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viation barriers below 170 kJ mol$^{-1}$. The production of primary and secondary radicals in $\beta$-scission reactions contributes to the incorporation of deuterium in $\beta$-positions.

CONCLUSIONS

The results of this work have shown that exchange and hydrogen transfer pathways operate simultaneously in general agreement with results of Heredy$^2$, Stock$^3$ and Cronauer$^5$. The early stages in the conversion of coal must involve the formation of stable and selective radicals from unimolecular homolysis of labile structure and facile molecule-induced homolytic pathways. However, reactive radicals may be produced via $\beta$-scission reactions, and if air is present, non-selective auto-oxidation intermediates may also lead to reactive radicals. The results of $^2$H n.m.r. show close similarity between different coals and indicate the need for maceral separation$^{13}$ to better distinguish reacting structures in the coals. Finally, the deuterium distributions in the coal products include substantial amounts of structure $\beta$ in aromatic rings or in comparable aliphatic structure. Future model studies of coal liquefaction should take into account the significant involvement of non-phenolic aliphatic structure, and steady-state concentrations of reactive radicals, particularly hydroxyl radical.

ACKNOWLEDGEMENT

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REFERENCES

14. Liotta, R., Fuel 1979, 48, 724
24. Barle, K. D., Snape, C. E., Martin, T. G. and Williams, D. F., Fuel 1979, 58, 413
27. Stein, S. E. ibid, 1981, 169, 97
32. Derbyshire, P. J. and Whisthurt, D. D., Fuel 1981, 60, 655
40. Ross, D., personal communication
42. Benson, S. W. and Nangia, P. S., Acc. Chem. Res. 1979, 12, 233
43. Vernon, L. W., Fuel 1980, 59, 102
44. Camaioni, D. M., Franz, J. A. and Beisilhine, unpublished results

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Application of FT-i.r. spectroscopy to the determination of COOH groups in coal

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FT-i.r. studies of acid-demineralized and cation-loaded lignites demonstrate that exchange methods presently being used to determine carboxylic acid groups in coal produce systematic errors. An i.r. method based on intensity measurements of the 1710 cm$^{-1}$ carboxylic acid C=O stretching mode is reported.

(Keywords: coal; COOH groups; instrumental methods of analysis; FT-i.r.)

It is well-known that carboxylate groups affect various coal reactions and conversion processes$^1$–$^4$. Recent work in this laboratory has demonstrated that these groups are relatively easily detected by i.r. spectroscopy in such processes as coal oxidation$^1$. Also of interest is the dual nature of carboxylate groups in lignites, where they may be found in either the acid (COOH) or salt (COO$^-$$^-$ M$^+$, M = metal cation) form. The cations associated with carboxylate groups can promote liquefaction$^2$ or give rise to deposits in liquefaction reactors$^3$. On pyrolysis, a lignite with metal carboxylates yields more CO$_2$ than one in which these groups are in the acid form$^4$. Similarly, Otake$^5$ has found that a corresponding increase can be obtained when the acid groups in a demineralized lignite are exchanged chemically with various metal cations.

Because of the variety of processes in which carboxylate groups are considered ‘important’ or ‘significant’, it is desirable to have an accurate method for quantitative analysis. Schafer$^6$ developed an ion-exchange procedure using barium acetate which has since become the standard method. A major conclusion of this study was that in the pH range 8.0–8.5 the exchange of carboxyl groups was complete. As evidence for this, Schafer cited a steady decrease in the absorbance of the 1700 cm$^{-1}$ vibration in the i.r. spectra of coal samples as pH increased to a value of $\approx$ 8.5, followed by a levelling off of absorbance at a constant value upon further pH increase. It was suggested that the residual absorbance at 1700 cm$^{-1}$ was due to the presence of some carbonyl groups (other than carboxyl).

However, it was also observed that additional exchange occurred at higher pH values. This was explained as being due to exchange of phenolic OH groups and is consistent with the behaviour of phenol–formaldehyde polymers, in which little or no exchange occurred until pH of $\approx$ 8. Thus, Schafer concluded that exchange reactions of COOH groups should be carried out at pH 8.3–8.5, to prevent interference from the exchange of phenolic groups.

This result is a key factor in exchange procedures, in which the extent of reaction (and thus the measured amount of COOH present) is determined by titration, assuming complete and specific exchange of COOH groups. Nevertheless, there is some lingering doubt concerning the completeness of the exchange. Is the equilibrium between acid and salt groups at pH 8 sufficiently tilted towards the latter to allow the assumption of complete exchange? In this context, the application of FT-i.r. procedures should allow accurate intensity measurements of the characteristic 1700 cm$^{-1}$ carboxylic acid mode in coal independent of other acidic entities, such as phenolic OH (which have bands in other regions of the spectrum).

Such procedures have been employed to measure changes in the carboxylate region of a Texas lignite upon exchange with various cations. Out of these studies has emerged a technique which uses an adaptation of Schafer’s method as a calibration of an FT-i.r. procedure for measuring carboxylic acids. This allows a determination of absorption coefficients from the curve-fitted carboxylic acid mode at 1700 cm$^{-1}$. With this information, the process of measuring COOH groups can be performed much quicker than by using the ion exchange method. Furthermore, in developing the procedure a systematic error was detected in previous measurements, due to incomplete exchange. This error can be eliminated using appropriate FT-i.r. methods.

**EXPERIMENTAL**

The coal sample employed in this study is a lignite from Texas, PSOC 623, described in Table 1. The coal was loaded with five different cations (Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$) by soaking in acetate solutions of each cation. Otake$^7$ determined the amount of COOH in the coal as 2.10 meq COOH g$^{-1}$ demineralized coal via Schafer’s method ($=6.72$ wt% O as COOH), assuming that in the Ba$^{2+}$ exchanged coal coverage of COOH groups is essentially complete.

As a test for further COOH exchange at higher pH, the Ba$^{2+}$ loaded sample was suspended in distilled water and dialysed against a large excess of 1N NaOH solution for 24 h. The lignite went partially into solution as the NaOH diffused through the semi-permeable membrane; however, upon subsequent soaking in distilled water most of
Table 1: Analyses of Texas (Darco Seam) lignite, PSOC 623

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Elemental analysis</th>
<th>(wt%, dry basis)</th>
<th>(wt%, dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>C</td>
<td>18.6</td>
<td>60.7</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>H</td>
<td>44.8</td>
<td>4.3</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>N</td>
<td>38.8</td>
<td>1.1</td>
</tr>
<tr>
<td>S (organic)</td>
<td>O (by diff)</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Cl</td>
<td></td>
<td></td>
<td>14.3</td>
</tr>
<tr>
<td>Mineral matter (including 0.36% Fe₂S₃)</td>
<td></td>
<td></td>
<td>0.03</td>
</tr>
</tbody>
</table>

Petrographic analysis

| Vitrinites       | Kaolinite | 80.9 | 41 ± 1.6 |
| Lipinites        | Quartz    | 2.3  | 12 ± 3.1 |
| Inertinites      | Anhydrite | 16.4 | 1 ± 0    |
|                  | Calcite   |      | nil      |
|                  | Pyrite    |      | nil      |
|                  | Other Clays|     | 24       |
|                  | Others    |      | 32       |

a After removal of exchangeable cations with 1N ammonium acetate

The material was re-precipitated and could be recovered by filtration.

FT-i.r. spectra were recorded on a Digilab 15 E FTS spectrometer. Samples were prepared by dispersing 1 mg of sample in 300 mg KBr using a Perkin Elmer Wig-L-Bug and a pre-grind procedure. Spectra were obtained by averaging 400 interferograms at a resolution of 2 cm⁻¹.

The program used to curve-resolve spectra fits the observed spectral profile to a set of bands as a linear sum of Gaussian and Lorentzian band shapes in the proportion f to (1−f), f being determined by a least squares iteration, as described in a previous publication. Naturally, it is always possible to 'fit' a given spectral profile to a set of bands. In order for the results to be meaningful it is necessary to determine the number of peaks in a given region of the spectrum and to have a good initial estimate of their frequency and intensity. Furthermore, any band so defined should correspond to some identifiable group frequency for the material in question. Maddams has reviewed the problems involved in curve-resolving at some length and outlined procedures that should be applied to obtain meaningful results. The general application of these procedures to coal spectra have previously been discussed and the specific problems encountered in curve-resolving the 1600 cm⁻¹ region have been considered.

RESULTS AND DISCUSSION

Figure 1 compares the FT-i.r. spectrum (between 2000 and 5000 cm⁻¹) of the demineralized lignite to that of the Ba⁺⁺ loaded sample. The difference spectrum obtained by spectral subtraction of the two (on a 1:1 weight basis) is shown in the same figure. It can be seen that the 1600 cm⁻¹ region of the spectrum broadens upon exchange. This is due to a shift of the COOH mode near 1700 cm⁻¹ to 1565 cm⁻¹ upon exchange. This change can be more clearly seen in the difference spectrum, where positive and negative (above and below the baseline) bands are clearly resolved. Similar results were obtained for the other four cation loaded samples. The assignments of these spectral bands are well established. The 1710 cm⁻¹ band is due to COOH groups, while the 1564 cm⁻¹ vibration can be assigned to structures of the type COO⁻M⁺. These differences demonstrate the ability of FT-i.r. to detect, qualitatively, changes in the coal upon exchange. To obtain quantitative results, however, it is necessary to separate the overlapping contributions of bands in this spectral region. This may be accomplished through the use of least squares curve-fitting procedures.

The importance of using the second derivative of a spectrum in curve-resolving studies has been discussed in general terms by Maddams and with particular reference to coal spectra in work performed in this laboratory. Typical examples are illustrated in Figures 2 and 3.
FT-IR spectroscopy for COOH groups in coal: M. Starinic et al.

Table 2 Normalized peak heights from curve-fitted spectra

<table>
<thead>
<tr>
<th>Sample</th>
<th>mg COOH g⁻¹</th>
<th>1710 cm⁻¹</th>
<th>1622 cm⁻¹</th>
<th>1564 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demineralized</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba²⁺-loaded</td>
<td>2.10</td>
<td>0.39</td>
<td>0.52</td>
<td>0.02</td>
</tr>
<tr>
<td>K⁺-loaded</td>
<td>1.53</td>
<td>0.20</td>
<td>0.59</td>
<td>0.40</td>
</tr>
<tr>
<td>Na⁺-loaded</td>
<td>1.61</td>
<td>0.28</td>
<td>0.62</td>
<td>0.24</td>
</tr>
<tr>
<td>Mg²⁺-loaded</td>
<td>2.06</td>
<td>0.17</td>
<td>0.50</td>
<td>0.44</td>
</tr>
<tr>
<td>Ca²⁺-loaded</td>
<td>2.04</td>
<td>0.25</td>
<td>0.56</td>
<td>0.52</td>
</tr>
<tr>
<td>Ba²⁺-loaded/24 h</td>
<td>0.13</td>
<td>0.13</td>
<td>0.56</td>
<td>0.57</td>
</tr>
<tr>
<td>NaOH soak</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

fraction Gaussian (bandshape), band intensities, widths at half-height, and locations are obtained, a second computer program was used to plot such bands, as illustrated in both Figures 2 and 3. Measurements of peak heights for all the exchanged samples, normalized to the equivalent of 1 mg of dry demineralized coal, are summarized in Table 2. There is a dramatic increase in intensity of the 1565 cm⁻¹ band upon exchange. This is accompanied by a decrease in intensity and an apparent shift in the COOH band from 1710 cm⁻¹ to ≈ 1705 cm⁻¹. The normalized intensity of the 1622 cm⁻¹ band, which should remain constant, varies slightly. Errors in curve-resolving, weighing pellets, etc., are certainly a factor in this variation. However, it should be kept in mind that a band due to adsorbed water also contributes to the intensity of this peak, so that slightly different amounts of water picked up during sample preparation would also lead to the observed differences.

The first surprise concerning the data shown in Table 2 is the fact that a band near 1705 cm⁻¹ remained so intense in the Ba⁺⁺ exchanged sample, for which exchange reactions are assumed in most cases to be complete. Second, the results also indicate that one cation, Mg⁺⁺, produced a greater reduction in intensity of the C=O vibration. There are two possible explanations for this: 1. the 1705 cm⁻¹ vibration is due in part to something other than carboxylic acids; or 2. the exchange reactions are not complete. If intensity changes in this band are to be related to COOH concentration in coal, this problem must be resolved.

Because the measurements of the band near 1700 cm⁻¹ are not affected by OH and other acidic groups upon exchange, an experiment was attempted which has been of some use in identifying COOH groups in coals and oxidized carbons. This involved soaking the Ba⁺⁺ exchanged sample in 1N NaOH solution in an attempt to obtain further exchange of COOH groups. Because this lignite is partially soluble in the NaOH solution, the procedure was modified as described in the experimental section. Figure 4 shows the curve resolved 1850-1500 cm⁻¹ portion of the spectrum of the NaOH soaked/Ba⁺⁺ exchanged sample along with its second derivative. Here a band may still be seen at 1699 cm⁻¹, however, its character (as indicated by the sharpness of the second derivative) is nothing like the vibration in either the demineralized or any of the exchanged samples. Furthermore, its intensity is significantly less than the corresponding band in any of the exchanged sample spectra (Table 2). These changes are accompanied by an increase in intensity of the 1564 cm⁻¹ band above that observed in any other cation-loaded sample. In addition, a decrease may be observed in the intensity and broadness.

Figure 3. Bottom: FT-IR spectrum between 1850 and 1500 cm⁻¹ or Ba⁺⁺-loaded lignite and component bands from curve resolving. Top: second derivative of spectrum.
of the 1250 cm⁻¹ vibration when the spectrum of the NaOH soaked sample is compared to that of the Ba⁺⁺ loaded coal, as shown in Figure 5. This band, assigned to the C-O stretch coupled to the O-H bending mode of COOH groups, would be expected to disappear upon exchange. The results would thus indicate that soaking in NaOH unquestionably promotes further COOH exchange, demonstrating that the exchange reaction using Schauer’s method is incomplete. Nevertheless, as will be demonstrated below, it is possible to build on this procedure to obtain more accurate numbers.

All of which still leaves unanswered the question of the residual 1700 cm⁻¹ vibration in the spectrum of the NaOH soaked sample. The most likely origin of this mode is either carbonate groups formed during NaOH exchange (by dissolution of atmospheric CO₂), residual (possibly inaccessible) C=O in COOH groups, or C=O vibrations in entities such as ketones. If the assignment to carbonate structure (sodium bicarbonate has bands near 1700 cm⁻¹) were correct, one would expect to observe a very strong stretching mode near 1400 cm⁻¹ as well as out of plane bending modes in the 700-800 cm⁻¹ spectral region. Figure 5 shows no evidence of such bands. While a band does appear in the NaOH soaked sample spectrum around 1400 cm⁻¹, no bands in the 700-800 cm⁻¹ region are observable. This 1400 cm⁻¹ vibration, which also appears in the difference spectrum of the Ba⁺⁺ loaded and demineralized samples (Figure 1), is most likely due to a symmetric stretch of the COO⁻ group. Thus, with no other evidence for carbonates in the infrared, it may be ruled out as a possible cause of the residual 1700 cm⁻¹ band in the NaOH soaked sample spectrum. It thus appears most likely that the vibration is due to other C=O structures in the coal; however, the question of still unexchanged COOH is legitimate. To assume that C=O as COOH is entirely removed would be to assume complete exchange. This may be unwise due to the equilibrium nature of the NaOH exchange reaction. Nevertheless, it would be anticipated that the concentration of any residual COOH groups would be relatively small and the 1695 cm⁻¹ band is assigned to other carbonyl groups, possibly ketones (aldehydes have a characteristic C-H stretching mode which was not observed).

The next task is to relate the intensity of the 1700 cm⁻¹ band to the concentration of COOH groups, taking into account the contribution of the 1695 cm⁻¹ mode discussed above. For the Texas lignite used in this study, Otaka determined (using Schauer’s method) that the concentration of oxygen present as COOH groups is 6.72%. It has been demonstrated that the exchange is incomplete and therefore this number is too low. It can, however, be directly related to the difference in the intensity of the 1710 cm⁻¹ band between the spectra of the demineralized original lignite and the barium exchanged sample. In addition, because a difference is used, the contribution of the 1695 cm⁻¹ band is subtracted out. Consequently, an absorption coefficient can be determined (or more accurately in terms of the definitions used, a conversion factor) relating band intensity to concentration of COOH groups, which in turn should allow a more accurate measurement of COOH groups.

It is usual in quantitative work to write the Beer-Lambert law in the following form:

\[ I = abc \]  

(1)

where: \( I = \) the band intensity (definitions in terms of peak heights or areas can be used); \( a = \) an absorption coefficient; \( b = \) the thickness of the sample; and \( c = \) the concentration of the species responsible for the band being measured. This equation can be rewritten in terms of weight fractions for solid samples. It is convenient to use the following form:

\[ \frac{I}{E} = c \]  

(2)

where: \( E = \) the quantity which will be referred to as a 'conversion factor'. It is equivalent to the reciprocal of an
extinction coefficient for a 1 mg dmmf coal sample (dispersed in 300 mg of KBr and made into a standard 13 mm dia. pellet). Using FT-i.r. instruments it is simple to normalize spectra and hence band intensities, to the equivalent of 1 mg of sample by weight. (The spectra also have to be adjusted to account for the weight of cations in the exchanged samples.) It follows that for these measurements:

\[ I_{1700}^{(demin)} - I_{1700}^{(Ba)} \times 100\% = 6.72\% \]  

(3)

The application of this equation raises several problems. The first of these lies in the contribution of the 1699 cm\(^{-1}\) vibration, the 'other C=O present', to the C=O as COOH vibration in the demineralized and Ba\(^{++}\)-loaded samples. If this contribution is different in these two samples, due to variances in band overlap between the two spectra, an element of error would occur in applying peak heights to the conversion factor calculation. As a check, the peak areas obtained from curve-resolving were also applied. Since areas of the C=O vibration in the demineralized and Ba\(^{++}\)-loaded sample spectra overlap almost completely, as can be seen in Figures 2 and 3, the 'other C=O' vibration should have nearly the same area contribution in both cases and will thus subtract out upon application of Equation (3).

The second problem arises during the determination of conversion factors from spectra of samples exchanged using cations other than Ba\(^{++}\). These calculations, which involve calibration of weight % COOH using the ratio of meq. COOH per gram of coal determined for each sample to that determined for the Ba\(^{++}\)-exchanged sample by Otak\(^{6}\), gave a range of values for conversion factors. This is perhaps most clearly illustrated by a plot of meq. COOH versus the intensity of the 1710 cm\(^{-1}\) band in the exchanged samples, illustrated in Figure 6. The m. equivalents of COOH are measured by the degree of exchange of the coal with various cations, so that the most intense band is observed in the unexchanged sample and the plot has a negative slope. The data from the Ba\(^{++}\)-exchanged sample are considered to be the most reliable, as the chemical procedures utilized in determining COOH were optimized specifically for barium exchange\(^{6,15}\). The variance in coverage by other cations can arise from problems in the choice of exchange time, temperature, and pH of washing solutions chosen to remove excess ions.

Application of Equation (3) to peak height and area differences (Tables 2 and 3, respectively) between the spectra of Ba\(^{++}\)-loaded and demineralized samples yields the conversion factors in Table 4. These conversion factors are then applied to the 1700 cm\(^{-1}\) peak height and the band area differences between the demineralized and NaOH soaked samples. This calculation yields 9.2% and 9.0% O as COOH respectively (Table 4). The fact that only a 0.2% difference can be determined between the two values indicates that sufficient overlap of the various C=O vibrations occurs to allow measurement by differences in peak height or area. Finally, the values obtained by FT-i.r. are significantly higher than the 6.72% value obtained chemically, suggesting the NaOH soaking/FT-i.r. method should be used for more representative % O as COOH values. Errors in curve-resolving etc. will unquestionably affect the numbers reported; nevertheless, it is believed that this work demonstrates that titration procedures significantly underestimate the concentration of COOH groups in coal and an attempt has been made to determine more accurate numbers.

![Figure 6 Plot of m. equivalents of COOH per gram of coal versus the intensity of the 1710 cm\(^{-1}\) band](image)

**Table 3** Normalized (to 1 mg dmmf sample) peak areas of the 1700 cm\(^{-1}\) vibration

<table>
<thead>
<tr>
<th>Sample</th>
<th>A 1700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demineralized</td>
<td>34.1</td>
</tr>
<tr>
<td>Ba(^{++})-loaded</td>
<td>15.2</td>
</tr>
<tr>
<td>Ba(^{++})-loaded/NaOH wash</td>
<td>9.2</td>
</tr>
</tbody>
</table>

**Table 4** Conversion factors and COOH content using the 1710 cm\(^{-1}\) vibration: peak height versus peak area

<table>
<thead>
<tr>
<th>Method</th>
<th>Conversion factor(^{a})</th>
<th>%O as COOH(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>36.4</td>
<td>9.2</td>
</tr>
<tr>
<td>Area</td>
<td>0.36</td>
<td>9.0</td>
</tr>
</tbody>
</table>

\(^{a}\) Obtained using differences in 1710 cm\(^{-1}\) vibration in Ba\(^{++}\)-loaded and demineralized sample spectra

\(^{b}\) Obtained using differences in 1710 cm\(^{-1}\) vibration in Ba\(^{++}\)-loaded/NaOH washed and demineralized sample spectra

**CONCLUSIONS**

It has been shown that traditional methods of measuring % O as COOH in lignites tend to underestimate actual amounts, due to incomplete exchange. Nevertheless, previous procedures can be improved to obtain a calibration method by quantitatively accounting for unexchanged groups. This allows us to obtain conversion factors relating intensity or area of the 1700 cm\(^{-1}\) COOH vibration in coal spectra to % O as COOH. Unlike titration methods, the fact that NaOH can also exchange OH groups has no bearing on the results. Contributions to 1700 cm\(^{-1}\) peak intensities and areas from a residual 'other C=O' vibration subtract out in difference calculations.
ACKNOWLEDGEMENTS

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REFERENCES

4 Schafer, H. N. S. Fuel 1979, 58, 673

6 Schafer, H. N. S. Fuel 1980, 59, 197
7 Topp, N. E. and Pepper, K. W. J. Chem. Soc. 1940, 3299
8 Elliot, J. J., Brown, J. P. and Balfour, J. P. personal communication, to be published
10 Maddams, W. F. Appl. Spectrosc. 1980, 34, 245
13 Painter, P. C., Starsinic, M., Squires, E. and Davis, A. Fuel 1983, 62, 742
15 Morgan, M. E., Jenkins, R. G. and Walker, Jr., P. L. Fuel 1981, 60, 189
Variation of rate during potassium-catalysed CO$_2$ gasification of coal char

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The instantaneous rate of catalysed CO$_2$ gasification of char at 800°C was measured at various levels of conversion. One important reason for the change in rate during the gasification is the change in the solid surface area, measured in the present study by CO$_2$ adsorption at 25°C. The models which have been successful in representing the char porous structure under noncatalytic conditions were found inadequate for catalytic gasification at low conversions. Other important factors contributing to the variation in rate during conversion are the catalyst loss and the change in the catalyst/carbon ratio. A model is presented which combines the effects of these contributing factors and gives a satisfactory representation of the experimental data.

(Keywords: coal; gasification; catalysis)

During the last decade, increased interest has been focused on the steam gasification of coal using alkali metal catalysis. Various investigators have studied the kinetics of catalytic H$_2$O–C and CO$_2$–C gasification reactions and comprehensive reviews are available$^{1-2}$. An important aspect of this gasification process is the variation in the reaction rate during conversion. The primary contributing factors are the change in the reaction area and the change in the amount and distribution of catalyst during gasification.

Because the gasification reactions occur at the gas–solid interface, the available catalysed surface area is of major importance. Most researchers have avoided the measurement and analysis of reaction area by evaluating rates on a sample mass basis. Only recently have some investigators considered the effect of surface area in the analysis of catalytic gasification reactions$^{4-5}$. The effect of catalyst loading on the rate has been the subject of several studies$^{6-8}$. However, the change in the effective catalyst concentration during gasification and its contribution to the variation in rate have received very little attention. In the present study the variation in rate during CO$_2$ gasification is investigated and the roles of the various contributing factors are analysed.

**EXPERIMENTAL**

All experiments were conducted with a char prepared from Utah bituminous coal by slow devolatilization at 1000°C. Using an air-jet sieve, the 53–63 μm size fraction was separated and retained for use. The analysis of the sieved char is given in Table 1.

The char was impregnated with KOH to various concentration levels using an incipient wetting technique. After drying at room temperature, the samples were stored under vacuum until use. The potassium content of the dried samples was determined by atomic absorption spectroscopy.

Char samples were gasified at 800°C with 15 kPa CO$_2$ and a total pressure of 100 kPa, the balance being He. The reactor was a quartz tube (6 mm o.d., 4 mm i.d.) heated inside a three-zone electric furnace. The initial sample size was held constant at 40 mg. Under these conditions, the reactor was considered differential; experiments showed that reducing the sample size below 40 mg did not result in a measurable rate increase. The change in CO$_2$ concentration was less than 10%. The concentration of CO was around or less than 1%, so its inhibition effect was negligible. Oxygen levels were maintained below 10 ppm during gasification. The gaseous products were analysed by an on-line gas chromatograph and CO–CO$_2$ i.r. analysers. The reaction rates and carbon conversions were calculated from the flow rates and the CO–CO$_2$ concentrations. A more detailed description of the experimental system and procedures is given elsewhere$^{8,9}$.

![Table 1 Analysis of char](https://example.com/table1.jpg)

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt% (dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>79.1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.7</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.6</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.1</td>
</tr>
<tr>
<td>Ash</td>
<td>16.8</td>
</tr>
<tr>
<td>Oxygen (by difference)</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The intraphase areas of the char samples were measured by a dynamic adsorption–desorption technique using CO$_2$ as the adsorbing gas with helium as the carrier gas. Samples were degassed overnight at 150°C in a pure helium atmosphere before adsorption. To minimize the diffusional limitations caused by the char micropores, adsorption was performed at 25°C for 3 h. The amount of CO$_2$ adsorbed on the char was determined by integrating the desorption peaks. This eliminated the effect of possible reaction between CO$_2$ and the catalyst. The Dubinin–Polanyi equation was used to find the total micropore volume. This method gave reproducible results and Dubinin–Polanyi plots with a high degree of linearity. The molecular cross-sectional area of CO$_2$ was taken as 0.218 nm$^2$ for surface area calculations. A detailed de-