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A REVIEW

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THE CHARACTERIZATION OF OXIDIZED
COAL - A REVIEW

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ABSTRACT

The presence of oxidized coal causes substantive problems in the coal industry. It would be of benefit to producers and end-users alike if the existence and extent of oxidation could be easily and reliably determined. Many methods have been proposed; unfortunately no completely acceptable method has yet been established. The extremely variable and complex nature of coal has been a major stumbling block in the development of a generally - applicable method of characterization. Most methods require comparison to results obtained on unoxidized samples of the same coal, a process which is obviously not always feasible. Moreover, the absolute measurement of degree of oxidation is not an end in itself, but must be related to changes affecting coal processing and relative technological properties.

This paper is an attempt to summarize methods which have been used to detect and/or quantify the oxidation state of a coal. Attention is focussed on problems encountered and limitations of the data obtained. The reader is referred to the bibliography for detailed descriptions of the various methodologies.

Keywords

Oxidized coal, characterization, oxidation, coal chemistry, physical properties, floatability, plastic properties.

INTRODUCTION

Oxidation of coal has been aptly described as a process of deterioration, since most of the end-uses of coal are adversely affected. Processing problems in the washery include reduced recovery in flotation circuits and decreased efficiency of dewatering processes.

Oxidation of reactive lithotypes (vitrain) in coal affects the plastic properties of metallurgical coals during carbonization and can result in significant lowering of coke strength. Thermal values and the yield of coke oven byproducts are also adversely affected.

With low-rank coals, the process of oxidation can result in spontaneous heating and/or combustion

during storage and transport. Natural oxidation (weathering) may also reduce the yield of conversion products during liquefaction. Conversely, the use of artificial selective oxidation to cleave connecting groups between aromatic aggregates may render the "process of deterioration" desirable in solvent refining of coal.

THE KINETICS AND MECHANISMS OF COAL OXIDATION

The manner in which atmospheric oxygen attacks coal has been the subject of numerous investigations. Early work was prompted by the spontaneous heating of coal storage piles. Schmidt (1) showed that coal exposed to air reacts continuously with oxygen at slow but measurable rates, even at room temperature, and developed mathematical expressions relating reaction rate to temperature, time, oxygen concentration and coal composition. Wood (2) noted that the oxidation reaction proceeds in distinct stages; a rapid initial sorption of oxygen followed by a marked decrease in oxidation rate and postulated that this represented a change in reaction mechanism. More recently, a mathematical model for the oxidation of bituminous coal was developed by Kam and co-workers (3) (the KHP model) and later modified by Avison (4) to account for the variability of pore sizes in coal. This model suggests that oxidation proceeds along two paths, the first being a direct "burn-off" reaction resembling combustion and the second being highly complicated, involving chemisorption, formation of oxygenated complexes and subsequent decomposition of the complexes. The mechanisms of low-temperature coal-oxygen interactions have also been extensively investigated by Marinov (5) who studied changes in weight, elemental composition, oxygen functional groups and yields of CO₂ and H₂O. Saranchuk (6) studied the effect of moisture on oxidation and concluded that below 70°C, the presence of water is critical to the chemisorption of oxygen on the coal surface; at higher temperatures, water has little effect on the type and intensity of oxidation processes.

The complex and variable nature of coal would suggest that oxidation involves at least several reactions. While models are useful in understanding the factors which control oxidation, the exact chemistry and reactions involved remain uncertain. Moreover, as noted by Kukharenko (7), among others, oxidation in the coal beds (in-situ weathering) cannot be

taken as identical to oxidation under laboratory conditions. Natural weathering of near surface coal may take place over thousands of years; the mechanisms and end products of this process cannot be duplicated in the laboratory with any degree of certainty. Laboratory - induced or controlled oxidation of coal is useful however, in producing samples of varying oxidation states for experiments aimed at solving processing problems and restoring desirable properties. It is essential therefore, that any method to detect and/or quantify the oxidation state of coal be applicable to both naturally and artificially oxidized samples.

METHODS OF CHARACTERIZATION OF OXIDIZED COALS

The process of oxidation results in physical and chemical changes in the coal; methods of characterization may thus be broadly classified as being based on measurement of these changes.

A. Methods Based on Physical Properties

Free Swelling Index

The free swelling index (FSI) as determined by ASTM Standard D720 or ISO Standard 501 is a rapid and simple test which can be used to indicate the level of caking propensity of coal. Oxidation reduces the FSI; we have found that coals normally having an FSI of up to 6 may be made completely non-caking by exposure to oxygen at 125°C for 72 hours. The method, however, does not appear to be sensitive to the presence of small amounts of oxidized coal, which can seriously affect flotation, coke strength, etc. nor is it sufficiently quantitative to indicate the bulk state of oxidation. It finds its main use as a rough screening test in delineating mining areas or reducing the number of laboratory tests from sampling programs. It is particularly useful when the FSI of the corresponding "fresh" coal is known.

Plastic Properties

The effect of oxidation on the plastic properties of coal has been studied by many workers (8, 9). Comprehensive reviews of the published literature have been given by Howard (10) and Loison (11).

In general, oxidation restricts the plastic temperature range and brings about a decrease in fluidity and swelling. Gibson (12) recently noted that plastic properties may be markedly affected by even mild oxidation. It was proposed by Orchin (13) and later Ignasiak (14) that the formation of cross-linkages by condensation reactions during oxidation contributes to a loss of plasticity and fusibility of the coal. The presence of oxygen-bearing groups particularly acidic -OH has been shown (15) to adversely affect the maximum Gieseler fluidity (ASTM Standard D 1812).

Measurement of plastic properties alone are not sufficient to quantify the degree of oxidation of an unknown coal. Pearson (16) noted that FSI, dilatation and fluidity of Western Canadian coals are characteristically low despite the fact that they

make good quality coke. For these coals, a comparatively low caking propensity is attributed to their inertinite-rich maceral composition. From a petrographic viewpoint, it has been established (11) that the macerals responsible for plastic properties of coal during carbonization, e.g. vitrinite, are those most subject to oxidative degradation.

Coke Strength

The major effect of oxidized coal in the coke oven is the production of inferior quality coke. Some operators (17) have used results from small test ovens as a means of selecting "unoxidized" coal seams prior to recovery. The resultant coke strength as determined by standard tumbler tests cannot be used to quantify the degree of oxidation of a coking coal or coal blend because of the indeterminate synergistic effect of other coal properties on coke strength.

Yield and Molecular Weight of Low Temperature Tar

It has been reported by Wackowska (18) that the yield of low temperature tar during coal pyrolysis is dependent upon the degree of oxidation of the coal. Laboratory oxidation at 200°C leads to destruction of those systems in a coal responsible for tar formation. Moreover, a five-fold increase in average molecular weight of low temperature tar was observed upon pyrolysis of oxidized vs non-oxidized coals. They concluded that oxygen attacks aliphatic chains and hydroaromatic groups in the coal and that the observed increase in molecular weight results from the condensation of hydroxyl groups formed during oxidation. Results obtained by Ignasiak (19) who oxidized coal with labelled oxygen (O_{18}) would appear to support this suggestion, as a major part of the labelled oxygen was found in the low-temperature tar fraction upon pyrolysis of the oxidized coal. Application of this method has not been suggested as a quantitative indicator of oxidation, nor has it been shown to be applicable to naturally weathered coals. The data obtained has been useful however, in explaining the deterioration of fluidity and dilatation during pyrolysis.

Hydrophobicity of Coal Surfaces

From a processing point of view, the major effect of oxidation is reduced hydrophobicity of coal surfaces, resulting in decreased floatability and increased problems in solid-liquid separation. Early work by Sun (20, 21) had shown the deleterious effect of oxidation on the floatability of coals. Heterogeneous coal was considered to consist of floatable hydrophobic components (hydrocarbons) and non-floatable hydrophilic components (moisture, mineral matter and oxygen-rich constituents). It is now well established that oxidation decreases the hydrophobicity of coal surfaces by changing their chemical composition, although the exact mechanisms and end products have not been fully elucidated.

The wide variation in hydrophobicity of "fresh" coals with rank, moisture content, mineral matter and petrographic composition makes it very difficult to quantify the degree of oxidation based on hydrophobicity alone. Moreover, mild oxidation may de-

crease hydrophobicity of particle surfaces without serious effects on the bulk oxidation state.

Relative hydrophobicity can be determined by several laboratory methods, including (1) static flotation (bubble pick-up method), (2) dynamic flotation, using hydrocarbon collectors (a variety of flotation cells are available) (3) contact angle, usually taken as the angle, measured across the water phase, that the air-water interface makes with the solid coal surface, and (4) oil agglomeration, which includes the phase inversion test (22) commonly used to make an estimate of floatability. Many operators favor floatability as an indicator of oxidation because its determination is rapid, simple and relates directly to washery performance. It has been reported (23) that the sensitivity of the flotation test is improved by using hexyl alcohol as a collector-frother. Samples of unoxidized coal from the same seam are required to eliminate the possible effect of variables other than degree of oxidation on flotation

Sorptive Properties of Coal

The selective adsorption of organic compounds on coal surfaces depends upon the nature of the coal surface. Changes in sorptive properties with oxidation forms the basis of several attempts to detect oxidized coal. Leeder (23) briefly investigated the use of inverse gas chromatography in the study of coal surfaces. In this method finely crushed coal forms the column; the emergence time and spread of the eluting probe is affected by the surface properties of the coal particles. Significant changes in the chromatogram were observed with bituminous coals that had been exposed to air for three months. More work is required to correlate these changes to degree of oxidation and to demonstrate general applicability of the technique.

Another technique, first applied to coal by Larsen (24) is chromatographic evaluation of the isosteric heat of adsorption of various organic compounds on coal surfaces. Al Taweel (25) has recently suggested application of this technique to oxidized coal. In preliminary tests using propane as an adsorbate, retention time for oxidized coal was significantly higher than that for fresh coal. The selective adsorption of organic compounds on coal surfaces is also postulated to effect the stability of fine coal suspensions. Recent results obtained by these methods are being reported by Dr. Al Taweel at this conference.

Sorptive techniques require samples of unoxidized coal for comparative purposes and may suffer in precision due to experimental difficulties.

Microstructure of Coal

Coal which is present near the surface may be repeatedly dried and wetted. The natural fissure pattern (cleat) in coal offers surfaces for moisture loss or gain as well as exposure to air. Weathering causes the natural crack pattern to become extended and enlarged, furthering susceptibility to oxidative attack. The changes produced in oxidation are often readily discernible under the microscope, especially with strongly caking coals. Fissure patterns

oxidation rings, excessive ultrafine particles at the surface of larger particles, are all indicators of oxidation. Again, these changes are most readily observed on the vitrinoid components of the coal. Porosity, surface area and susceptibility to size degradation can all be expected to increase with oxidation. The difficulty lies in quantitatively relating observed changes in microstructural properties to degree of oxidation. Conjointly, mild oxidation may not be detectable.

Reflectance

The reflectance of polished coal samples, as measured by the mean maximum reflectance of vitrinite in oil (R_o) has been used primarily to indicate the rank of the coal. While changes in reflectance have been observed between outcrop and mine samples, no consistent correlation with degree of oxidation has been found. Chandra (26) observed significant reductions in reflectance of two high volatile British coal outcrop (oxidized) samples. Nandi (27) on the other hand, reported an increase in reflectance when going from unoxidized to oxidized portions of vitrinite grains which had been artificially oxidized. The data of Pearson (28) who tested ten consecutive channel samples from a Crowsnest coal-field seam, indicate that reflectance is a relatively insensitive indicator of oxidation.

Recently, Pearson and Creaney (29) described a method using the mean maximum reflectance and the bireflectance ($R_o \text{ max} - R_o \text{ min}$) of vitrinitic char as a measure of the degree of oxidation of the original coal. The method, while somewhat long, appears promising, provided fresh and fully oxidized samples are available.

Microhardness

The effect of artificial oxidation on the microhardness of vitrinite grains in coal was studied by Alpern and Maume (30) who concluded that microhardness is always greater near the edges of grains. Nandi (27), also working with laboratory oxidized coals, showed that the plastic state of fresh vitrinite is transformed into an elastic state with oxidation. The progress of oxygen penetration into the particles can thereby be determined. Microhardness measurements may be of limited usefulness when applied to weathered coals, wherein vitrinite grains may be expected to be of uniform hardness.

Colorimetric (Staining) Techniques

A method developed at U.S. Steel (22) and now used in many petrographic laboratories, involves immersing a polished pellet of coal in potassium hydroxide saturated with Safranin "O" (a red stain). After washing in water, the pellet is examined under the microscope. Highly oxidized portions become dark green, less oxidized portions brighter green and fresh coal remains unstained. The amount and degree of oxidation is claimed to be easily detected and may be analysed by a normal point-count procedure. Staining, however, is apparently not applicable to all ranks of coal, pending development of appropriate selective dyes.

METHODS BASED ON CHEMICAL PROPERTIES

The process of oxidation results in many complex chemical changes in the coal substance and may also affect the mineral matter present. In general, oxygen content increases, carbon and hydrogen decreases, pyritic sulphur may be converted to sulfate, etc. Some organic structures are modified or destroyed; new compounds and functional groups are generated; soluble oxidation products may be formed. Many attempts have been made to quantify the extent of these chemical changes and relate them to changes in technological properties.

Oxygen Content of Coal

The chemical changes occurring during metamorphism to higher rank coals involve the removal of oxygen; oxidation reverses this process. Oxygen is present in coal in a variety of forms; oxygen-containing groups include hydroxyl (-OH), carbonyl (C=O), carboxyl (-COOH), methoxyl (O-CH₃) and ether-type linkages. Pitt (31) has stated that the majority of oxygen in bituminous coals is present in carbonyl and phenolic hydroxyl groups, the remainder being in ether and carboxyl groups or heterocyclic ring systems. Oxygen also forms an essential part of the inorganic constituents of coal as silica, alumina, sulfate etc. The determination of oxygen in coal has been the subject of numerous studies. Analytical methods should distinguish between organic and inorganic oxygen, especially in studies involving oxidation or coal conversion processes. Analytical methods include:

A. Oxygen by Difference

Oxygen in coal has historically been determined by difference (32) due to the lack of a completely satisfactory direct method. Carbon, hydrogen, sulfur, nitrogen and ash are determined directly after drying and the balance is assumed to be oxygen. Analytical errors are cumulated in the oxygen content - an obvious shortcoming if subtle changes resulting from mild oxidation are to be detected.

B. Activation Analysis

In activation analysis the amount of an element present in a sample is determined by measuring the intensity of activity induced in that element by bombardment with suitable nuclear projectiles. Neutrons are most often used, the method then being known as neutron activation analysis.

The method was first applied to determination of oxygen in coal by Martin (33) and has since been used by a large number of workers in the field (34, 35, 36). The major problem in using activation techniques is that they do not distinguish between organic and inorganic oxygen. Gray (22) has suggested use of an empirical correction factor to correct for oxygen in the ash. The variable nature of ash forming constituents would require a different correction factor for each coal. Extensive work using neutron activation has been done on oxygen stoichiometry in coal by Volborth and co-workers (37, 38). They concluded that accurate determination of oxygen in coal before ashing, in the coal ash and in the

corresponding low-temperature ash are necessary to provide a reliable estimate of the organic oxygen in coal on a moisture and ash-free basis.

Recent work at the Brookhaven National Laboratory by Schlyer (39) used the alternate technique of charged particle activation analysis. Coal samples are irradiated with ³He ions and a direct comparison of the amounts of carbon and oxygen present in the coal sample can be obtained. The advantages of charged particle activation analysis are claimed to be ease of sample preparation, short irradiation time, easily automated counting and analysis and the elimination of complex correction factors. An added feature is the ability to vary the depth to which the charged particles penetrate by varying the energy of the particles. It is therefore possible to obtain an oxygen depth profile, which may provide useful information on the progress and extent of oxidative attack.

In summation, activation analysis is rapid, non-destructive and can determine many elements simultaneously. However, a source of nuclear particles is required, the instrumentation is expensive and is not readily available to all potential users.

C. Pyrolysis Methods

Kinson and Belcher (40) have presented results of organic oxygen determinations in Australian coals based on a radio frequency heating method. Pyrolysis gases are passed through a five stage purification and conversion train and oxygen is determined gravimetrically from the CO₂ adsorbed. Elaborate corrections for inorganic oxygen were required if the ash content of the coal was greater than five percent.

Hasegawa (41) determined oxygen in Japanese coals by pyrolyzing samples in flowing argon; converting pyrolysis gases to CO, the CO₂, which liberated iodine from an I₂O₅ solution. Colorometric determination of iodine allowed calculation of the oxygen content; pyrolysis values for total oxygen were always lower than those determined by neutron activation, in one case by a factor of three.

A more successful pyrolysis technique was reported by Abernethy and Gibson (42) at the U.S. Bureau of Mines, who applied a modified Unterzaucher method to coals which had first been demineralized by hydrochloric - hydrofluoric acid treatment. Results obtained had a precision of approximately 0.1% absolute. The procedure is laborious however, and has not yet been adopted as a standard method for oxygen determination in coal.

D. Electron Microprobe

The electron microprobe was used by Wen (43) to determine the oxygen content of artificially oxidized coals. Oxygen contents were uniformly low when compared to those obtained by difference (ultimate analysis). Discrepancies were attributed to loss of physically adsorbed oxygen by the vacuum necessary to operate the instrument and to the lack of a suitable standard (1 - 10% oxygen) for the microprobe analysis.

The foregoing list of methods of oxygen determination

is by no means complete. While attempts have been made for years, no simple, accurate method for directly determining (organic) oxygen in coal has evolved. In any event, precise measurement of oxygen is not sufficient to quantify the degree of oxidation unless comparison can be made with unoxidized samples of the same coal.

Coal Slurry Acidity

In this test, a known amount of fine coal is added to a fixed amount of distilled water; after equilibrium is reached, the pH of the slurry is measured. It has been found (22, 43) that acidity increases with degree of oxidation. The effect is attributed to acids produced during oxidation reactions (44); distinction between organic acids formed and acidity produced by oxidation of inorganics, e.g. pyrite, is not made. The test would appear to be semi-quantitative, at best.

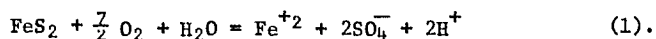
Alkali Solubility

This test, somewhat similar to the acidity test above was first applied in England and is now used extensively in the eastern United States. Atkinson and Hyslop (45) found that the solubility of coal in an alkali solution is dependent upon its rank, type and state of oxidation. For coals of a given rank and type, the greater the degree of oxidation, the greater the solubility. Light transmittance of the filtered alkali extract solution is measured; lower values indicate a higher degree of oxidation. Successful application of this method depends upon the conversion of organic material of the coal to acidic oxygen-bearing groups by the oxidative process. These alkali-soluble, acid-insoluble products are commonly designated "regenerated humic acids". While these reactions occur with Carboniferous British and American coals, Berkowitz (46) found that air oxidation of Cretaceous Western Canadian coals produced virtually no acidic -OH groups. Further work appears necessary to evaluate the applicability of this method to Canadian coals.

Mineral Matter in Coal

The process of oxidation affects the inorganic mineral matter as well as the organic substance of the coal. The formulae of Parr (47) have been extensively used to calculate mineral matter from (high temperature) ash. Miller (48) pointed out the shortcomings of these formulae and described a new method for determining the mineral matter content based on low-temperature ashing of the coal in an oxygen plasma. The resultant low temperature ash (LTA) is purported to contain the minerals in as unaltered a condition as possible (49, 50) making the study of oxidative changes possible.

The oxidation of pyrite and/or marcasite present in coal by moist air is given by:



The liberated (soluble) iron concentration will increase as oxidation progresses and may be conveniently determined by atomic absorption spectroscopy.

Other inorganic cations, e.g. calcium, may also increase with degree of oxidation, probably due to solubilization by the acid generated in pyrite oxidation. The analysis of soluble inorganic oxidation products is useful in monitoring the progress of artificial oxidation experiments.

Pearson and Kwong (28) studied LTA mineralogy of samples taken from an exploration adit in the Crow's nest coalfield, British Columbia. They found that the mineral bassanite ($\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$) was developed in oxidized and partially oxidized samples. No bassanite was detected (by X-ray diffraction) in unoxidized portions of the seam. The sequence of events producing bassanite is: (i) oxidation of pyrite to produce hydrated ferrous sulfate (ii) reaction of ferrous sulfate with calcite to produce gypsum (iii) partial dehydration of gypsum during low temperature ashing. A definite inverse relationship existed between bassanite development in LTA and the swelling character (FSI) of the coal. The procedure, however, is lengthy and further work is required to show general applicability.

Infrared Absorption Spectroscopy

Of all the spectroscopic techniques, infrared absorption has been most used in the investigation of coal structure. The first successful spectra were produced in 1945 by Canon and Sutherland (51). More recently (52, 53), infrared spectroscopy has been used to investigate the type and amount of oxygen introduced into the coal as a result of oxidation. Oxidation is believed to effect primarily the periphery of the coal macromolecule, i.e. the functional groups. The assignment of absorption bands in the infrared spectra to various oxygen containing and carbon-hydrogen functions is fairly well established (54). The spectra, however, are somewhat limited in resolution and are essentially qualitative in nature. Conventional dispersive infrared spectroscopy is limited by the highly absorbing nature of the coal and the sample preparation techniques employed. Dispersive instruments, using monochromators, record spectra by scanning the desired frequency range at successive resolution intervals. The slit system, required to achieve good resolution, limits the energy throughput from the infrared source. The scanning rate must subsequently be decreased in order to achieve acceptable signal to noise ratios. Additionally, infrared detectors such as thermocouples and pyroelectric devices have a relatively high internal noise.

A common sample preparation technique consists of mounting the finely ground coal (typically $< 2 \mu\text{m}$) in a potassium bromide pellet. The long grinding time may result in inadvertent oxidation of the coal surface, the sample may be contaminated by the grinding elements and the adsorption of water in the pellet is almost unavoidable.

Infrared spectroscopy has been greatly extended by the use of an interferometer and the application of Fourier transform techniques to the interferogram obtained. The advantages and applications of Fourier transform infrared spectroscopy have been summarized by Koenig (55). Higher energy throughput (by a factor of up to 200); combined with the speed and

improved resolution make FTIR a potentially powerful tool in the study of oxidized coal. The application of data processing, whereby two digital spectra can be stored and/or compared (difference spectroscopy) is probably the most important benefit of FTIR. Thus, small changes in samples as oxidation progresses, can be detected.

Very recently, a new type of detector has been developed, the technique being known as photo acoustic spectroscopy (PAS). The sample is placed in a sealed cell containing a very sensitive microphone. If the sample absorbs infrared radiation of a certain wavelength, it is converted to thermal energy, resulting in a corresponding pressure wave in the cell which is detected by the microphone. Sample preparation problems are avoided as fine grinding is not necessary and no mounting medium is required. The technique has been applied to coal by Rockley (56) and most recently by Lynch and Donini. Dr. B.M. Lynch will present a paper on the application of FTIR and PAS-FTIR to the study of oxidized coals at this conference.

Other Spectroscopic Methods

A myriad of spectroscopic techniques are available for the study of surfaces (57). Incident beams of photons, electrons or ions interact with the surface; resulting emissions can be used to characterize the surfaces chemical composition, either on an elemental or molecular basis. These methods include: (i) electron spectroscopy for chemical analysis (ESCA) and the related X-ray photoelectron spectroscopy (XPS) (ii) Auger electron spectroscopy (AES) (iii) (molecular) secondary ion mass spectrometry (SIMS) (iv) ion scattering spectroscopy (ISS) (v) X-ray fluorescence (XRF). Depth profiling can in many cases be accomplished by sputtering techniques, wherein the surface layers are progressively removed by the incident beam. The applicability of these methods to oxidized coal has not in general been fully evaluated. The quantitating of spectra is fraught with difficulties peculiar to each specimen and each analytical tool. West (58) recently applied the advanced spectroscopic techniques known as electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) to samples of fresh and oxidized Crowsnest coals and their low temperature chars. Significant spectroscopic differences were observed between fresh and highly oxidized coal, with the ENDOR response being more sensitive to the oxidation history of the coal. A relevant paper (Pearson and West) is scheduled for presentation at this conference.

Chemical Analysis of Functional Groups

Oxidation of coal results in the formation of additional oxygen containing functional groups, primarily at the expense of aliphatic C-H groups. Various investigators have reported peroxide complexes, acidic hydroxyl, carboxylic acid, ketonic, ether and ester groups in oxidized coal.

Chemical methods have been summarized by Van Krevelen (59). The extraction and analysis of the functional groups is inherently difficult due to the intractable nature of the coal, i.e. the functional groups are not readily accessible to the reagent. Fine grinding

is required, reaction times are long and results are not always reproducible.

It would appear that chemical derivatization of oxygen containing groups would be useful in confirming spectroscopic indications and may provide a reliable means of quantification when correlated with FTIR spectral subtraction results. Further work is required in this area.

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