

INVESTIGATIONS OF ANODICALLY OXIDISED COAL

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A number of studies carried out on the electrolysis of coal in basic media(1-7) support the conclusion that electrooxidation of coal in NaOH forms soluble products similar to humic acids. Upon further electrolysis the humic acids - like material decomposes to liberate CO₂ at the anode. Hydrogen is liberated at the cathode with high efficiency and, depending upon the electrode potential and other conditions, relatively small amounts of O₂ and traces of CH₄ and C₂H₂ form at the anode. Different cell geometries have been explored, ranging from a stirred - cell reactor(1-5) to a reactor with an anode made of anthracite coal(6); other electrodes which have been used include Pt, graphite, Pb and Ni. The effect of catalysts, such as vanadium pentoxide and cobalt chloride, on the oxidation rates have also been studied(3). Some researchers(3) reported that horizontal electrodes caused higher rates of coal conversion than vertical electrodes. Belcher(4) characterized the various coal electrolysis products by separating them into acetone - soluble and acetone - insoluble products. Khundkar(5) showed that peat displays higher electrochemical activity than coal under similar conditions. Excepting recently reported work(7) coal electrolysis has usually been done galvanostatically. Senftle and coworkers(6) argued that OH• radicals are the most probable agents for hydrogen abstraction and/or addition to aromatic rings. In addition to containing an excellent review of the oxidising species formed during the electrolysis of water, this paper(6) also gives some experimental data as to the products of coal electrolysis.

The present study reports more details as to products formed during coal electrolysis in basic media and considers various possible reaction pathways for electrochemical oxidation of coal. Constant potentials were employed in this work and the reaction products were analysed by FTIR, and for elemental compositions.

Reaction mechanisms of coal oxidation by electrolysis are neither very well understood nor widely studied. Guidance may be gleaned, however, from a number of experimental investigations of the mechanism of the oxidation of coal by chemical reagents. It has been reasoned

from such results that free radicals formed during the early stages combine to form larger entities; then this is followed by an essentially oxidative - hydrolytic process in later stages(8). For example, air - oxidation makes coal increasingly soluble in alkali during the later stages with ultimate conversion of about 20 - 30% (wt) of the carbon to carbon - oxides and about 40 - 50% of the hydrogen to water(8). The solubilised portion of the coal, considered to be "humic acid" is spectroscopically similar to the parent coal molecule except for increased concentrations of oxygen - rich functional groups, including phenolic -OH, -COOH and =CO (ketone and/or quinone). The limiting elemental compositions of these humic acids depend strongly on the temperature of oxidation and vary slightly with the rank of the coal.

Humic acid is a term usually applied to certain dark amorphous substances which occur in soil, peat and low - rank coal. Humic acid are alkali - soluble, can be precipitated by acids, and have molecular weights in the range of 20,000 - 50,000 daltons(9). A "typical" humic acid has a "core" which is partly aromatic in nature with other structural features derived from lignin, e.g. phenols and resorcinols(9). In addition, alcohol, carboxyl, carbonyl and quinoid groups and heterocyclic nitrogen are present in humic acids.

The humic acids formed by oxidising coal can be oxidised further to produce low molecular weight water - soluble acids. All the aromatic carboxylic acids (with the exception of benzoic acid), oxalic, succinic and acetic acids have been identified(9) in the products. Intense oxidation of coal if carried out for a sufficiently long time, consumes intermediate products such as humic acids and yields CO_2 and H_2O as ultimate products(9). Rates of coal oxidation are accelerated by higher temperatures and higher oxygen partial pressures. At even higher temperatures above 250 °C in air, a virtual low - temperature combustion sets in. Humic acids are used as drilling muds, boiler scale removers, pigments for printing inks, carriers of fertilizers and growth hormones for plants, transporters of trace minerals in soil and soil conditioners.

The rate of oxidation of coal is enhanced by the presence of alkali. When coal is slurried with aqueous sodium hydroxide and reacted with oxygen under pressure, and at temperatures up to 200 °C, the organic portion of the coal is completely solubilized and large amounts of aromatic carboxylic acids(11,12) are formed. Thirty to forty - five percent of the total carbon is recovered as carboxylic acids, and the remainder is converted to carbon dioxide. Jensen et al.(13) proposed that with coal in air, the predominant primary process is rapid generation of humic acids followed by decomposition of the carboxyl groups. In wet oxidation, the humic acids are presumed to form at the outer regions of the particles. The humic acids then dissolve and get further oxidised in the homogeneous solution phase, thereby exposing fresh reactive surface on the shrinking coal particle for continuing "primary" oxidation. This mechanism for the oxidation of coals in aqueous NaOH at 50 to 100 °C is discussed in detail by Deno and coworkers(14).

EXPERIMENTAL

North Dakota lignite of particle size less than 77 μm was electrolysed in 1M NaOH at room temperature in a stirred reactor made of Pyrex, using Pt electrodes. Experimental details and properties of the lignite are given elsewhere(7).

The lignite was weighed before and after the electrolysis. After electrolysis, the solid residue was filtered from the slurry, washed with distilled water and dried under vacuum at 40 $^{\circ}\text{C}$. The aqueous filtrate was acidified thereby causing a precipitate to form and gases to evolve. The gases produced during this operation were collected and analysed. The two solid products (solid electrolysed lignite residue and precipitate from acidified electrolyte) were characterized by transmission measurements using a Nicolet 7199 Fourier Transform Infrared Spectrometer (FTIR); these samples were also subjected to elemental analysis using a Perkin Elmer Model 240 analyzer. The parent lignite was similarly subjected to FTIR investigations and elemental analysis.

RESULTS AND DISCUSSIONS

When lignite was electrolysed in 1M NaOH slurries using Pt electrodes, products similar to humic acid were produced in addition to CO_2 , H_2 , relatively small amounts of O_2 and traces of CH_4 and C_2H_2 . The potential applied to the cell influences the production distribution; for example, increasing the electrode potential from 1.2 V to 2.5 V vs. SCE gave correspondingly greater humic acid production(7). Increasing the potential still further, however, lowers the amount of humic acid formed.

Elemental Analysis of Reacted Coal

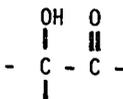
Table I provides a comparison of the elemental analyses of electrolysed lignites with those of a virgin lignite and a lignite that had been treated with 1M NaOH for 24 hours but not electrolysed. The most striking feature of the data seems to be the monotonic decrease of the oxygen content of the residual particulate material as electrode potential is increased. The decrease of oxygen content of the partially reacted lignite particles with increasing electrode potential may well be related to the greater solubility of the more oxygen - rich fragments produced during electrolysis. The outermost oxidised portions of the coal particles may be viewed as possessing large populations of carboxylic groups which render them potentially alkali - soluble. As these oxidised outer portions dissolve in the basic electrolytes, the inner coal residue would become relatively richer in carbon and poorer in oxygen. Figure 1 shows one hypothetical course of such a reaction in basic electrolytes in which nucleophilic addition of OH^- at an aliphatic carbonyl causes an adjacent C-C bond to rupture, thereby

producing a soluble carboxylic fragment and an insoluble residue richer in C and H than the initial composition. The result is that a molecule near the surface of the coal particle breaks along an aliphatic linkage to leave a relatively oxygen - poor residue on the coal particle while contributing a soluble, oxygen - rich, humic - acid - like fragment to the electrolyte solution. The larger population densities of carboxylic groups produced at higher potentials will have a greater tendency to decarboxylate. Such behavior probably underlies the increasing production of CO₂ with potential(7).

FTIR Results

Transmission infrared spectra of the parent lignite and its reaction production were obtained using a Nicolet Model 7199 Fourier Transform Infrared Spectrophotometer. The i.r. beam was passed through pellets prepared from a dry, finely ground (20 minutes in a "Wig-L-Bug") coal sample (10 mg) mixed with 300 mg of KBr. Thirteen - mm diameter pellets were pressed in an evacuated die under 20,000 lbs pressure for one minute and dried overnight at 105 °C. The spectra of the samples were corrected by subtracting background absorption in the 2000 - 4000 cm⁻¹ region.

In the i.r. spectrum of virgin NDL coal in Figure 2 various peaks are assigned as shown based on the work of Bouwman(15). A very low signal/noise ratio is observed for wave numbers greater than about 3600 cm⁻¹. This is attributed to scattering and low intensity of the i.r. source in this region. The broad band at 3400 cm⁻¹ arises from hydrogen bonding involving hydroxyl groups in free or bound H₂O. Bands at 2920 and 2860 cm⁻¹ (due to -CH stretching vibrations), indicate the presence of aliphatic hydrocarbon species. The band at 2360 cm⁻¹ is attributed to the presence of CO₂ and that at 1700 cm⁻¹ can be assigned to the carbonyl C=O stretching vibration of, e.g., carboxylic acids; the latter is a relatively small peak in most coals including the NDL used here. The band at about 1600 cm⁻¹ in Figure 2 (and which can occur anywhere between 1580 - 1620 cm⁻¹) is characteristic of solid carbonaceous system and is usually attributed to the ring vibrations in poly-nuclear condensed aromatic carbon structures. Contributions can also occur in this region from attenuated carbonyl vibrations of compounds in which intramolecular H-bonding bridge formation takes place between the -OH and the -C=O group, e.g.,



The bands at 1440 and 1380 cm⁻¹ correspond respectively to the presence of CH₂ and CH₃ groups (C-H bonding vibrations). Aromatic structures (C-H in-plane bending) can also contribute to 1440 cm⁻¹ band. The 1250 cm⁻¹ band can be assigned to the C-O-C ether group. The bands at 910, 800 and 750 cm⁻¹ are difficult to assign but are believed to arise from

minerals in the coal samples and out-of-plane C-H bending in aromatic structures. The most notable observations from a comparison of the i.r. spectra of: (1) lignite contacted with NaOH but not electrolysed, (2) residual lignite particles after electrolysis at 3.1 V vs. SCE and (3) of the humic acid - like products formed from the coal and later precipitated from the electrolyte is the large intensity in the 1700 cm^{-1} region (carbonyl band) for the dissolved residue compared to much lower intensities for both the residual lignite particles and the parent lignite. This indicates that the oxidised portion of the coal gets dissolved from the coal particles into the basic electrolyte. The 1700 cm^{-1} band is also enhanced for the solid residue after electrolysis but not nearly as much as for the soluble residue. The insoluble solid residues from electrolysed lignite were also Soxhlet extracted with an equivolumetric mixture of benzene and ethanol(16). The i.r. spectra of these residual solids after extraction showed greater oxygen functionality than the corresponding solids remaining after the parent lignite was extracted in the same way.

Using the 1580 - 1620 cm^{-1} band as an internal standard representative of the aromatic portion of the coal, the I_{1700}/I_{1600} intensity ratio gives a qualitative measure of the extent of the carbonyl functionality in the coal. The intensity ratio I_{1380}/I_{1600} and, to some extent the I_{1440}/I_{1600} ratio, are indicative of the content of alkane groups(15). Figures 3 and 4 show the variation of these intensity ratios of the solid residue after electrolysis as a function of electrode potential. The curve for the I_{1700}/I_{1600} ratio suggests that the oxygen content increases with an increase in the electrode potential, reaches a maximum due to the formation of carbonyl groups and then declines with further increase in potential. The later decrease in the ratio could be attributed to the dissolution of carboxylic material in NaOH where it reacts via Kolbe's mechanism to form CO_2 ; Figure 5 shows a monotonic dependence of CO_2 production on the applied electrode potential. The variation of the I_{1380}/I_{1600} , and I_{1440}/I_{1600} ratios with the electrode potential permit speculation that at the lower potentials the soluble products that dissolve away from the solid particles are more aromatic than the lignite; this dissolution process then leaves behind solid particles, the surfaces of which get relatively higher in alkane concentrations as the electrode potential increases. Increase of electrode potential beyond the maxima of Figures 3 and 4 may cause additional oxidation of the surface alkane groups to soluble products or CO_2 , thereby reducing the relative alkane intensity observed at higher potentials.

CONCLUSIONS

The nature of coal oxidation products is a strong function of the applied electrode potential. As the oxidising power is increased, oxygen containing functional groups are formed on the surface of coal, however, a further increase in the electrode potential results in formation of alkali - soluble carboxylic groups leaving behind an oxygen - poor reacted coal particle. The research work to date suggests that by selectively controlling the electrode potential, desirable coal oxidation products may be obtained.

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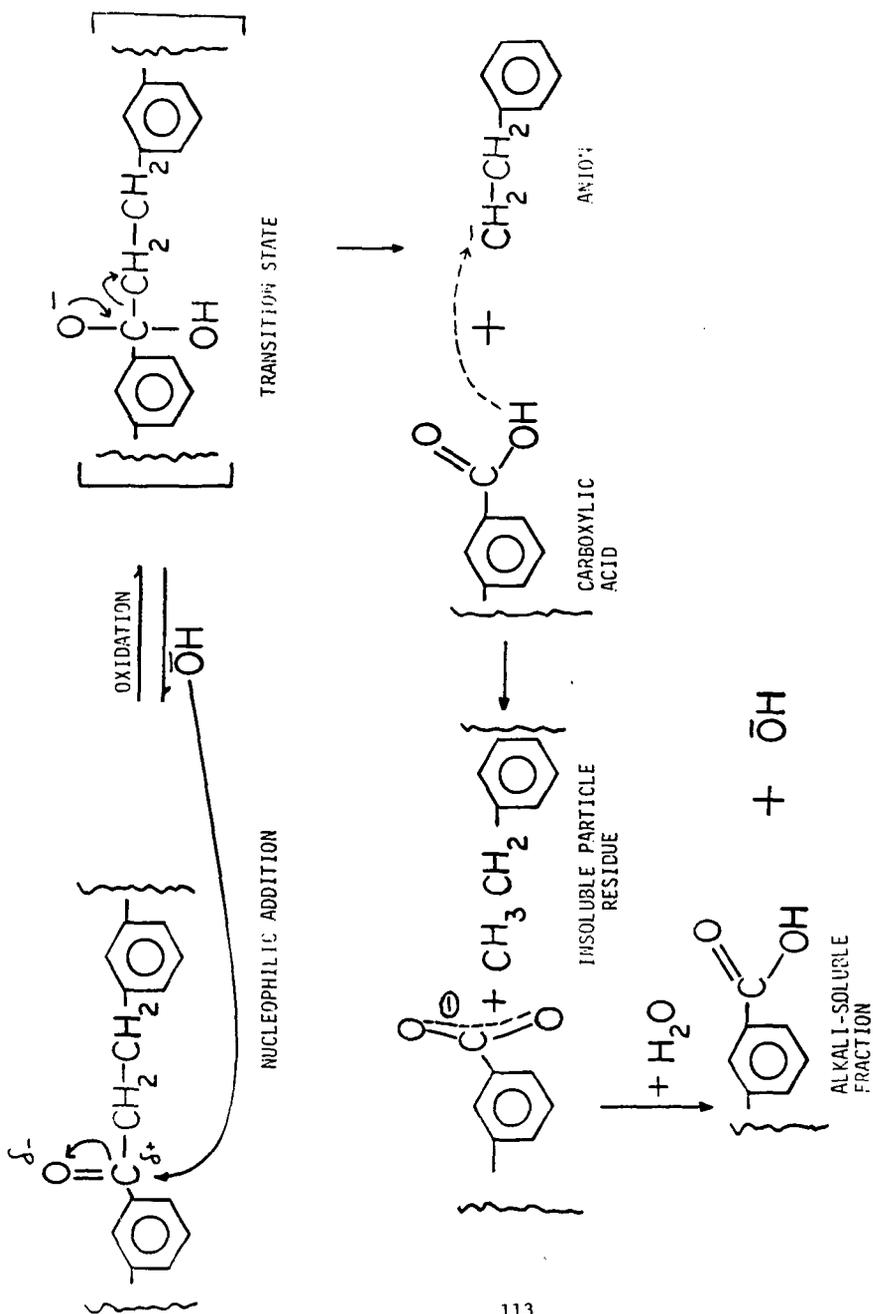


Figure 1. A proposed overall mechanism for coal oxidation.

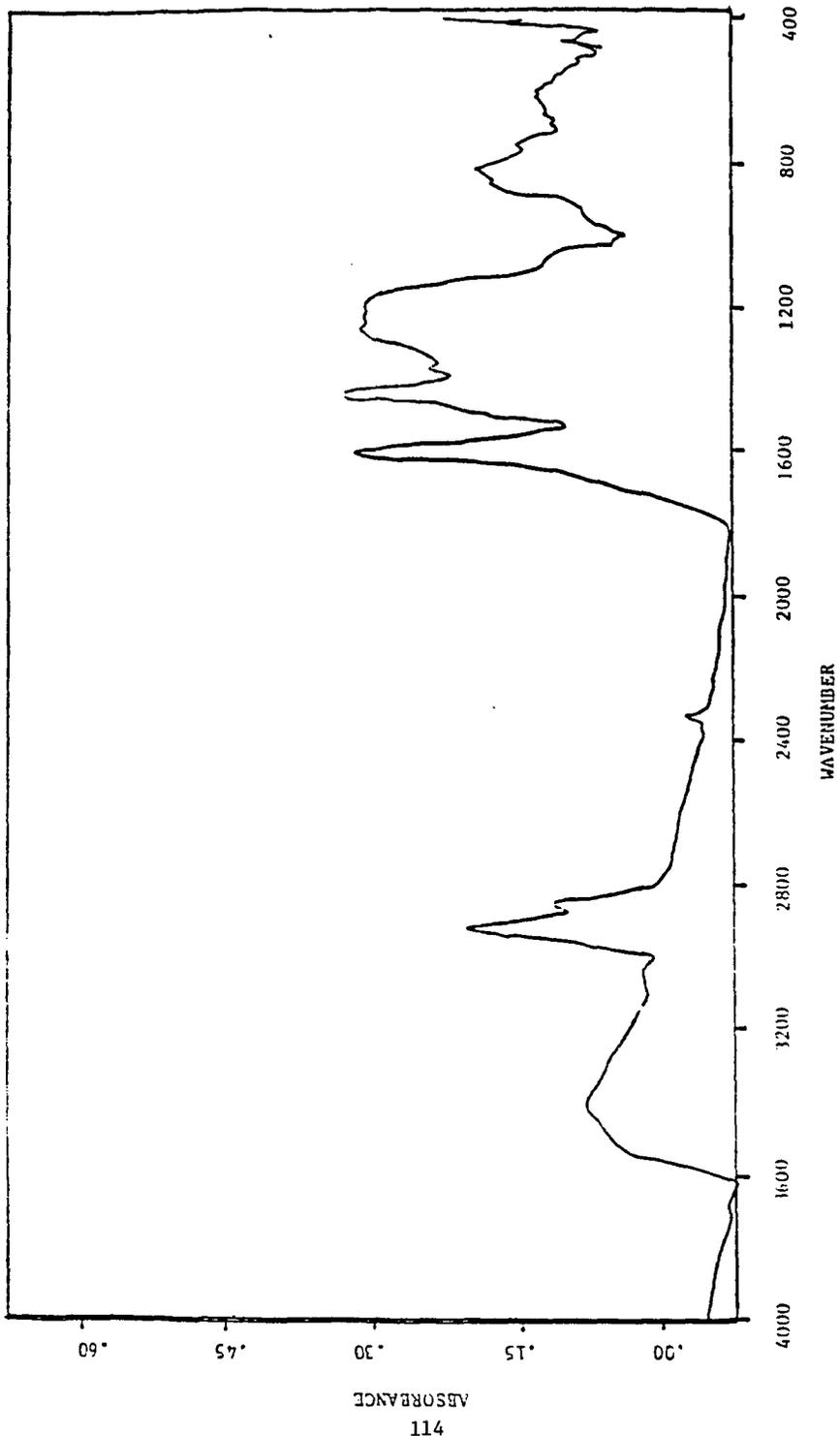


Figure 2. FTIR spectrum of virgin NDL coal.

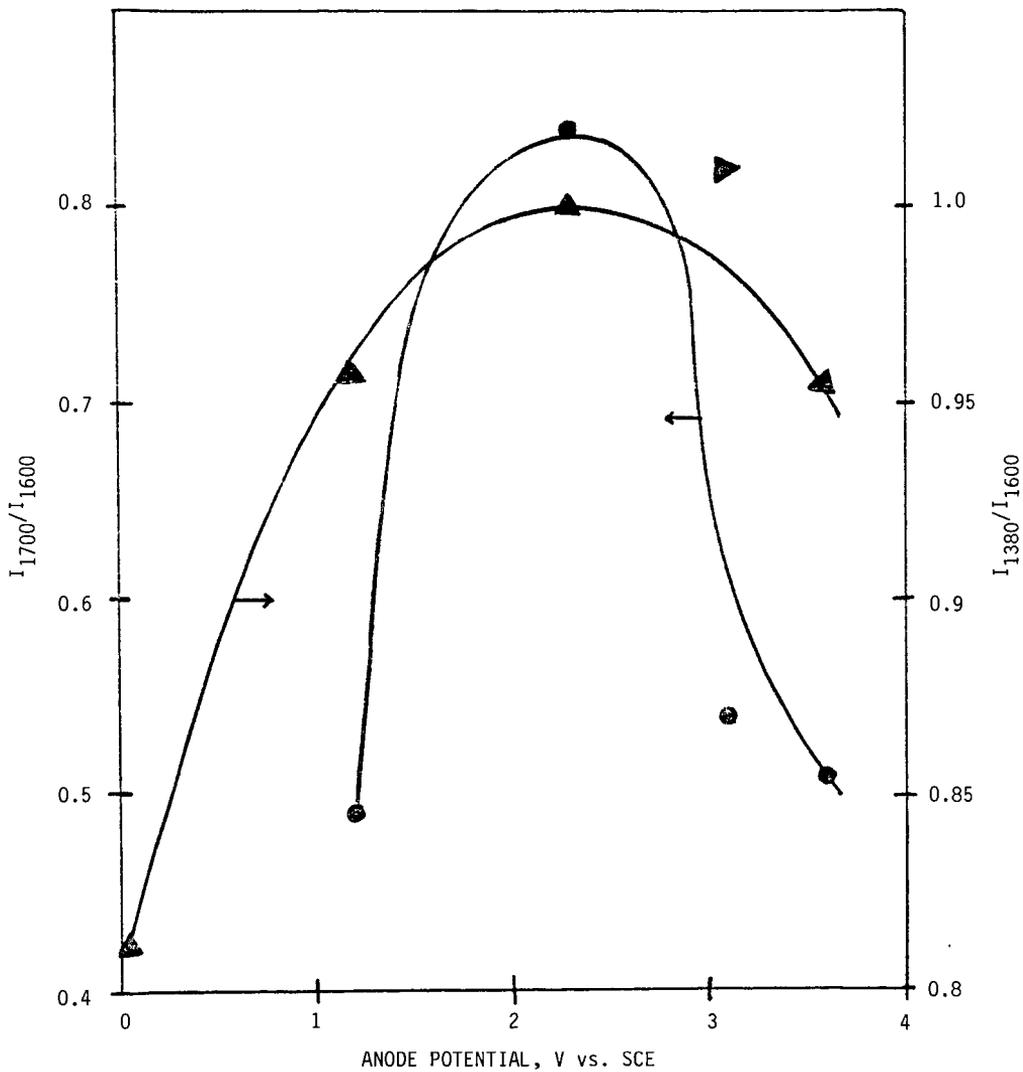


Figure 3. FTIR band intensity ratios of insoluble lignite residues as a function of electrode potential. Experimental conditions as in Table 1.

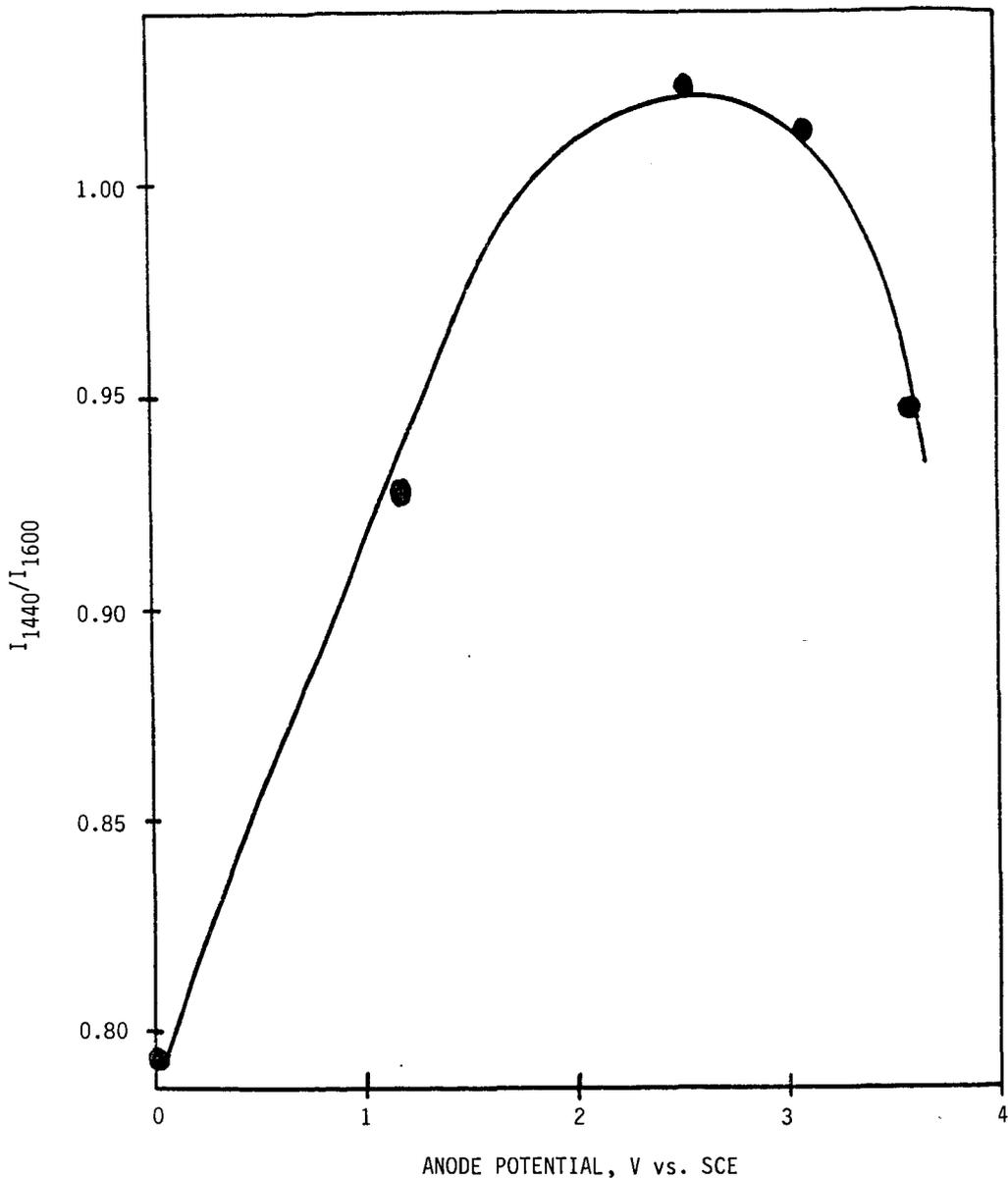


Figure 4. FTIR band intensity ratios of insoluble lignite residues as a function of electrode potential. Experimental conditions as in Table 1.

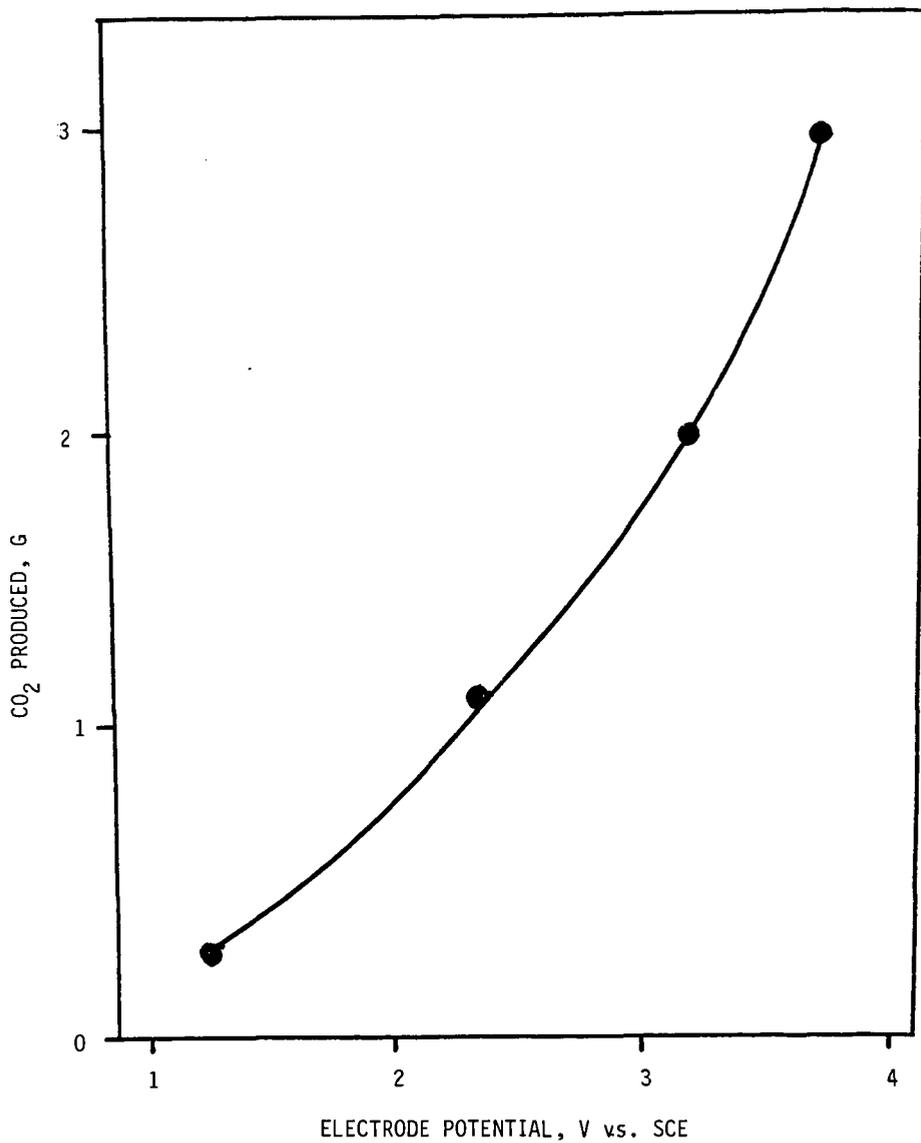


Figure 5. Influence of potential on amount of CO₂ liberated after acidification of electrolyte. Experimental conditions as in Table 1.