

Pyrolysis of demineralized and metal cation loaded lignites

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A Texas lignite was treated with HCl and HF to remove its mineral matter and its cations associated with carboxyl groups, converting them to their acidic form. Part of this demineralized lignite was then treated with metal acetate solutions to exchange hydrogen on some of the carboxyl groups with metal cations, producing Na, K, Mg, Ca and Ba loaded samples. These loaded lignites and the demineralized lignites were then pyrolysed in N₂ at 5°C min⁻¹ up to 1000°C. The pyrolysis process was monitored by using both chromatography to analyse for the major gases (CO₂, H₂O, CO, H₂ and CH₄) and TGA to determine total weight loss. The presence of cations on the lignite produces significant changes in the composition of the gas released but little effect on total weight loss. The role of secondary reactions, which involve participation of the gases initially released from the coal, is discussed.

(Keywords: lignite; ion exchange; pyrolysis)

Carboxyl contents in American lignites vary from about 2–3 meq g⁻¹ according to Morgan *et al.*¹. Further, about 40–60% of the hydrogen associated with the carboxyl groups has been exchanged with cations, primarily Ca and Mg. Upon lignite pyrolysis, the carboxyl groups decompose, liberating CO₂ and depositing well dispersed inorganic species on the char surface^{2–7}. In this laboratory, we have been particularly interested^{8–16} in the activity of the inorganic species for catalysing subsequent char gasification in air, CO₂, steam and H₂. Such activity is particularly high for reactions involving oxygen transfer¹⁷. It is not surprising then that these inorganic species have also been found to be active in catalysing secondary reactions once the primary devolatilization products have been released from the lignite structure^{2–5, 18–24}. Secondary reactions of importance include tar cracking or condensation, char gasification, steam reforming of hydrocarbons and the water–gas shift reaction.

In this study, demineralized and cation loaded Texas lignites were pyrolysed by slow heating up to 1000°C. Rates of evolution of all the major gases (CO₂, CO, H₂O, CH₄ and H₂) were determined, as well as rates of total weight loss. Changes in yields of products during pyrolysis result in changes in the structure of lignite char ultimately produced and, hence, its reactivity.

EXPERIMENTAL

Lignite sample

Lignite coal from Texas, PSOC 623, was used in this study. Proximate, elemental and petrographic analyses for this lignite, shown in *Table 1*, were supplied by the Coal Research Section, The Pennsylvania State

University. The mineral matter analysis and cation content were previously reported by Morgan *et al.*¹.

Preparation of demineralized lignite

Coal was ground in a N₂ atmosphere to size fractions of 40 × 70 and 200 × 270 mesh. These coals were then demineralized. This process converts essentially all of the carboxyl groups that had metal cations associated with them back to the hydrogen form, and it removes essentially all discrete minerals. The procedure is as follows. Coal (20 g) was mixed with 120 ml of 5 N HCl in a plastic beaker. This solution was stirred at 55–60°C for 45 min. The coal was then filtered and mixed with 120 ml of concentrated HF, and stirred again at 55–60°C for 45 min. The coal was filtered again and mixed with 150 ml of concentrated HCl. The heating and stirring procedure was then repeated for 45 min. The coal was filtered and repeatedly washed with distilled water until no chloride ions were detected upon the addition of silver nitrate. The coal was then dried at 105°C in a vacuum oven overnight and stored in a desiccator under a N₂ atmosphere. The high temperature ash content of the demineralized lignite was 0.41%.

Preparation of cation loaded lignites and determination of carboxyl group content

Cation loaded coals were prepared from demineralized lignite samples by exchange with Mg, Ba, Ca, K and Na acetate solutions. Cation exchange was effected by soaking 5.0 g of demineralized coal in 500 ml of a solution of 1.0 M acetate-triethanolamine at 80°C. A stream of N₂ was continuously bubbled through the solution during the exchange, while the pH was maintained constant at 8.2 ± 0.1 by addition of triethanolamine solution. After a designated exchange time of 24 h, the samples were filtered and washed with cold distilled water

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Table 1 Analyses of Texas (Darco seam) lignite

Proximate analysis (wt%, db)	
Ash	16.6
Volatile matter	44.6
Fixed C	38.8
Elemental analysis (wt%, db)	
C	60.67
H	4.27
N	1.07
S (organic)	0.84
O (difference)	14.29
Cl	0.03
Mineral matter (including 0.36% FeS ₂)	18.86
Petrographic analysis (vol%, dmmf)	
Vitrinites	80.9
Liptinites	2.3
Inertinites	16.4
Mineral matter analysis ^a (wt% LTA) ^b	
Kaolinite	41 ± 1.6
Quartz	12 ± 3.1
Anhydrite	1 ± 0
Calcite	nil
Pyrite	nil
Other clays	24
Others	32
Cation content (10 ⁻⁴ g g ⁻¹ , dmmf) ^b	
Mg	22.6
Ca	129
Na	8.7
K	3.4
Ba	3.4
Sr	2.4

^aAfter removal of exchangeable cations with 1N ammonium acetate

^bRef. 1

until the filtrate was free from excess cations. It was determined experimentally that the pH of the exchange solution did not change after about 18 h. Therefore, an exchange time of 24 h was adopted. The absence of excess cations in the filtrate was checked by a flame test using a platinum wire. The amount of cation loading was determined by extracting it for 14 h with 0.2 N perchloric acid and measuring the cation in the filtrate by atomic absorption.

The amount of carboxyl groups was calculated from the content of carboxyl groups covered by Ba cations, assuming that two carboxyl groups are exchanged with one Ba cation. This procedure followed the method used by Schaefer^{2,5}.

Determination of total acidity

In a study of the pyrolysis of a lignite coal, it is necessary to determine the phenolic hydroxyl content as well as the carboxyl group content. This procedure involves determination of the total acid group content of the coal (phenolic hydroxyl plus carboxyl) followed by determination of the carboxyl group content. Thus, the difference between the total acid group content and the carboxyl group content yields the acidity attributed to phenolic groups. The total acid group content was determined following the method of Schaefer^{2,5}.

Pyrolysis procedure

Pyrolysis of each coal sample was carried out in a 9.2 × 1.6 × 1.1 cm silica boat placed in a horizontal tube furnace. One gram of lignite was usually used, while packed to a depth of 1.4 mm in the boat. It was heated at 105°C overnight in a flow of N₂ of 99.99% purity.

The inlet flow rate of N₂ was 25 cm³ min⁻¹. After this overnight drying procedure, the sample was heated at 5°C min⁻¹ to 1000°C under a stream of N₂.

Analysis of gaseous products

The gases evolved during pyrolysis were analysed for CO₂, CO, CH₄, H₂ and H₂O using a gas chromatograph (Fisher model 1200 gas partitioner) which was connected directly to the horizontal furnace. Details of this analysis are presented elsewhere²⁶.

Weight loss measurements

In this experiment, devolatilization of lignite samples was followed using a conventional vertical TGA system (Fisher Thermogravimetric analyser model 422) operating at atmospheric pressure. The weight loss was monitored as a function of temperature under conditions simulating those used with the g.c. runs. During TGA runs, about 40 mg of sample was placed in a platinum pan. The depth of the sample was the same as that used in g.c. runs. After flushing out the whole system with N₂ for 2 h, the sample was heated at a rate of 2°C min⁻¹ to 105°C. Once the sample weight reached a constant value at 105°C, the temperature was raised to 1000°C at a rate of 5°C min⁻¹.

X-ray diffraction

X-ray diffraction patterns of -200 mesh pyrolysed chars produced from the various cation exchange lignites were taken. Cu K α radiation produced at 40 kV and 20 mA was used. The scanning rate was 1°(2 θ) min⁻¹. X-ray diffraction was used to identify major crystal phases which were present on the chars after pyrolysis.

Equilibrium calculations

In order to investigate the importance of secondary reactions, experimental mole fractions of the gaseous products were compared with theoretical equilibrium mole fractions obtained by a computer program. This program can calculate equilibrium mole fractions of CO₂, CO, H₂O, CH₄ and H₂ for any pressure, temperature and gas ratio of hydrogen to oxygen in an excess of solid carbon. The hydrogen/oxygen ratio at a particular temperature can be calculated from CO₂, CO, H₂O, CH₄ and H₂ concentrations analysed by g.c. runs. Equilibrium calculations for this system are described in detail elsewhere²⁶.

RESULTS

Carboxyl and hydroxyl contents in lignite

Table 2 shows the results of the carboxyl group analysis, as well as the total acid group analysis. The phenolic group content is calculated as the difference between these two determinations. Percentages of the total oxygen contained in the carboxyl and hydroxyl groups and the sum of these functional groups are also given in Table 2.

Cation contents in lignite

Amounts of inorganic cations resulting from 24 h exchange on the demineralized lignite with Ca, Ba, Mg, Na and K acetates are given in Table 3. Assuming that two carboxyl groups are associated with one divalent cation and one carboxyl group is associated with one

Table 2 Carboxyl and hydroxyl contents in demineralized lignite

COOH (mmol g ⁻¹ demin. coal)	2.1
Total acidity (OH + COOH) (mmol g ⁻¹ demin. coal)	5.4
OH groups (by difference) (mmol g ⁻¹ demin. coal)	3.3
COOH groups (% of total O)	31.1
OH groups (% of total O)	24.1
(COOH + OH) groups (% of total O)	55.2

Table 3 Cation contents in exchanged demineralized lignite

	g g ⁻¹ demin. coal	mmol g ⁻¹ demin. coal	meq of COOH g ⁻¹ demin. coal
K	0.060	1.53	1.53
Na	0.037	1.61	1.61
Mg	0.025	1.03	2.06
Ca	0.041	1.02	2.04
Ba	0.144	1.05	2.10

monovalent cation, the carboxyl groups exchanged with cations are also given. For the divalent cations, the carboxyl groups exchanged are in good agreement with the total carboxyl group content determined experimentally by Morgan *et al.*¹ with the same lignite. However, in the case of monovalent cations, cation coverages are considerably lower than the total carboxyl group content in the lignite.

Questions have been raised about whether washing the cation loaded lignite with cold distilled water (pH = 7.0) would affect the final amount of different metals loaded on the lignite. In order to check this effect, a sodium hydroxide solution (pH = 8.2) was used as the washing solution. After washing with these two different wash solutions, the cation loaded lignites were extracted with 0.2 N perchloric acid for 24 h and the amount of cation released was analysed by atomic absorption. Results indicated that, in the case of a Texas lignite, these washings gave the same results for each of the metals. Thus, it can be concluded that washing the cation loaded lignite with cold distilled water does not remove the cations exchanged on carboxyl groups.

In further studies employing Na and K acetate, 30 min was used as the exchange time instead of 24 h. After each 30 min period, concentrations of Na and K exchanged were analysed by atomic absorption. It was demonstrated that exchange was complete within a 30 min contact period.

The exchange solution was changed from a Mg acetate-triethanolamine reagent to a Mg(Cl)₂-NaOH reagent in order to check for the presence of the exchange reagent on the lignite structure. If significant amounts of the Mg acetate-triethanolamine reagent are held on the coal structure, changes in the evolution of CO₂, CO and CH₄ during pyrolysis should be observed. However, there was no effect on gas evolution, suggesting the absence of significant amounts of acetate-triethanolamine on the surface of cation loaded lignites prior to studying their pyrolysis. To the extent that the reagent was physically adsorbed during exchange, it was obviously removed during subsequent washing in cold distilled water.

Pyrolysis of lignite samples

Effect of experimental conditions. Different particle sizes (40 × 70 and 200 × 270 mesh) of Na loaded lignites

were studied to examine the effect of particle size on rates of CO₂, CO and CH₄ evolution. Also, in order to study the effect of sample depth (*D*) on rates of gas evolution, a 9.2 × 1.6 × 1.1 cm high silica boat (boat A) was used as well as a 2.3 × 1.6 × 1.1 cm high silica boat (boat B). With these two different sizes of boat, the depth of sample could be changed over a wide range, while the surface areas of contact to flowing N₂ were different by a factor of four. Figures 1–3 show results of these studies for the Na loaded lignite. In all cases, volume of gas is given in cubic centimetres at standard temperature (0°C) and pressure (0.1 MPa). It is concluded that there is no effect of particle size. Also, changing the depth of the sample bed has no effect on the rate of evolution of CO₂, CO and CH₄ under the experimental conditions used.

Different heating rates of 2, 5 and 10°C min⁻¹ were used in order to study the effect of heating rate upon pyrolysis of the raw lignite. Within this heating rate range, no effect was found for the release of CO₂, CO, H₂, H₂O or CH₄.

Rate of gas evolution. Experiments were performed using 40 × 70 mesh particle sizes of lignite and a 5°C min⁻¹ heating rate. Measured rates of gas evolution on the demineralized, cation loaded and raw lignites are shown in Figures 4–10. Data points in these figures are the average for at least two individual runs. The maximum experimental error for each point based on the total amount of gas evolved was ±2.5%. After the pyrolysis runs, the colour of the sample boat was light brown. This implies that tar vapours cracked on the surface of the boat. However, since the geometrical surface area of the boat is 0.4 m² compared to

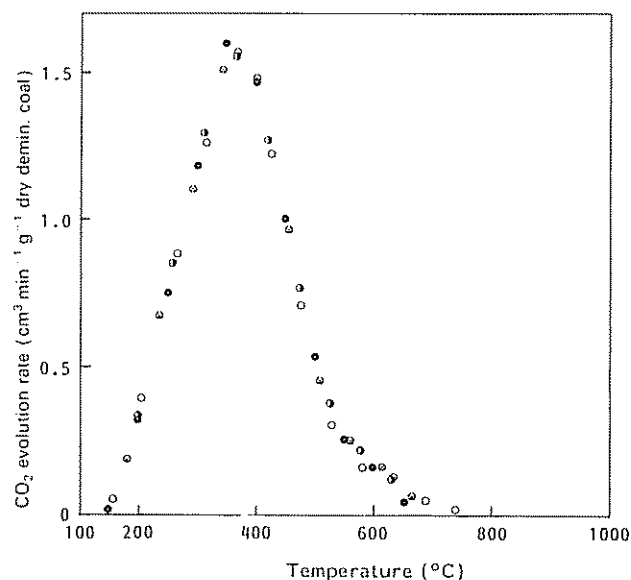


Figure 1 Evolution rate of CO₂ as a function of temperature for Na loaded lignite

Symbol	Particle size (mesh)	<i>D</i> (mm)	Boat	Sample weight (g)
○	40 × 70	9.1	B	2.2437
●	40 × 70	1.4	A	1.3807
⊗	200 × 270	1.1	A	1.0849
⊙	200 × 270	8.8	B	2.1697

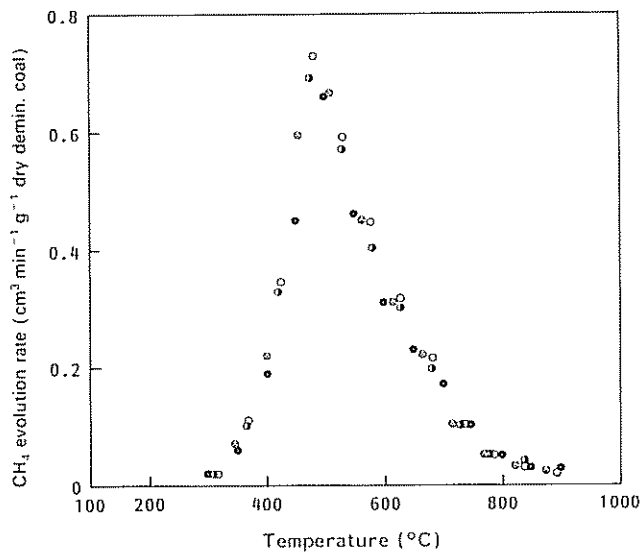


Figure 2 Evolution rate of CH₄ as a function of temperature for Na loaded lignite

Symbol	Particle size (mesh)	D (mm)	Boat	Sample weight (g)
○	40 × 70	9.1	B	2.2437
●	40 × 70	1.4	A	1.3807
⊗	200 × 270	1.1	A	1.0849
⊕	200 × 270	8.8	B	2.1697

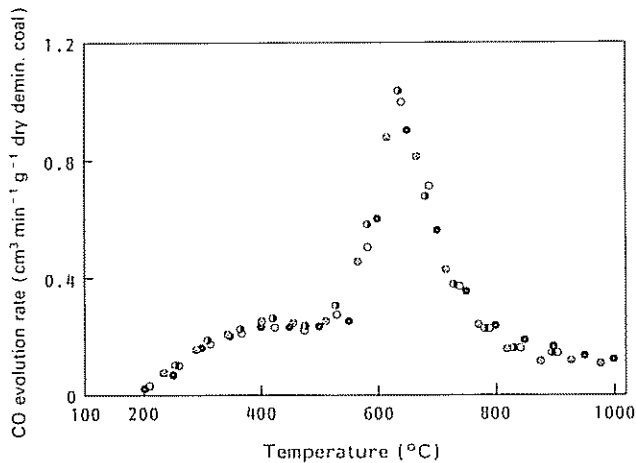


Figure 3 Evolution rate of CO as a function of temperature for Na loaded lignite

Symbol	Particle size (mesh)	D (mm)	Boat	Sample weight (g)
○	40 × 70	9.1	B	2.2437
●	40 × 70	1.4	A	1.3807
⊗	200 × 270	1.1	A	1.0849
⊕	200 × 270	8.8	B	2.1697

~250 m² g⁻¹ of coal surface area (measured by CO₂ adsorption at 25°C), the contribution of cracking in the boat to overall cracking is expected to be negligible.

The cations present as carboxylates in a lignite may form different mineral phases. Thus, rates of gas evolution

in Figures 4–10 are expressed on a cation-free basis. The rate of gas evolution from the raw lignite (Figure 10) is expressed on a dry mineral matter free basis or demineralized coal basis. Although mineral carbonates may decompose to yield CO₂ and H₂O of hydration associated with mineral matter, which may then be evolved during pyrolysis of the raw lignite, these effects are neglected since there is no method for resolving the quantities of gases evolved from the coal from those evolved from the mineral matter.

For the demineralized lignite (Figure 4) H₂O starts to evolve at about 100°C, having a maximum evolution rate at 450°C. Carbon dioxide starts to emerge at 140°C, with a maximum rate at 390°C. Carbon monoxide evolves above 200°C, with a maximum evolution rate at 580°C. Methane starts to evolve at 290°C, with a maximum rate at 460°C. Hydrogen initially emerges at 450°C, exhibiting a maximum rate at 700°C.

Rates of gas evolution from raw and Ca loaded lignites are similar, as expected since the Ca cation is by far the

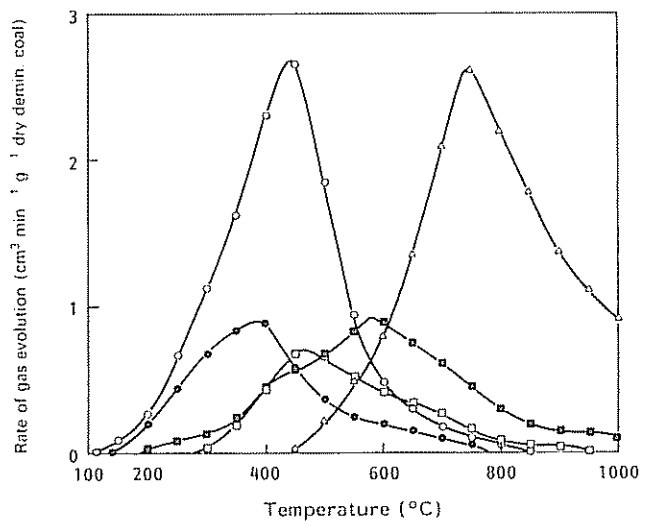


Figure 4 Rate of gas evolution from demineralized lignite as a function of temperature. ●, CO₂; ■, CO; □, CH₄; △, H₂; ○, H₂O

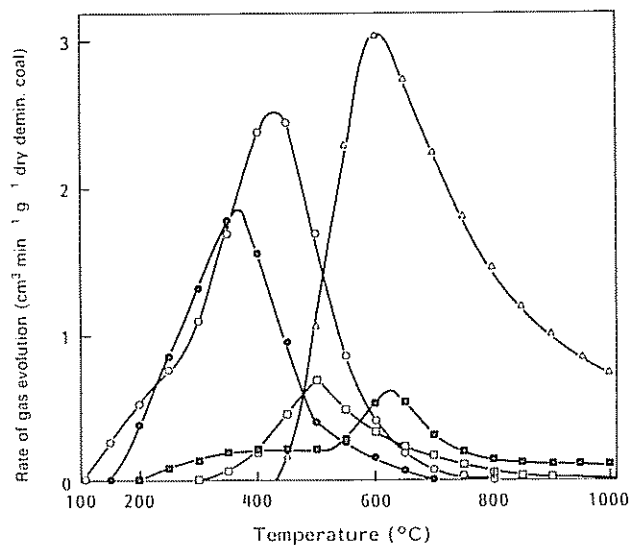


Figure 5 Rate of gas evolution from K loaded lignite as a function of temperature. ●, CO₂; ■, CO; □, CH₄; △, H₂; ○, H₂O

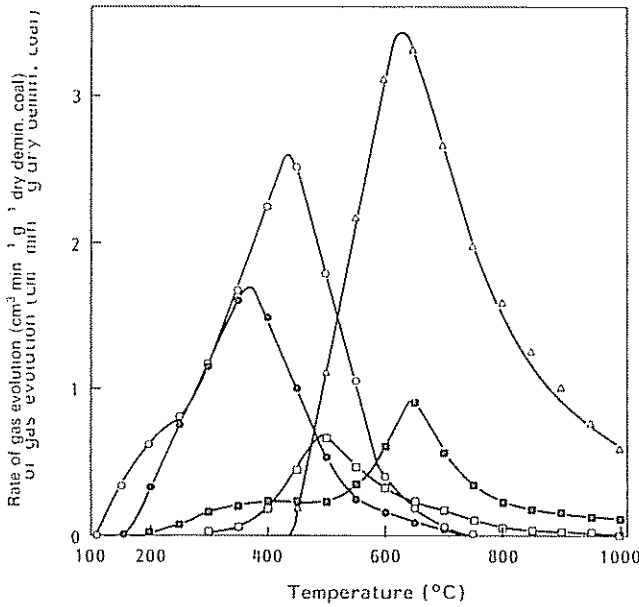


Figure 6 Rate of gas evolution from Na loaded lignite as a function of temperature. ●, CO₂; ■, CO; □, CH₄; △, H₂; ○, H₂O

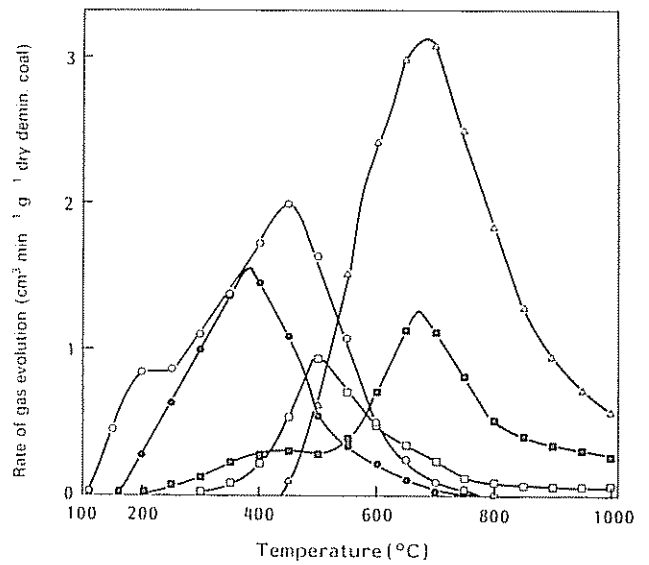


Figure 9 Rate of gas evolution from Ba loaded lignite as a function of temperature. ●, CO₂; ■, CO; □, CH₄; △, H₂; ○, H₂O

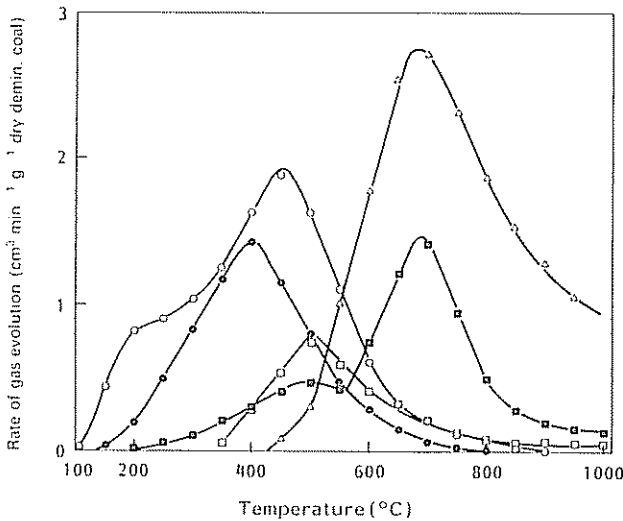


Figure 7 Rate of gas evolution from Ca loaded lignite as a function of temperature. ●, CO₂; ■, CO; □, CH₄; △, H₂; ○, H₂O

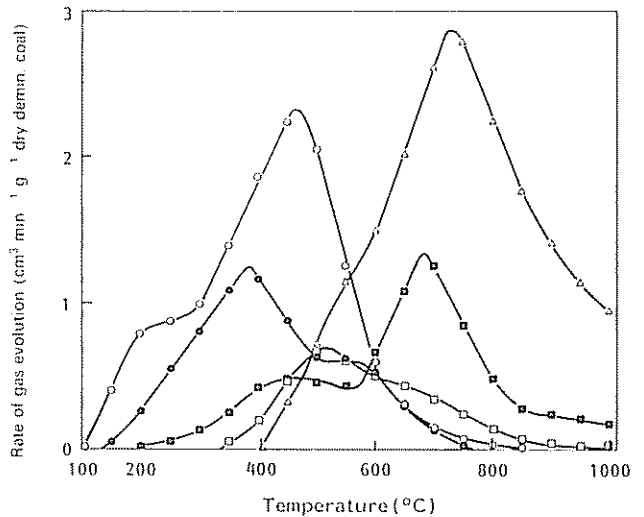


Figure 10 Rate of gas evolution from raw lignite as a function of temperature. ●, CO₂; ■, CO; □, CH₄; △, H₂; ○, H₂O

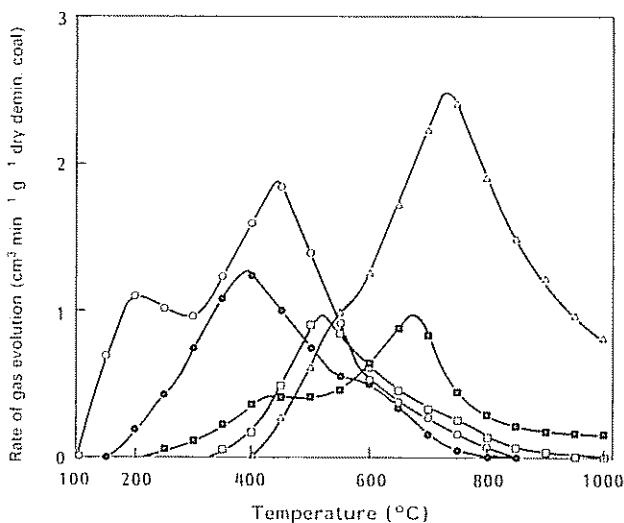


Figure 8 Rate of gas evolution from Mg loaded lignite as a function of temperature. ●, CO₂; ■, CO; □, CH₄; △, H₂; ○, H₂O

most abundant in the raw lignites. Figures 5–10 exhibit a large peak at about 450°C, with a shoulder near 200°C due to H₂O evolution. In contrast, H₂O evolution from the demineralized lignite showed only one peak at about 450°C. In the case of cation loaded lignites where the proton of the carboxyl group has been exchanged with a metal cation, hydration of the cation occurs²⁷ and some of this water is not evolved on heating at 110°C. It is therefore assumed that the first shoulder is due to the evolution of hydrated H₂O. The amount of hydrated H₂O was calculated by assuming that it starts to evolve at 100°C, shows a maximum rate at 200°C, and is completely eliminated at 300°C. This hydrated H₂O content was then subtracted from the total H₂O evolved up to 1000°C. This corrected H₂O is shown in Table 4. Hydrated H₂O contents vary with the cation present in the exchanged coal in the order: Mg > Ba > Ca > Na > K > demineralized coal. It is of interest to compare this order with the order of hydrated radii of the cations, since a correlation might be expected²⁷. The latter order

Table 4 Hydrated water content in demineralized and cation loaded lignites

Coal	H ₂ O evolved (cm ³ g ⁻¹ dry demin. coal)		
	Total	Hydrated	Corrected
Demin.	124.9	4.2	120.7
K	118.2	9.9	108.3
Na	120.7	11.2	109.5
Mg	113.8	25.8	88.0
Ca	115.5	14.6	96.9
Ba	111.5	18.8	92.7

Table 5 Total yield of gases evolved up to 1000°C (wt%, dry demin. coal)

Coal	CO ₂	CO	CH ₄	H ₂	H ₂ O ^a	Total
Demin.	9.0	7.7	2.6	1.2	10.0	30.5
K	14.9	4.2	2.0	1.6	9.5	32.2
Na	14.2	5.1	2.2	1.7	9.7	32.9
Mg	13.4	7.1	3.1	1.4	9.1	34.1
Ca	13.2	8.7	3.1	1.4	9.3	35.7
Ba	13.5	8.6	2.6	1.6	9.0	35.3

^aNo correction for H₂O of hydration

is: Mg (0.30), Ca (0.27), Ba (0.25), Na (0.22) and K (0.18 nm). For some reason(s), the order for Ba and Ca is inverted.

The behaviour of demineralized lignite and cation loaded lignites with respect to the evolution of CO₂, CO, CH₄, H₂ and H₂O is compared below.

1. For all samples studied, temperatures of maximum rate of H₂O, CO₂ and CH₄ evolution are at about 450, 375 and 500°C, respectively.
2. A strong CO peak appears at about 650–700°C for both the raw and cation loaded lignites. Both samples also show a smaller CO peak at about 450°C.
3. The temperature of maximum rate of H₂ evolution is at about 750°C for the demineralized lignite. It shifts to lower temperatures for the cation loaded lignites. Temperatures (in °C) for maximum rates of H₂ evolution during pyrolysis were as follows: demineralized coal (750) > Mg (730) > raw coal (725) > Ca (680) > Ba (675) > Na (625) > K (600).

Total gases evolved. Integration of the evolution envelopes provides the total volume of each gas given off during pyrolysis. Volumes can be converted to weights of gases. Total amounts of gases evolved, expressed as weight per cent of dry demineralized lignite, are given in Table 5. Also, total yields of the five gases are listed in Table 5. From Table 5 it is seen that cation loaded lignites yield larger amounts of H₂ and CO₂ upon pyrolysis and smaller amounts of H₂O. K and Na loaded lignites produce less CO and CH₄ compared to lignites loaded with divalent cations.

Yields of each gas evolved from both demineralized lignite and cation loaded lignites are plotted as a function of temperature in Figures 11–15. It is seen in Figures 11 and 12 that cation loaded lignites yield more CO₂ and H₂ than the demineralized lignite above 250°C and 500°C, respectively. The order of cation loaded lignites in which increasing amounts of

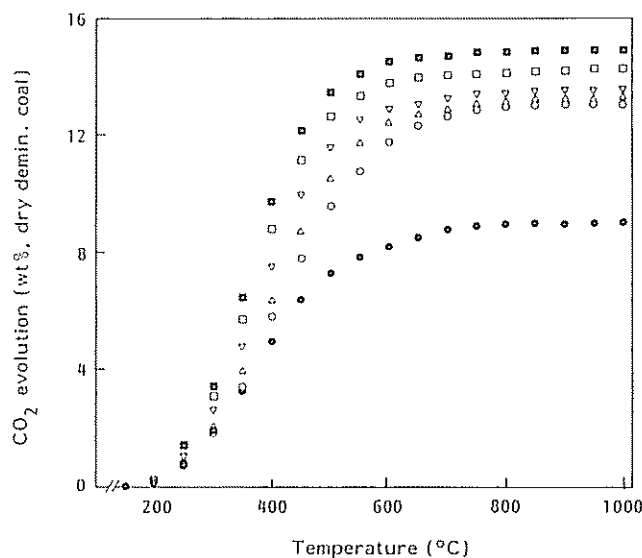


Figure 11 Yield of CO₂ from demineralized and cation loaded lignites upon pyrolysis. Cation: ■, K; □, Na; ○, Mg; △, Ca; ▽, Ba; ●, demineralized coal

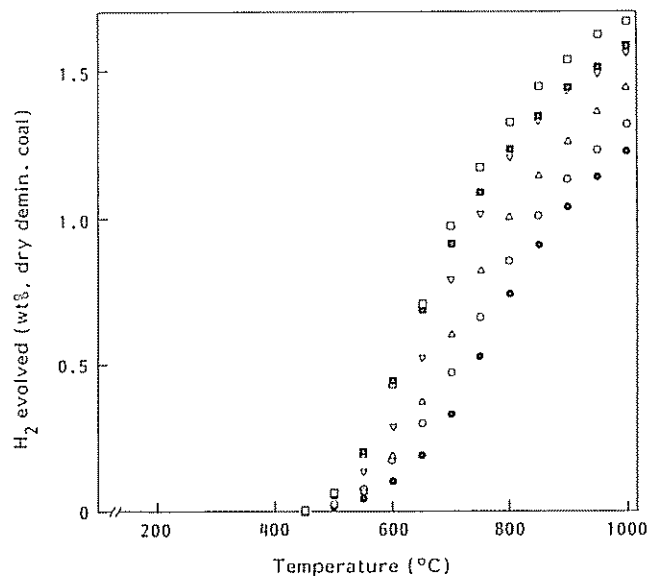


Figure 12 Yield of H₂ from demineralized and cation loaded lignites upon pyrolysis. Cation: ■, K; □, Na; ○, Mg; △, Ca; ▽, Ba; ●, demineralized coal

CO₂ and H₂ are produced is K ~ Na > Ba > Ca > Mg > demineralized coal. This order also corresponds essentially to the order in which the yield of CO decreases up to 700°C. Finally, at about 800°C, Ca and Ba loaded lignites release more CO than the demineralized lignite (Figure 13).

For the yield of H₂O, lignites loaded with divalent cations exhibit less production of H₂O, compared to demineralized and monovalent cation loaded lignites (Figure 14). Further, all loaded lignites yield less total H₂O than does the demineralized lignite.

There is more production of CH₄ starting at 500°C for divalent cation loaded lignites compared to the demineralized lignite. On the other hand, monovalent cation loaded lignites show less yield of CH₄ above 650°C than does the demineralized lignite (Figure 15).

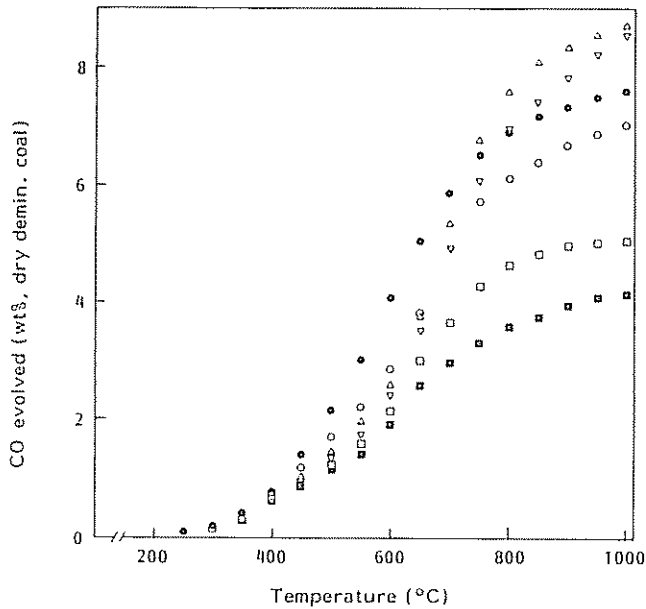


Figure 13 Yield of CO from demineralized and cation loaded lignites upon pyrolysis. Cation: ■, K; □, Na; ○, Mg; △, Ca; ▽, Ba; ●, demineralized coal

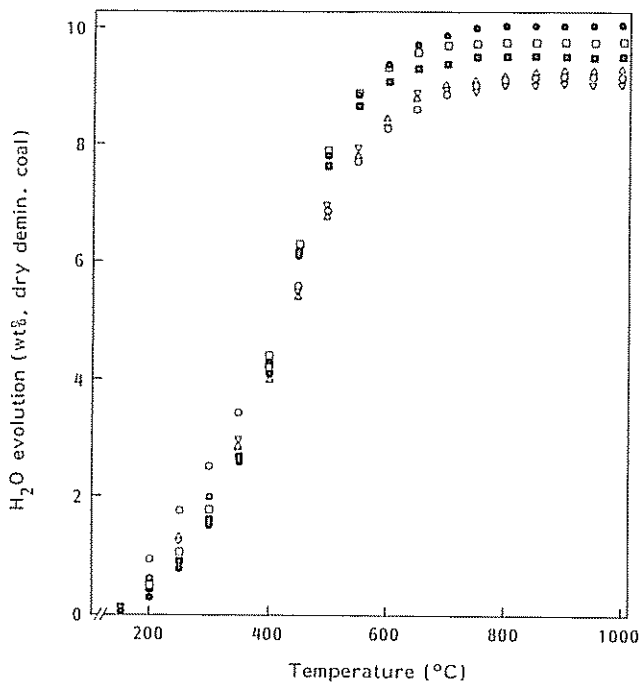


Figure 14 Yield of H₂O from demineralized and cation loaded lignites upon pyrolysis. Cation: ■, K; □, Na; ○, Mg; △, Ca; ▽, Ba; ●, demineralized coal

Figure 16 presents results for cumulative weight loss of the five gases studied during pyrolysis of demineralized and cation loaded lignites up to 1000°C. It is noted that cation loaded lignites yield a greater total weight of volatile gases (CO₂, CO, H₂O, H₂ and CH₄) than does the demineralized lignite over the entire temperature range.

TGA results. Total volatile matter evolved from demineralized and cation loaded lignites is shown as a function of temperature in Figure 17. Total weight

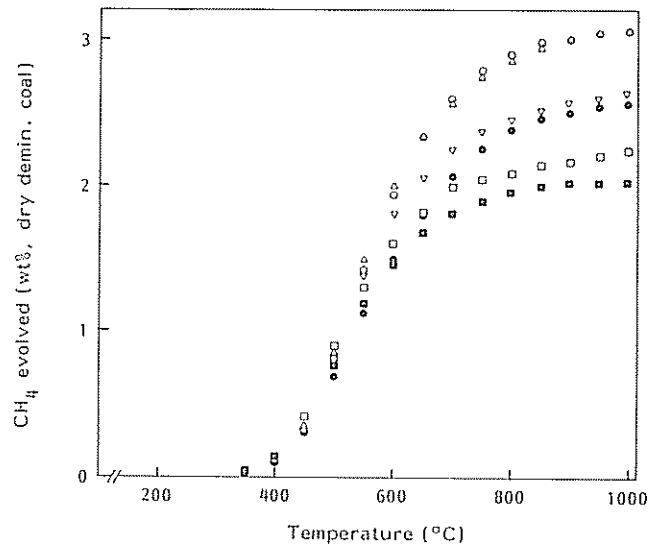


Figure 15 Yield of CH₄ from demineralized and cation loaded lignites upon pyrolysis. Cation: ■, K; □, Na; ○, Mg; △, Ca; ▽, Ba; ●, demineralized coal

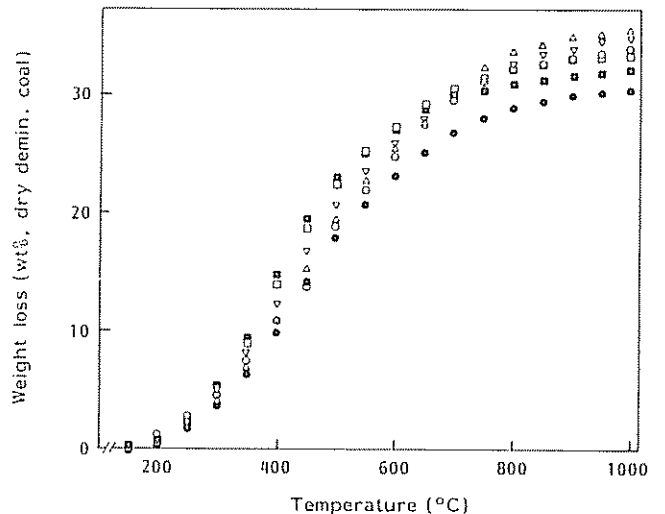


Figure 16 Total weight loss of five gases from demineralized and cation loaded lignites. Cation: ■, K; □, Na; ○, Mg; △, Ca; ▽, Ba; ●, demineralized coal

loss at 1000°C is essentially the same for all samples. Comparing Figures 16 and 17, it is seen that 64–73% of the total weight loss measured by TGA can be attributed to loss of the five gases. The remainder of the weight loss is attributed to release of hydrocarbons of higher molecular weights, and tar. Table 6 summarizes results for total weight loss, weight loss due to the five gases, and weight loss of higher hydrocarbons and tar upon pyrolysis of the samples up to 1000°C.

X-ray diffraction studies

The fates of cations present in the lignites during pyrolysis were examined qualitatively by X-ray diffraction. With Ca and Mg loaded lignite chars produced at 1000°C, CaO, Ca(OH)₂ and MgO were identified. However, no diffraction peak was detected, except for the broad (0 0 2) band of carbon, for the Ca and Mg loaded coal chars produced at 375 and 630°C. X-ray

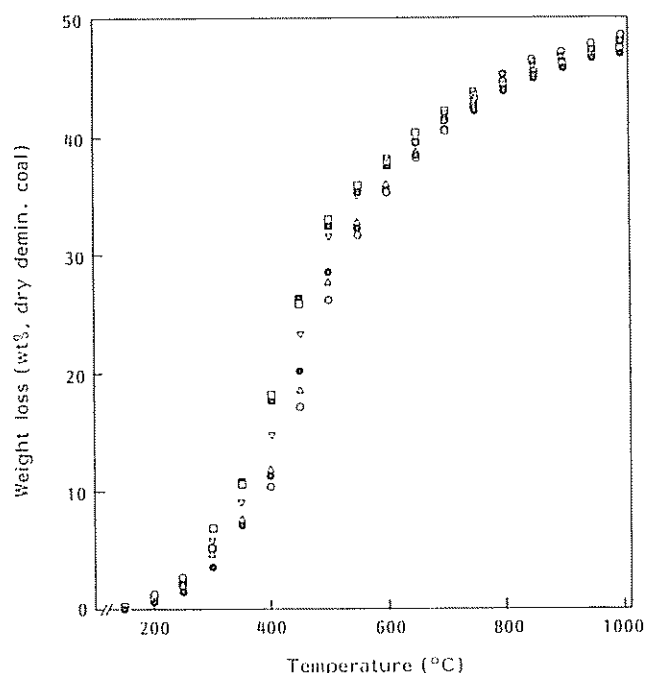


Figure 17 Weight loss during lignite pyrolysis as a function of temperature. Cation: \square , K: \square , Na: \circ , Mg: \triangle , Ca: ∇ , Ba: \odot , demineralized coal

Table 6 Weight loss upon pyrolysis of lignites up to 1000°C

Coal	Weight loss (wt%, dry demin. coal)		
	TGA	Gas analysis	Difference
Demin.	47.3	30.5	16.8
K	48.3	32.2	16.1
Na	48.0	32.9	15.1
Mg	48.9	34.1	14.8
Ca	48.6	35.7	12.9
Ba	48.3	35.2	13.1

diffraction patterns of Na containing chars prepared at 630°C and 1000°C indicated several unknown peaks. These peaks occurred at the same diffraction angle for both chars. A similar result was obtained with K loaded coal chars prepared at 630°C and 1000°C. Thus, it appears that inorganic phases that exist at 1000°C are formed at no higher than 630°C. With the Ba loaded coal chars, no peaks were detected, not even the (0 0 2) band of carbon. This is attributed to Ba having a high absorption coefficient for Cu K α radiation.

Analyses of organic phase in lignites and chars

In this study, demineralized lignite and cation loaded lignites, which were prepared after demineralization, were used. Since demineralization removed over 95% of all ash forming materials, minerals left after the demineralization will have a negligible effect on the calculations of the composition of the organic phase in the lignites studied.

It was assumed that the first peak of H₂O evolution in Figures 5-10 is due to hydrated H₂O on the cations. Hydrogen contents associated with the organic phase of the lignites (H_{org}) can then be calculated from H_{org} = H_{ult} - H_w, where H_{ult} is the hydrogen content from ultimate analysis (wt%) and H_w is the hydrogen content evolved as hydrated H₂O (wt%). Using the

Table 7 Elemental analyses of the organic phase in demineralized and cation loaded lignites (g/100 g dry coal)

Element	Cation					
	Demin.	K	Na	Mg	Ca	Ba
C	70.4	65.9	67.2	66.3	65.5	58.0
H _{org}	4.73	4.40	4.69	4.59	4.51	3.93
N	1.54	1.57	1.70	1.49	1.65	1.40
S	1.14	1.05	1.05	1.07	0.99	0.90
Cation ^a	0.21 ^b	5.64	3.56	2.44	3.93	12.33
H ₂ O ^c	0.34	0.75	0.87	2.02	1.13	1.32
O	21.6	20.7	20.9	22.1	22.3	22.1
O ^d	19.6	20.9	21.1	20.1	21.5	21.4

^aCation content (g/100 g dry coal)

^bHydrogen as COOH (g/100 g dry coal)

^cHydrated water content (g/100 g dry coal)

^dTotal oxygen evolved as CO₂, CO, H₂O (g/100 g dry, demin., hydrated water free coal)

Table 8 Elemental analyses of chars produced at 1000°C from demineralized and cation loaded lignites (g/100 g of original dry demin. coal)

Element	Cation					
	Demin.	K	Na	Mg	Ca	Ba
C	47.3	46.3	46.6	46.1	46.7	45.8
H	0.16	0.25	0.36	0.27	0.31	0.35
N	0.64	1.04	0.96	0.66	0.99	0.88
S (total)	0.36	0.48	0.53	0.40	0.54	0.68

cation contents in each coal, as well as the C, N and S contents determined by ultimate analysis and H contents calculated in the above equation, oxygen by difference was calculated for the lignites and is presented in Table 7. Also, oxygen evolved as the total of CO₂, CO and H₂O during pyrolysis to 1000°C is listed in Table 7.

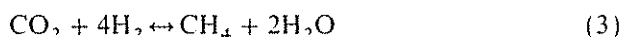
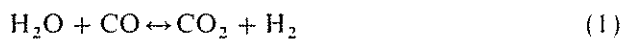
Elemental analyses of chars produced at 1000°C, based on 100 g of original dry demineralized coal, are shown in Table 8. It is seen that cation loaded chars contain more N and S than the demineralized char. Obviously the cations are getting some of the N and S that would otherwise escape from the coal. This has been noted previously⁸.

DISCUSSION

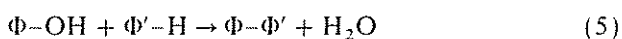
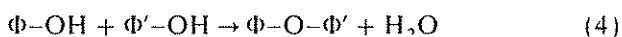
Coal pyrolysis can be divided into two steps. In the primary step, functional groups are liberated from the periphery of the coal building blocks, cross-links are broken releasing some of the aromatic and hydroaromatic building blocks, and aromatic groups (Φ) lose hydrogen and condense as they are converted to small, trigonally bonded carbon crystallites. In the other step, primary products can undergo secondary reactions as they diffuse from the coal particles through an extensive micropore system. Frequent collisions with the pore walls occur as the devolatilization products travel through the micropores by a combination of activated and Knudsen diffusion. In this study collisions can occur with surfaces derived both from the organic phase of the coal and from the metal carboxylate groups on the cation loaded lignite. The latter surface is composed of well dispersed inorganic species. The slow heating rate used in this study allows maximum time for secondary reactions to occur.

Pyrolysis of demineralized lignite

Let us consider results for the demineralized lignite first. In agreement with Schaefer²⁻⁵ and others, there is good agreement between the total CO₂ released upon pyrolysis to 1000°C (9.0 wt%, dry) and the amount that would be expected assuming that the decomposition of each carboxyl group (Φ-COOH) yields one molecule of CO₂ (9.2 wt%, dry). This means that the CO₂ released from carboxyl groups underwent negligible secondary reactions that would either increase or decrease the amount of CO₂ diffusing from the lignite particles. Possible reactions would have included:



Next, consider the release of H₂O. In the present study, the demineralized lignite was dried overnight at 105°C in N₂ prior to pyrolysis. The hydrated H₂O content is estimated to be only 4.2 cm³ g⁻¹ (Table 4) for the demineralized lignite. Thus, most of the H₂O was evolved from functional groups on the coal. Since it is concluded that decomposition of carboxyl groups leads only to CO₂, H₂O evolution must come from other functional groups. Solomon and Colket⁶ conclude that H₂O is derived from hydroxyl groups via the reactions:



The demineralized coal employed in this study contained 3.3 meq g⁻¹ of hydroxyl groups which could evolve a maximum of 36 cm³ H₂O g⁻¹ via reaction (4) and 72 cm³ H₂O g⁻¹ via reaction (5). This is considerably less than the 120 cm³ H₂O g⁻¹ recovered experimentally. Assuming that an insignificant amount of H₂O is produced by secondary reactions for the demineralized lignite, it is concluded that the extra H₂O is derived from other functional groups on the coal. Schaefer came to the same conclusion from his studies on brown coal²⁻⁵.

An approximate, empirical chemical formula for the demineralized lignite used in the study is C₁₀₀H₈₀O₂₃N_{1.8}S_{0.6}. Roughly 31% O is in carboxyl groups and 24% O is in hydroxyl groups. This leaves roughly 10 O atoms to be accounted for, primarily in ether crosslinks, carbonyl and methoxyl groups and in ring structures. It is suggested that the H₂O unaccounted for is derived primarily from the cleavage of ether crosslinks, producing aldehydes. They, in turn, react with mobile H atoms in the coal, yielding H₂O as one of the products^{28,29}. Mobile H atoms can also react with carbonyl groups in the coal³⁰ to produce H₂O.

Carbon monoxide is thought to come from a number of sources: cyclic ether which exists in the coal⁶, aldehydes resulting from the cleavage of ether crosslinks, methoxyl groups, and/or carbonyl groups. The low temperature side of the CO gas evolution peak is not symmetrical (Figure 4), which suggests that the CO originated from, at least, two types of processes. A total of 62 cm³ CO g⁻¹ is recovered experimentally upon pyrolysis to 1000°C.

Hydrogen is thought to come primarily from the aromatic building blocks in the coal⁶. Loss of H from these building blocks results in the production of free

radical species, which condense into larger entities³¹, leading eventually to small, trigonally bonded carbon crystallites which compose the lignite derived char. All of the H released from aromatic species does not yield H₂; some is added to other aromatic species through internal hydrogen transfer reactions converting them to hydroaromatic species and ultimately to tar³¹ and hydrocarbon gases.

Methane is expected to be derived, at least in part, from methoxyl groups in the lignite. For a lignite of ~70 wt% carbon content, ~0.9 wt% oxygen is found in methoxyl groups³². Since the total oxygen content of the demineralized lignite is 21.6% of the total weight of the coal in the above study, the oxygen in the methoxyl groups represents ~4% of the total oxygen. Or for the chemical formula of the coal in this study, of the 23 O molecules, ~0.9 are attributed to methoxyl groups. Since one CH₄ molecule should be released for each methoxyl group, 12 cm³ CH₄ g⁻¹ should be produced upon pyrolysis. For the demineralized lignite, a total of 36.4 cm³ CH₄ g⁻¹ were recovered upon heating to 1000°C. Methane, as a primary product, is also expected to be derived from methyl and methylene groups in the coal. Methylene groups are thought to exist as bridges between aromatic structures in coal³³. At this time, there does not appear to be a good estimate of the total methyl and methylene groups in lignites. Assuming that the CH₄ not originating from methoxyl groups originates totally from the above groups, the 24 cm³ CH₄ g⁻¹ recovered would come from ~1.1 mmol g⁻¹ demineralized coal.

It is of interest to compare the composition of the gas released experimentally during pyrolysis of the demineralized lignite with the calculated equilibrium composition of the gas. As described in the Experimental section, and elsewhere²⁶, this can be done in a closed system, in an excess of carbon, as a function of temperature, total pressure of the five gases, final H/O ratio, and free energy of formation (ΔF) of the carbon relative to β-graphite. There is some question as to the values of total pressure to be used in the calculation as a function of temperature. The total pressure of the five gases at the exit of the furnace can be calculated from the ratio of the total flow rate of the five gases to the total flow rate of all volatiles plus N₂. However, if there are secondary reactions involving the primary volatiles, they are expected to occur primarily within the pores of the lignite particles and not in the gas phase above the boat. In this case, the total pressure of the five gases could be greater than that calculated at the exit of the furnace. There is also uncertainty as to what value to use for ΔF of the carbon phase relative to β-graphite. Because the char is composed of disordered, turbostratic carbon³⁴, it is known that its ΔF is greater than that of β-graphite. Calculations presented elsewhere explore the effects of changing pressure and ΔF on equilibrium mole fraction values for the five gases²⁶. Pressures explored were those at the exit of the furnace, which ranged from ~1–20 kPa for the five gases as temperature changed, 100 kPa (atmospheric pressure) and 1000 kPa. Free energies of formation explored ranged from zero to 3 kcal mol⁻¹ relative to β-graphite.

The results summarized in Table 9 are for just one set of conditions: the total pressure of the five gases at the exit of the furnace and a ΔF of zero. Equilibrium mole fraction values can be compared with experimental values at 600°C for the demineralized lignite. It is seen, under

Table 9 Comparison of experimental gas composition released at 600°C with equilibrium composition for several lignites

Gas	Demineralized lignite		Na loaded lignite	
	Experimental mole fraction	Equilibrium mole fraction	Experimental mole fraction	Equilibrium mole fraction
CO ₂	0.063	0.095	0.034	0.041
H ₂ O	0.170	0.076	0.091	0.077
CO	0.311	0.223	0.136	0.128
H ₂	0.313	0.580	0.671	0.699
CH ₄	0.143	0.108	0.068	0.055

the conditions selected, that experimental mole fractions are higher than equilibrium values for H₂O, CO and CH₄. They are lower for CO₂ and H₂. An increase in total pressure used in the calculations would have raised the equilibrium mole fractions of CO₂, CH₄ and H₂O and lowered those of CO and H₂. An increase in Δ*F* used would have raised the equilibrium mole fractions of CO₂, CO and CH₄ and lowered those of H₂O and H₂. Selection of correct values for total pressure of the gases and Δ*F* obviously presents a difficult problem, particularly when they are expected to be functions of temperature. As temperature increases and more volatiles have left the char particle, the porosity of the particle is expected to increase. This could decrease the total pressure of the volatiles within the lignite particle. Also, as temperature increases, the char structure is expected to become more ordered, thus decreasing Δ*F* relative to β-graphite.

Pyrolysis of cation loaded lignites

Changes in lignite particle size, depth of sample in the boat, area of the boat and heating rate had a negligible effect on the rate of release of CO, CO₂ and CH₄ from the Na loaded lignite during its pyrolysis. This is interpreted to mean that Na is a good catalyst for secondary reactions involving the primary gases evolved during pyrolysis; under the slow heating rates used in this study, equilibrium was essentially attained prior to the volatile gases leaving the coal particles. In addition to the possible secondary reactions given by Equations (1)–(3), other possible reactions include:



The five cations used in this study are excellent catalysts for carbon gasification in H₂O and CO₂ and the water–gas shift reaction^{8,9,11,13,15,16,35–37}; they are fair catalysts for the methanation reactions³⁷. Their efficiency as catalysts is enhanced in this case since, following decomposition of the carboxylate groups, the inorganic species are highly dispersed on the lignite surface¹¹. The water–gas shift reaction is thought to be an especially important secondary reaction in this study since it is usually a more rapid reaction than the gasification of carbon³⁸ by H₂O, and it is also particularly favoured by thermodynamics (equilibrium) over most of the temperature range used for pyrolysis.

Equilibrium calculations were made for pyrolysis of the Na loaded lignite at 600°C and are compared with experimental results for the composition of the gas in

Table 9. Again, the total pressure of the five gases was taken as that at the exit of the furnace and Δ*F* for the carbon was taken as zero relative to β-graphite. It is seen that agreement between experimental mole fractions and equilibrium values is much better for the Na loaded lignite than for the demineralized char. The mole fraction of the H₂ in the product gas is quite high and is closely predicted by equilibrium calculations.

As seen in Table 6, total weight loss upon pyrolysis to 1000°C is essentially the same for all the lignite samples. However, the breakdown of weight loss between the five gases and the tar and higher molecular weight hydrocarbons is different. The weight of higher molecular weight hydrocarbons and tar lost during pyrolysis is highest for the demineralized lignite, apparently due to the absence of secondary cracking reactions. By contrast, the weight of gases lost during pyrolysis is greater for the cation loaded lignites, apparently due to the presence of some secondary carbon gasification reactions occurring.

CONCLUSIONS

The presence of exchangeable cations associated with carboxyl groups on lignites affects the composition of the gas (composed of CO, CO₂, H₂O, H₂ and CH₄) released upon pyrolysis to 1000°C. Amounts of CO₂ and H₂ are particularly enhanced for the cation loaded lignites over the demineralized coal. The total weight loss during pyrolysis is essentially the same for all lignites but the breakdown between the weight lost in the gases compared to that lost in the tar and higher molecular weight hydrocarbons changes. Differences are attributed to secondary reactions occurring among the primary products in the case of the cation loaded lignites. It is concluded that negligible secondary reactions occur for the demineralized lignite, under conditions of slow heating rate (5°C min⁻¹) used in this study.

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