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vation barriers below 170 kJ mol^{-1} .²⁷ The production of primary and secondary radicals in β -scission reactions contributes to the incorporation of deuterium in β -positions.

CONCLUSIONS

The results of this work have shown that exchange and hydrogen transfer pathways operate simultaneously in general agreement with results of Heredy², Stock³ and Cronauer⁴. 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 β -scission reactions, and if air is present, non-selective auto-oxidation intermediates may also lead to reactive radicals. The results of ²H n.m.r. show close similarity between different coals and indicate the need for maceral separation¹² to better distinguish reacting structures in the coals. Finally, the deuterium distributions in the coal products include substantial amounts of structure β to aromatic rings or in comparable aliphatic structure. Future model studies of coal liquefaction should take into account the significant involvement of non-benzylic aliphatic structure, and steady-state concentrations of reactive radicals, particularly hydroxyl radical.

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REFERENCES

- 1 'Proceedings of the International Conference on Coal Science', Verlag Glückauf GmbH, Essen, 1981, pp 327-331
- 2 King, H.-H. and Stock, L. M. *Fuel* 1980, **59**, 447 and *ibid* 1982, **61**, 257
- 3 Heredy, L. A., Skowronski, R. P., Ratto, J. J. and Goldberg, I. B. *Am. Chem. Soc. Div. Fuel Chem. Prepr.* 1981, **26**, 84
- 4 Ratto, J. J., Heredy, L. A. and Skowronski, R. P. *Am. Chem. Soc. Symp. Ser.* 1980, **139**, 347
- 5 Skowronski, R. P., Heredy, L. A. and Ratto, J. J. *Am. Chem. Soc. Div. Fuel Chem. Prepr.* 1978, **23**(4), 255
- 6 Cronauer, D. C., Jewell, D. M., Shah, Y. T., Modi, R. J., Seshandri, K. S. and Young, D. C. *Am. Chem. Soc. Symp. Ser.* 1980, **139**, 371
- 7 Cronauer, D. C., Jewell, D. M., Shah, Y. T. and Modi, R. J. *Ind. Eng. Chem. Fundamentals* 1979, **18**, 153
- 8 Cronauer, D. C., McNeil, R. I., Young, D. C. and Ruberto, R. G. *Fuel* 1982, **61**, 610
- 9 Franz, J. A. *Am. Chem. Soc. Div. Fuel Chem. Prepr.* 1979, **24**, 263
- 10 Franz, J. A., Camaioni, D. M. and Skien, W. E. 'Coal Structure' (Eds. M. L. Gorbaty and K. Ouchi), *Adv. Chem. Ser.* 192, Am. Chem. Soc., Washington, DC, 1981, pp 75-94
- 11 Franz, J. A. *Fuel* 1979, **58**, 405
- 12 Franz, J. A. and Camaioni, D. M. *Fuel* 1980, **59**, 803
- 13 Franz, J. A. and Camaioni, D. M. *J. Org. Chem.* 1980, **45**, 5247
- 14 Liotta, R. *Fuel* 1979, **48**, 724
- 15 Hagaman, E. W. and Woody, M. E. *Fuel* 1982, **61**, 53
- 16 Pugmire, R. J., Zilm, K. W., Woolfenden, W. R., Grant, D. M., Dyrkacz, G. R., Bloomquist, C. A. A. and Horwitz, E. P. 'Proceedings of the International Conference on Coal Science', Düsseldorf, FRG, September 7-9, 1981, Verlag Glückauf GmbH, Essen, FRG, p. 798; and Ref. 18.
- 17 Dyrkacz, G. R. and Horwitz, E. P. *Fuel* 1982, **61**, 3
- 18 Pugmire, R. J., Grant, D. M., Zilm, K. W., Anderson, L. L., Oblad, A. G. and Wood, R. E. *Fuel* 1977, **56**, 295
- 19 Zilm, K. W., Pugmire, R. J., Larter, S. R., Allen, J. and Grant, D. M. *Fuel* 1981, **60**, 712
- 20 Gerstein, B. C., Ryan, L. M. and Murphy, P. D. 'Coal Structure' (Eds. M. L. Gorbaty and K. Ouchi), *Adv. Chem. Ser.* 192, Am. Chem. Soc., Washington DC, 1981, pp. 15-22
- 21 Stothers, J. B. in 'Organic Chemistry' Academic Press, New York, 1972, Vol. 24, p. 203
- 22 Brevard, C. and Kintzinger, J. P. in 'NMR and the Periodic Table' (Eds. Robin K. Harris and Brian R. Mann) Academic Press, New York, Chap. 5, p. 112
- 23 See, for example Pouchert, C. J. and Campbell, J. R. 'The Aldrich Library of NMR Spectra, Volume IV, Aromatic Hydrocarbons' The Aldrich Chemical Company, Milwaukee, Wisconsin
- 24 Bartle, K. D., Snape, C. E., Martin, T. G. and Williams, D. F. *Fuel* 1979, **58**, 413
- 25 Snape, C. E., Ladner, W. R. and Bartle, K. D. *Anal. Chem.* 1979, **51**, 2189
- 26 Bockrath, B. C. and Schroeder, K. T. *Am. Chem. Soc. Symp. Ser.* 1981, **169**, 191
- 27 Stein, S. E. *ibid.* 1981, **169**, 97
- 28 Heusing, A. and Muellers, W. *Chem. Ber.* 1980, **113**, 9
- 29 Benson, S. W. 'Thermochemical Kinetics' 2nd Edn., Wiley and Sons, New York, NY, 1976
- 30 Braude, E. A., Jackman, L. M. and Linstead, R. P. *J. Chem. Soc.* 1954, 3548
- 31 Whitehurst, D. D., Mitchell, T. O. and Farcasiu, M. 'Coal Liquefaction—The Chemistry and Technology of Thermal Processes', Academic Press, New York, NY, 1980, Chapter 9
- 32 Derbyshire, F. J. and Whitehurst, D. D. *Fuel* 1981, **60**, 655
- 33 Petrakis, L., Grandy, D. W. and Jones, G. L. *Fuel* 1982, **61**, 21
- 34 Poutsma, M. L., Youngblood, E. L., Oswald, G. B. and Cochran, H. D. *Fuel* 1982, **61**, 314
- 35 Heredy, L. A. and Goldberg, I. US Seminar on Chemistry of Coal Liquefaction, Salt Lake City, Utah, January 11-14, 1982
- 36 Benjamin, B. M., Raaen, V. F., Maupin, P. H., Brown, L. L. and Collins, C. *Fuel* 1976, **55**, 269
- 37 Deno, N. C., Curry, K. W., Greigger, B. A., Jones, A. D., Rukitsky, W. G., Smith, K. A., Wagner, K. and Minard, R. D. *Fuel* 1980, **59**, 694
- 38 Lloyd, R. V. and Wood, D. E. *J. Am. Chem. Soc.* 1974, **96**, 659
- 39 McMillen, D., Ogier, W. and Ross, D. *J. Org. Chem.* 1981, **46**, 3322
- 40 Ross, D. personal communication
- 41 Howard, A. J. 'Free Radicals' (Ed. J. K. Kochi) Wiley and Sons, New York, NY, 1973, Chap 3
- 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 Beishline, R. unpublished results
- 45 Gangwer, T. W. *J. Phys. Chem.* 1981, **85**, 575

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 processes¹⁻⁵. Recent work in this laboratory has demonstrated that these groups are relatively easily detected by i.r. spectroscopy in such processes as coal oxidation¹. Also of interest is the dual nature of carboxylate groups in lignites, where they may be found in either the acid (COOH) or salt ($\text{COO}^- M^+$, M = metal cation) form. The cations associated with carboxylate groups can promote liquefaction² or give rise to deposits in liquefaction reactors³. On pyrolysis, a lignite with metal carboxylates yields more CO_2 than one in which these groups are in the acid form⁴. Similarly, Otake⁵ has found that a corresponding increase can be obtained when the acid groups in a demineralized lignite are exchanged chemically with various metal counterions.

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. Schafer⁶ 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 ≈ 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 $\approx 8^7$. 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 adaption 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^{++} , Ca^{++} , Ba^{++}) by soaking in acetate solutions of each cation. Otake⁵ determined the amount of COOH in the coal as $2.10\text{ meq COOH g}^{-1}$ demineralized coal via Schafer's method ($=6.72\text{ wt\% O as COOH}$), assuming that in the Ba^{++} exchanged coal coverage of COOH groups is essentially complete.

As a test for further COOH exchange at higher pH, the Ba^{++} 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

Proximate analysis (wt%, dry basis)		Elemental analysis (wt%, dry basis)	
Ash	16.6	C	60.7
Volatile matter	44.6	H	4.3
F C	38.8	N	1.1
		S (organic)	0.8
		O (by diff)	14.3
		Cl	0.03
		Mineral matter	18.9
		(including 0.36% FeS ₂)	
Petrographic analysis (vol%, dmmf)		Mineral matter analysis ^a (wt%, LTA ⁴)	
Vitrinites	80.9	Kaolinite	41 ± 1.6
Liptinites	2.3	Quartz	12 ± 3.1
Inertinites	16.4	Anhydrite	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 procedure⁸. 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 publication⁹. 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. Maddams¹⁰ 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 spectra⁹ have previously been discussed and the specific problems encountered in curve-resolving the 1600 cm⁻¹ region have been considered^{11,12}.

RESULTS AND DISCUSSION

Figure 1 compares the FT-i.r. spectrum (between 2000 and 450 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⁺.¹² 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 Maddams¹⁰ and with particular reference to coal spectra in work performed in this laboratory⁹. Typical examples are illustrated in Figures 2 and

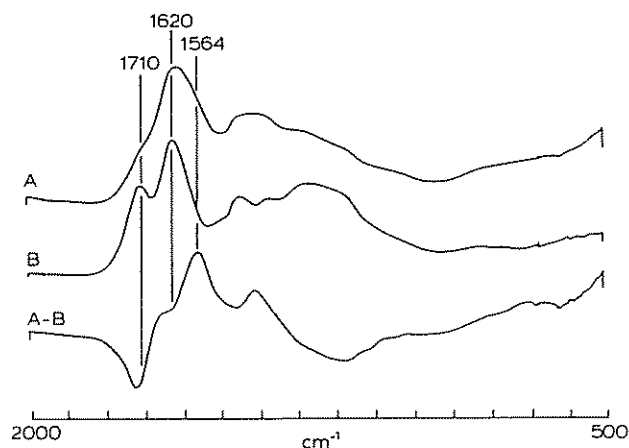


Figure 1 FT-i.r. spectra between 2000 and 5000 cm⁻¹; A, Ba⁺⁺-loaded lignite; B, demineralized lignite; A-B, difference spectrum

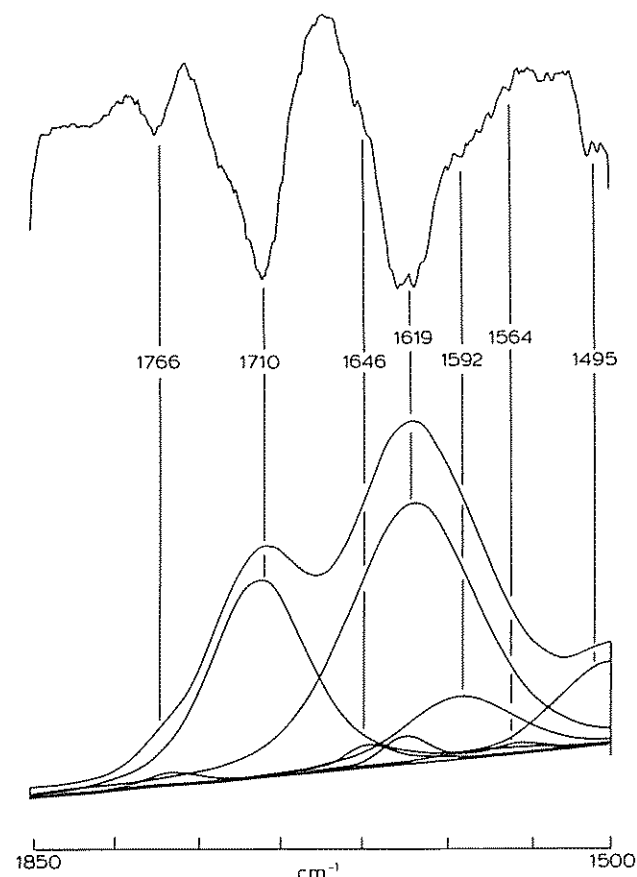


Figure 2 Bottom: FT-i.r. spectrum between 1850 and 1500 cm⁻¹ of demineralized Texas lignite and component bands from curve resolving. Top: second derivative of spectrum

3 for spectra (between 1850 and 1500 cm^{-1}) of the demineralized and Ba^{++} -loaded coals, respectively. The second derivatives not only provide information as to the number of bands which should be curve fitted to a particular spectral profile, but also estimates of band positions and widths at half-height. There are limitations, however, and bands that overlap significantly (usually by less than half their half-width) are poorly separated in the second derivative. Theoretically, a fourth derivative should provide further separation, but because the signal-to-noise ratio degrades geometrically with successive derivative operations this is often a pointless exercise. Because of this, the broad overlapping bands near 1600 cm^{-1} are not easily distinguished. Some modes are identified in what can only be described as an uncertain fashion by shoulders on the second derivative profile. In coals of higher rank, however, similar bands are much more clearly resolved and can be identified with certainty¹³. In part, the curve-fitting rests on this previous experience, but in any event the principle aim was to separate the overlapping contributions of the strongest bands near 1700 and 1600 cm^{-1} to measure the intensity of the former. These bands are relatively well separated so that the area and peak height of the curve-fitted 1710 cm^{-1} band can be determined with some confidence (see Figures 2 and 3). Unfortunately, this confidence does not extend to the COO^- band curve-fitted at 1564 cm^{-1} , where overlap with a number of other poorly identified bands could lead to significant errors in intensity measurements.

A total of eight bands were curve-fitted to the spectral profiles shown in Figures 2 and 3. After refined values of

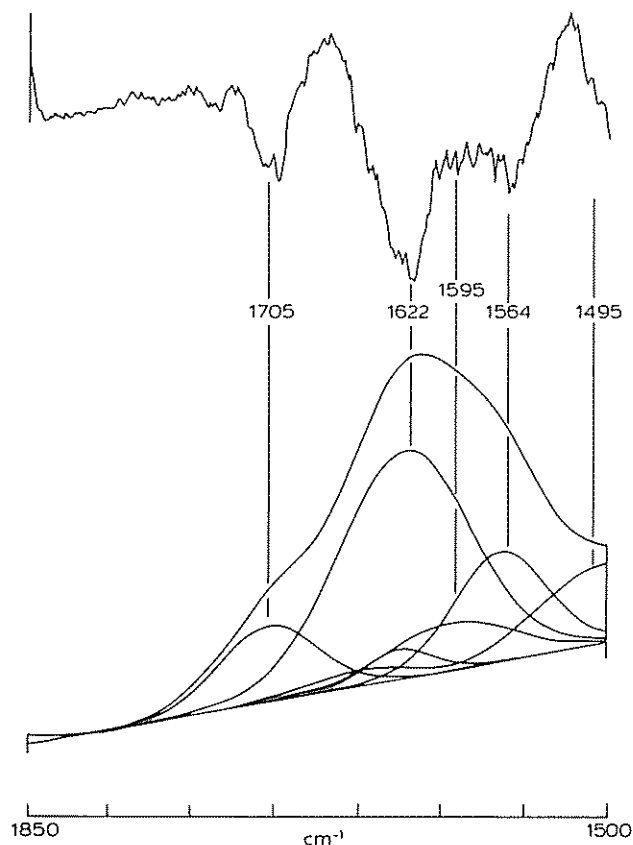


Figure 3 Bottom: FT-i.r. spectrum between 1850 and 1500 cm^{-1} of Ba^{++} -loaded lignite and component bands from curve resolving. Top: second derivative of spectrum

Table 2 Normalized peak heights from curve-fitted spectra

Sample	meq. COOH g^{-1} demin coal (from ref 5)	1710 cm^{-1}	1622 cm^{-1}	1564 cm^{-1}
Demineralized		0.39	0.52	0.02
Ba^{++} -loaded	2.10	0.20	0.59	0.49
K^+ -loaded	1.53	0.31	0.50	0.25
Na^+ -loaded	1.61	0.26	0.52	0.24
Mg^{++} -loaded	2.06	0.17	0.50	0.44
Ca^{++} -loaded	2.04	0.25	0.56	0.52
Ba^{++} -loaded/24 h NaOH soak		0.13	0.56	0.57

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 $\approx 1705 \text{ cm}^{-1}$. 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 complete⁴⁻⁶. Second, the results also indicate that one cation, Mg^{++} , produced a greater reduction in intensity of the $\text{C}=\text{O}$ 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^{9,14}. 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

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 groups¹², 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 Schafer'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

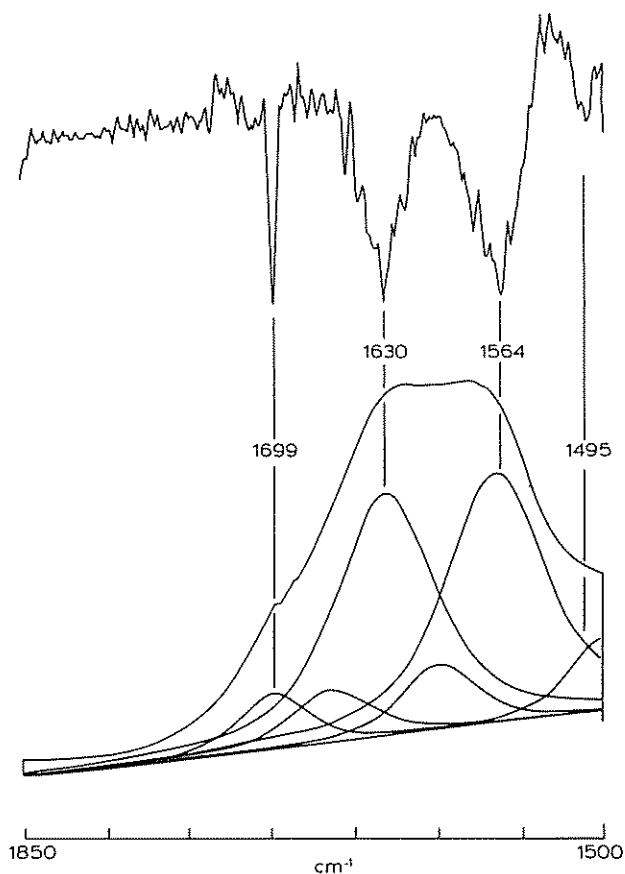


Figure 4 Bottom: FT-i.r. spectrum between 1850 and 1500 cm^{-1} of Ba^{++} -lignite soaked 24 h in 1 N NaOH and component bands from curve resolving. Top: second derivative of spectrum

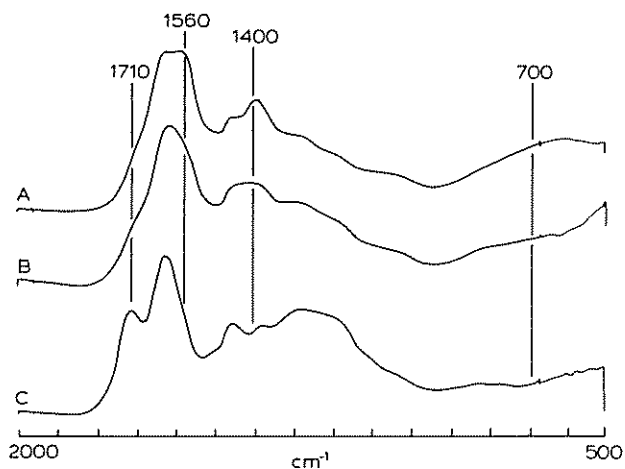


Figure 5 FT-i.r. spectra between 2000 and 500 cm^{-1} ; A, Ba^{++} -loaded lignite soaked 24 h in 1 N NaOH; B, Ba^{++} -loaded lignite; C, demineralized lignite

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 CO_2), 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 $700\text{--}800\text{ cm}^{-1}$ 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 $700\text{--}800\text{ cm}^{-1}$ 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, Otake⁵ determined (using Schafer'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:

$$I = abc \quad (1)$$

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:

$$IE = c \quad (2)$$

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:

$$[I_{1700}(\text{demin}) - I_{1700}(\text{Ba})]E = 6.72\% \quad (3)$$

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 Otake⁵, 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.

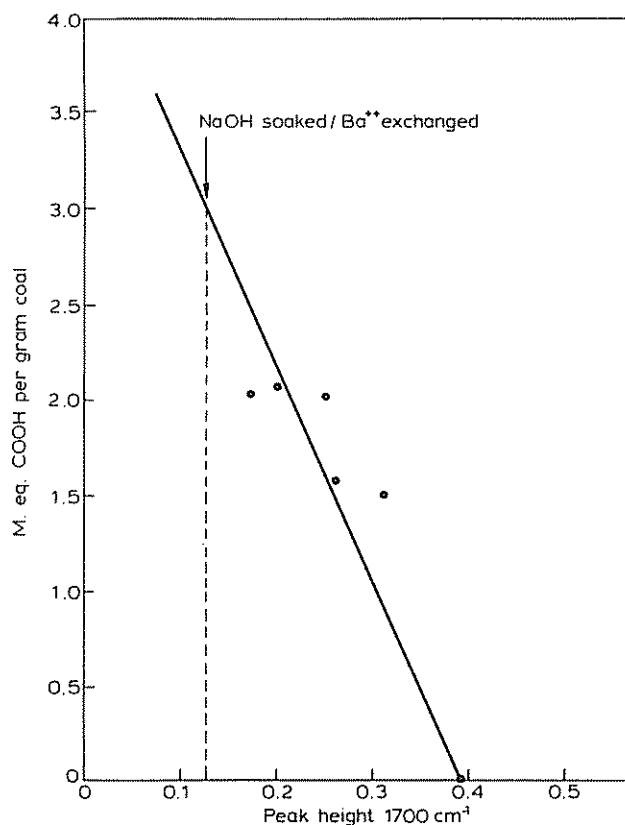


Figure 6 Plot of m. equivalents of COOH per gram of coal versus the intensity of the 1710 cm^{-1} band

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

Sample	A 1700
Demineralized	34.1
Ba^{++} -loaded	15.2
Ba^{++} -loaded/NaOH wash	9.2

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

Method	Conversion factor ^a	%O as COOH ^b
Height	35.4	9.2
Area	0.36	9.0

^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.

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REFERENCES

- 1 Painter, P. C., Snyder, R. W., Pearson, D. E. and Kwong, J. *Fuel* 1980, **59**, 282
- 2 Jackson, W. R., Larkins, F. R., Marshall, M., Rash, D. and White, N. *Fuel* 1979, **58**, 281
- 3 Wakeley, L. D., Davis, A., Jenkins, R. G., Mitchell, C. D. and Walker, Jr., P. L. *Fuel* 1979, **58**, 673
- 4 Schafer, H. N. S. *Fuel* 1979, **58**, 673
- 5 Otake, Y. *Ph.D. Thesis*, The Pennsylvania State University, 1982
- 6 Schafer, H. N. S. *Fuel* 1980, **59**, 197
- 7 Topp, N. E. and Pepper, K. W. *J. Chem. Soc.* 1949, 3299
- 8 Elliot, J. J., Brown, J. P. and Baltrous, J. P. personal communication, to be published
- 9 Painter, P. C., Snyder, R. W., Starsinic, M., Coleman, M. M., Kuehn, D. W. and Davis, A. *Appl. Spectrosc.* 1981, **35**(5), 474
- 10 Maddams, W. F. *Appl. Spectrosc.* 1980, **34**, 245
- 11 Rhoads, C., Senftle, J. T., Coleman, M. M., Davis, A. and Painter, P. C. *Fuel* 1983, **62**, 1387
- 12 Colthup, N. B., Daly, L. H. and Wiberly, S. E. 'Introduction to Infrared and Raman Spectroscopy', Academic Press, New York, 1975
- 13 Painter, P. C., Starsinic, M., Squires, E. and Davis, A. *Fuel* 1983, **62**, 742
- 14 Starsinic, M., Taylor, R. L., Walker, Jr., P. L. and Painter, P. C. *Carbon* 1983, **21**(1), 69
- 15 Morgan, M. E., Jenkins, R. G. and Walker, Jr., P. L. *Fuel* 1981, **60**, 189

Variation of rate during potassium-catalysed CO₂ gasification of coal char

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The instantaneous rate of catalysed CO₂ 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 CO₂ 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 H₂O-C and CO₂-C gasification reactions and comprehensive reviews are available¹⁻³.

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 studies⁶⁻⁸. 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 CO₂ 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 used. The potassium content of the dried samples was determined by atomic absorption spectroscopy.

Char samples were gasified at 800°C with 15 kPa CO₂ and a total pressure of 100 kPa, the balance being He. The

Table 1 Analysis of char

	Wt% (dry basis)
Carbon	79.1
Hydrogen	0.7
Nitrogen	1.5
Sulphur	1.1
Ash	16.8
Oxygen (by difference)	0.8

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 CO₂ 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-CO₂ i.r. analysers. The reaction rates and carbon conversions were calculated from the flow rates and the CO-CO₂ concentrations. A more detailed description of the experimental system and procedures is given elsewhere^{8,9}.

The intraphase areas of the char samples were measured by a dynamic adsorption-desorption technique using CO₂ 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 CO₂ adsorbed on the char was determined by integrating the desorption peaks. This eliminated the effect of possible reaction between CO₂ 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 CO₂ was taken as 0.218 nm² for surface area calculations. A detailed de-