxidation products but lead to misinterpretation of results. The Turkish group under Olcay oxidised lignites and coals with alkaline nitrobenzene at 190-240°C for 2-4 h. The oxidation products were characterised by UV, IR and NMR spectroscopy and also by chemical methods. The presence of aromatic aldehydes, aromatic ketones having phenolic OH and aliphatic substituents were detected. However, individual compounds were not seperated and identified. They however concluded that soluble products obtained from oxidation of lignites and coals by alkaline nitrobenzene were derived from the whole coal/lignite and not just from the low molecular weight constituents. However in 1979, Dogru et al. solvent extracted reductively ethylated (by Sternberg’s method) lignite (%C 71.9) and a coking coal (%C 89.0) using consecutively 5 different solvents. Each extract was then oxidised by nitrobenzene oxidation using the method of Olcay et al. Each solution was subjected to steam distillation and the solution remaining was extracted by the same set of solvents. Each extract was subjected to GCMS. Stationary phase was 5% SEQ 30 and 3% OV101 combined on GCQ (diatomaceous earth after standard
treatment) was used with nitrogen as carrier gas in the GC, which was connected to quadrupole mass spectrometer. Ionisation was carried out at 1.33 mpa pressure with 70 eV electrons. In many of the compounds identified, carbonyl groups were found to be α to an aromatic ring which indicated that the reductively ethylated coals were branched at this position.

**Oxidation by alkaline cupric oxide**

The alkali solutions of metal oxides (copper(II), silver(I), mercury(II) and cobalt(II) oxides) are known to selectively oxidise lignins, humic acids and coals without degradation of aromatic rings. Oxidation by alkaline cupric oxide is milder than similar oxidation by other metal oxides and though similar to oxidation by alkaline nitrobenzene, is more advantageous due to much lesser undesirable byproducts. For the first time, Hayatsu et al. applied alkaline cupric oxide oxidation to coals. Seven coals of varied rank from lignite to anthracite were oxidised at 20°C for 8 — 10 h as 170°C for 2 — 4 h which is normally used to oxidise lignin and marine sediments was found to be too mild to oxidise coal particularly those having high rank. To obtain detailed information about the oxidation behaviour oxidation of 25 pure compounds and polymers were carried out. The acidic solution containing the organic acids was extracted with benzene:ether (1:3). Derivatisation was done using d₆ dimethyl sulphate to yield d₆-methyl esters which were characterised by Gas Chromatography using 15m × 0.5mm OV-17 SCOT column, temperature programmed from 100 to 250°C at 4°C/min with 4 mL/min He flow. Further characterisation was done by HRMS. For coals Hayatsu et al. have suggested inter alia that the phenolic acids found are derived mainly from the cleavage of ether linked aromatic systems present in the structure of coals.

**Oxidation by potassium permanganate**

The oxidation of coal using potassium permanganate has been studied extensively and the first systematic reaction was carried out during 1920s and 30s mainly by Bone and co-workers and details of literature of this period are available in reviews by van Krevelen, Lowry, Berkowitz. Young and Yen isolated aliphatic dicarboxylic acids together with benzene dicarboxylic and benzene tricarboxylic acids from single step permanganate oxidation of a lignite (C, 69.3%). Methanol soluble part of the products was dried and esterified to obtain methyl esters, which were extracted with heptane, and the heptane soluble part was analysed by GC. No aliphatic carboxylic acid were detected. In order to characterise the aliphatic structures in low rank coals, Hayatsu et al. used a two-step buffer controlled permanganate oxidation. Solvent extracted coal was methylated and each methylated sample was oxidised at 80°C with buffer controlled permanganate (300 mL of 4.3% aqueous KMnO₄ and 11.5 g of MgSO₄, 7H₂O) with stirring till the reagent was consumed and the final pH of the solution was neutral. The oxidation process was repeated with the non-oxidised residue. The methyl esters of the organic acid fractions of both steps were characterised by GCMS (45.9m × 0.5mm glass SCOT column coated with OV-17 and temperature programmed from 70-250°C at 4°C/min) and HRMS. Straight chain aliphatic dicarboxylic acids were the most abundant component in organic acid fraction obtained from first step oxidation, of lignites. In the second step oxidation, the major products were aromatic acids. In the case of bituminous coals, first step oxidation products contained large amount of aromatic acids with smaller amount of dicarboxylic acids. No long chain aliphatic acids were detected. From these results Hayatsu et al. suggested that lignite is made up of two components, the first being aliphatic rich kerogen type of material which is the main source of aliphatic dicarboxylic acids in the organic acid fraction of the first step. The second is aromatic type of material and makes the coal macromolecule. However, Speight has suggested caution while making structural deductions based on permanganate data as different reaction conditions produce a different series of products. A remarkable observation regarding the nature of solid residue left after permanganate oxidation was made by Banerjee et al. They found that during oxidation of coal by KMnO₄, irrespective of the medium (acidic alkaline or neutral) in which carried out, the oxidation residue left over at any stage/duration of reaction remained virtually a replica of the original coal both in terms of elemental composition and gross properties like caking properties, etc.

**Oxidation by molecular oxygen-alkali**

Fischer and Schrader in 1920 observed that coal could be oxidised to soluble acids by oxygen-alkali at 200-250 °C. This reaction was extensively used in 1960s for structural characterisation and also as a possible method for production of commercially
useful chemicals. This has been well reviewed\textsuperscript{49,50}. Generally, the coal is suspended in aqueous alkaline solution and oxidised with air or oxygen under pressure. Many groups attempted to characterise the oxidation products\textsuperscript{51-58}. Holly et al.\textsuperscript{53,54} characterised the acidic fraction obtained after oxidation of a bituminous coal with oxygen (270ºC and 900 psig). Nearly 50% of the coal is converted to carbon dioxide, and the rest to water soluble acids, which were converted to methyl esters and identified by mass spectroscopy. Nearly 39% of these acids could be identified either positively or approximately. Of these, benzene tricarboxylic acid was most abundant and constituted nearly 21% of the total. The three isomers of benzene dicarboxylic acids were also identified which constitute nearly 16% of the total. The unidentified acids with constituted nearly 61% of the total were more highly condensed. Kamiya\textsuperscript{59} observed that there is increasing yields of benzene penta and hexa carboxylic acids with increasing rank of coal. Kamiya\textsuperscript{50} also observed that temperature range 260-270ºC is ideal. However, high severity of the reaction generates high carbon loss as CO\textsubscript{2}, which made the process unattractive, and thus slowly lost relevance. Interest was renewed by Hayashi et al.\textsuperscript{50} who used mild condition (80ºC at atms. pressure) to convert low rank coal to generate 70-90% extractable THF/methanol soluble product. Original coal and oxidised coal samples were analysed by DRIFT. While phenolic, carboxylic and alcoholic groups were introduced into the oxidised coal there was reduction in alkyl and ether groups.

**Photochemical oxidation**

Although photochemical degradation of polymers has been extensively studied, very few studies have been done on the photochemical oxidation of coals. Bent and Brown\textsuperscript{61} conducted photochemical oxidation of coal in water and found no major structural change. However, Hayatsu et al.\textsuperscript{1,20} subjected lignite, HV bituminous coals and anthracite to photochemical oxidation by irradiating slurry of the samples in 10% aqueous HCl for 8 days with ultraviolet light while bubbling air or oxygen through the HCl slurry. Negligible photochemical oxidation was observed in case of anthracite while lignite and the bituminous coals were oxidised in the yields of nearly 25 and 30%, respectively. Repeat of the oxidation on the unreacted residue resulted in further degradation to the extent of about 22%. Benzenecarboxylic acids are the most abundant (~60%) apart from chlorobenzenecarboxylic acids, polynuclear aromatic acids, heterocyclic acids, aliphatic acids and others. The oxidation products of both the lignite and bituminous coal exhibited similar distribution patterns. Model compounds including phenols, polynuclear aromatic hydrocarbons, heterocyclic aromatics and a polystyrene polymer were oxidised to study the chemistry and nature of the photochemical oxidation of coal\textsuperscript{52}.

**Electrochemical oxidation**

Only few studies on electrochemical oxidation of coal and lignite in basic medium have been reported. Lynch and Collet\textsuperscript{63} conducted electrolysis of pulverised coal in alkaline media at an applied density of 10 mA/cm\textsuperscript{2} on platinum electrodes and opined that 3 N NaOH to be the best medium for maximum yield of humic acid by elecrochemical oxidation. Lalwani et al.\textsuperscript{64} conducted electrochemical oxidation of lignite slurries in 1 N NaOH at Pt electrodes to produce humic acids. Gaseous products produced were analysed by GC and were found to contain CO\textsubscript{2}, H\textsubscript{2}, small amounts of O\textsubscript{2} and traces of hydrocarbon gases. The humic acids produced and the residual reacted coal were extracted by suitable solvents and finally characterised by GCMS. On the basis of the data, a reaction mechanism was proposed. They further observed that the amount of humic acid that could be precipitated from the electrolyte (alkaline lignite slurry) increased with applied potential and reached a maximum at E=2.7V SCE and decreased when electrode potential was further increased. They also observed that reaction rates were higher by about two to three times with graphite electrodes when compared with platinum electrodes although graphite electrodes got electrochemically oxidised themselves. There have also been few studies of electrochemical oxidation of coal slurry in acidic media\textsuperscript{65-67}. The general observation of these authors is that electrochemical oxidation of coal slurry in acidic media causes pyrite to react and dissolve resulting in the production of H\textsubscript{2} at cathode. The oxidation of small amount of carbonaceous matter at anode with production of CO\textsubscript{2} was also observed.

**Conclusion**

Coal is a complex macromolecular solid; the exact detail of the structure of continues to elude coal scientists. Various oxidizing agents, which are used for degradation of coal to generate smaller fragments, do not degrade coal identically in terms of centre of
attack, severity, and the nature of products generated. No oxidising agent is successful in degrading coal completely into soluble fragments and oxidation in most cases leads to generation of some products, which are complex and difficult to characterise. On the other hand, high severity reaction conditions, in spite of not degrading coal completely, increase carbon loss in form of CO₂. Although a number of sophisticated instrumental techniques have been used to characterize the oxidation products of coal, much more needs to be done for better characterisation and understanding of the mechanism of various oxidation reactions of coal and structural details of coal. More studies are needed for the identification of the reaction residues left after coal oxidation.

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