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A thermal analysis study of the influence of exchangeable cations on the pyrolysis of Victorian brown coal

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Abstract

A thermal analysis study of the pyrolysis of some cation-loaded brown coals has revealed that most of these cations have no significant effect on the total volatile matter released during slow pyrolysis; however, the results of infrared evolved gas analysis show that cation-loaded coals release more CO_2 at lower temperatures than an acid-washed reference coal. Among the cations investigated, Cu^{2+}, Fe^{2+} and Pb^{2+} have the most significant catalytic effect on the pyrolysis of brown coal. The pyrolysis kinetics indicate that the Cu^{2+}, Fe^{2+} and Pb^{2+} loaded coals have a lower average pyrolysis activation energy than the acid-washed reference coal.

INTRODUCTION

Victorian brown coal is a low rank coal with high moisture and oxygen contents. Air-dried brown coal has a large internal surface area and the high content of carboxyl and phenolic functional groups promotes excellent cation exchange properties of the coal. The cation-exchange properties of Victorian brown coal have been widely recognised [1] and used for removal of heavy metals from aqueous solutions [2–7]. Brown coals have inherent cation exchange capacities of up to 4 meq g^{-1} [3]. The heavy metals loaded onto the coal can be readily removed by acid washing thereby enabling re-use of the coal for cation exchange. Alternatively, the coal can be re-utilized in pyrolysis or combustion processes. Combustion of "metal-loaded" coal is a simple route to the recovery of precious metals, since such metals remain in the ash residue. In order to develop the metal recovery method and to make use of metal-loaded coals, it is essential to understand

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the role of the included metal cations on the coal pyrolysis and combustion characteristics, particularly the effects of heavy metals.

It is known that some metal cations act as catalysts for coal gasification, pyrolysis and combustion [8–30]. The cation-exchange property of brown coal can be used to load the catalyst onto the coal.

In this study, a variety of metals, particularly heavy metal cation-loaded coals, are investigated systematically by TG–DTG–DTA and by infrared evolved gas analysis.

EXPERIMENTAL

A series of cation-loaded coals was prepared from the acid-washed Loy Yang coal. The proximate and ultimate analysis data for the raw Loy Yang coal and the corresponding acid-washed reference coal are listed in Table 1. To prepare cation-loaded coal, the acid-washed coal was suspended in a series of solutions (0.1 M) containing various metal cations and anions for 24 h. The slurry was then filtered, washed with distilled water and then air dried and ground to pass an 80 mesh sieve. In order to maximize cation loading, a pH 5.23 buffer solution was used in the case of some heavy metal loading. The cation content of cation-loaded coals was determined on sub-samples by extracting the cation-loaded coal with 2 M HCl and analysing the extract solutions by atomic absorption spectrophotometry. The cation contents of cation-loaded coals are shown in Table 2.

Thermal analysis experiments were carried out using a Rigaku-Denki, Type 8085 (Thermoflex) TG–DTG/DTA thermal analysis system. Pyrolysis conditions were: heating rate, 10°C min^{-1}; temperature range, 20–950°C; atmosphere, nitrogen; flow rate, 0.1 $\text{dm}^3\ \text{min}^{-1}$; reference, Al_2O_3; sample size, 10 mg.

Metal cation content was determined by a Varian AA-275 atomic absorption spectrophotometer.

For the evolved gas analysis, 0.2 g coal sample was placed in a silica tube and heated in nitrogen (flow rate, 100 $\text{cm}^3\ \text{min}^{-1}$) in a tube furnace. The evolved gases were collected in an IR sample cell at different temperatures up to 800°C and IR spectra were obtained over the range 4000–400 cm^{-1} using a Perkin-Elmer 1430 ratio recording infrared spectrophotometer.

RESULTS AND DISCUSSION

TG–DTG results

The TG and DTG curves of the acid-washed reference coal, raw Loy Yang coal and some cation-loaded coals are shown in Figs. 1 and 2. Some characteristics can be derived from TG and DTG profiles and are listed in Table 3. Since cation contents of the cation-loaded coals are different, dry

TABLE 1

Chemical analysis of brown coal samples

Sample	Raw Loy Yang coal	Acid-washed coal
Proximate analysis		
Moisture (%ar) [a]	13.9	12.2
Volatile matter (%db) [b]	51.6	51.9
Fixed carbon (%db)	47.2	47.5
Ash (%db)	1.2	0.5
M&I [c] (%db)	1.3	0.7
Ultimate analysis (%db)		
C	67.9	68.1
H	5.1	5.1
N	0.58	0.63
S	0.25	0.25
Mineral and inorganic constituents		
Coal minerals (%db)		
SiO_2	0.70	0.43
Al_2O_3	< 0.1	< 0.1
K_2O	0.01	0.01
TiO_2	0.01	0.01
FeS_2	0.1	0.1
Coal inorganics (%db)		
Al	0.02	0.02
Fe (non-pyritic)	0.06	0.01
Ca	0.05	0.01
Mg	0.07	0.00
Na	0.12	0.01
Cl	0.14	0.10
S total	0.28	0.28
Fe total	0.09	0.04
Al_2O_3 total	0.08	0.06

[a] ar, as received. [b] db, dry basis. [c] M&I, minerals and inorganics.

TABLE 2

Cation-loading concentration for Loy Yang brown coal

Sample	Cation concentration (mmol per g dry coal)
$CuAc_2$ coal	1.200
$ZnAc_2$ coal	0.122
$PbAc_2$ coal	0.933
$FeCl_2$ coal (pH 5)	0.583
$NiCl_2$ coal (pH 5)	0.489
$CoCl_2$ coal (pH 5)	0.484
$MnCl_2$ coal (pH 5)	0.381
$CaCl_2$ coal (pH 5)	0.402

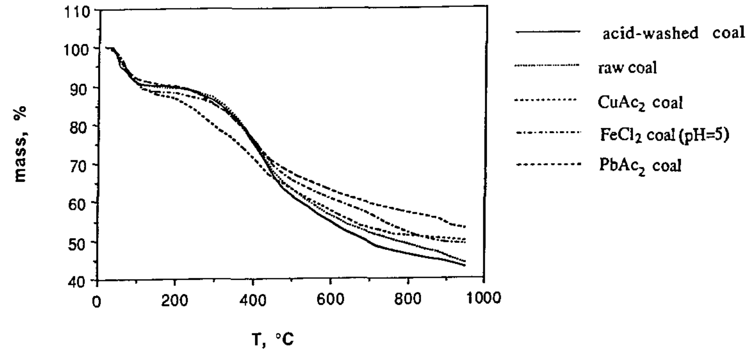

Fig. 1. TG profiles for the pyrolysis of brown coal samples.

and ash-free basis final volatile matter released V_f and maximum rate of mass loss R_m values are determined in order to obtain comparable results.

From Table 3, the raw coal has a lower initial pyrolysis temperature T_{in} and higher maximum rate temperature T_m and R_m values than the acid-washed reference coal. The Ca^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} coals have lower T_{in} and higher T_m values than the acid-washed reference coal. The Zn^{2+} loaded coal appears to have a slightly higher T_{in} value than the acid-washed reference coal. The Cu^{2+}, Fe^{2+} and Pb^{2+} loaded coals have much lower T_{in} and T_m values than the acid-washed reference coal. For the $CuAc_2$ loaded coal, the T_{in} value is lowered by more than 100°C. The Fe^{2+} loaded coal has the lowest T_m value.

Most of the cations investigated have no significant effect on the total volatile matter released in the pyrolysis process. For all the coal samples studied, an average of total volatile matter $V_f = 52.8 \pm 1.4$ is obtained. Schafer [10] has studied barium and magnesium cation-loaded coals at slow heating rates, and has shown that the char yields for these cation-loaded coals are the same as those for the corresponding cation-free coal, which

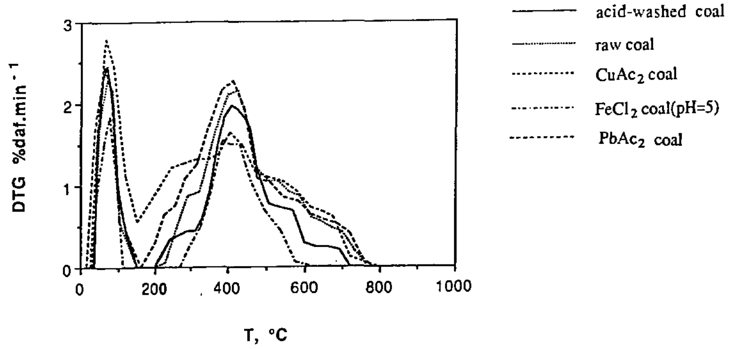

Fig. 2. DTG profiles for the pyrolysis of brown coal samples.

TABLE 3

Pyrolysis parameters of cation-loaded coals

Sample	M [a] (%)	V_f [b] (%daf) [c]	T_{in} [d] (°C)	T_m [e] (°C)	R_m [f] (%daf min^{-1})
Acid-washed coal	10.5	52.1	320	410	1.9
Raw Loy Yang coal	10.7	53.1	305	427	2.2
$ZnAc_2$ coal	10.0	51.2	325	419	1.8
$CuAc_2$ coal	11.7	51.9	210	420	1.6
$PbAc_2$ coal	10.0	53.1	275	413	2.3
$FeCl_2$ coal (pH 5)	11.5	54.0	293	386	1.5
$NiCl_2$ coal (pH 5)	10.9	54.3	305	422	1.1
$CoCl_2$ coal (pH 5)	10.7	54.8	319	427	1.8
$MnCl_2$ coal (pH 5)	11.4	53.3	309	427	2.0
$CaCl_2$ coal (pH 5)	10.0	50.6	297	423	1.4

[a] M, moisture. [b] V_f, final volatile matter released. [c] daf, Dry and ash free. [d] T_{in}, initial pyrolysis temperature. [e] T_m, maximum rate temperature. [f] R_m, maximum rate of mass loss.

suggests that cation-loading only alters the composition of the volatile constituents but not the total volatile matter yield. The results obtained at slow heating rates are different from those obtained at high heating rates. As reported by Morgan and Jenkins [12–14], Tyler and Schafer [11] and Morgan and Scaroni [15], in rapid pyrolysis studies, the total volatile matter released decreases with cation loading, suggesting [15] an increase in secondary char-forming reactions involving these exchangeable cations and volatile matter components, particularly tars. The difference between the total volatile matter yields obtained from rapid and slow pyrolyses was also noted by Morgan and Jenkins [12–14] and Morgan and Scaroni [15], for the ASTM volatile matter contents indicate no variation with cation loading. The final volatile matter yield of Victorian brown coal, as measured by TG [31], is similar to the volatile matter content, as determined by the standard method. Hence it is apparent that at slow heating rates, the total volatile matter content is independent of cation loading. However, in rapid industrial pyrolysis, due to the high heating rates (10^4–10^5°C min^{-1}), the proportion of secondary reactions, involving interaction of the pyrolysis products, is largely reduced [14], which results in a decrease of total volatile matter as cation loading increases. In rapid pyrolysis at 900°C [14], the total volatile matter released is much higher than the ASTM volatile matter content of the corresponding coal. However, at slow heating rates, the proportion of secondary char-forming reactions is increased, which contribute to the final char yield and lead to no variation in overall total volatile matter yield with cation loading.

Kinetic analysis

The kinetics of the catalytic effect of cations on coal pyrolysis has been studied by TG. The kinetic parameters for the pyrolysis process are obtained using the KNIS program [32]. The model used is a three dimensional diffusion control model D_3 [33]. The kinetic parameters corresponding to the primary and secondary pyrolysis stages are given in Table 4 together with the weighted mean apparent activation energy E_{m}. The raw coal has a higher activation energy in the primary pyrolysis stage and a higher E_{m} value than the acid-washed reference coal. Similar results are apparent for the Zn^{2+} and Ca^{2+} loaded coals. The Mn^{2+} and Ni^{2+} loaded coals have similar activation energy E_1, for the primary pyrolysis stage, to that of the acid-washed reference coal. Those cations associated with the most significant catalytic effect, such as Cu^{2+}, Fe^{2+} and Pb^{2+}, the activation energy for the primary pyrolysis stage E_1 and weighted mean apparent activation energy E_{m} are considerably lower than those of the acid-washed reference coal. The $CuAc_2$ coal has the lowest E_1 and E_{m} values. Hence the catalytic effect of these cations is primarily a chemical effect which results in a decreased apparent activation energy. The activation energy of the secondary pyrolysis stage appears to be independent of cation loading and hence the cation catalytic effect is essentially associated with the

TABLE 4

Kinetic parameters of coal pyrolysis

Sample	T (°C)	F [a]	E (kJ mol^{-1})	A (s^{-1})	r	E_{m} (kJ mol^{-1})
Acid washed coal	268–459	0.46	81.7	1.07×10^{2}	0.9993	46.9
	459–824	0.43	22.4	2.94×10^{-3}	0.9956	
Raw Loy Yang coal	280–450	0.43	94.9	1.29×10^{3}	0.9972	49.7
	450–876	0.47	18.9	1.45×10^{-3}	0.9862	
$CuAc_2$ coal	195–420	0.46	55.4	1.98	0.9921	35.4
	420–747	0.44	22.5	3.94×10^{-3}	0.9983	
$PbAc_2$ coal	242–442	0.48	73.0	3.85×10	0.9959	43.0
	442–880	0.42	15.2	8.14×10^{-4}	0.9973	
$MnCl_2$ (pH 5)	256–469	0.47	78.3	5.67×10	0.9973	47.0
	469–858	0.45	23.3	2.82×10^{-3}	0.9976	
$FeCl_2$ (pH = 5)	240–448	0.42	64.7	4.58	0.9993	38.3
	448–820	0.50	24.4	3.09×10^{-3}	0.9963	
$CoCl_2$ (pH = 5)	287–451	0.37	92.3	5.35×10^{2}	0.9990	50.2
	451–881	0.53	30.2	7.17×10^{-3}	0.9984	
$NiCl_2$ (pH = 5)	273–460	0.48	84.5	2.23×10^{2}	0.9959	49.5
	460–832	0.43	22.6	2.82×10^{-3}	0.9982	
$CaCl_2$ (pH = 5)	251–465	0.44	87.8	2.69×10^{2}	0.9961	51.1
	465–833	0.47	26.0	3.95×10^{-3}	0.9957	

[a] F, reaction fraction.

TABLE 5

Effect of Cu^{2+} content on the pyrolysis of $CuAc_2$ coal

Cu^{2+} content (mmol per g dry coal)	M [a] (%)	V_f [b] (%daf)	T_{in} [c] (°C)	T_m [d] (°C)	R_m [e] (%daf min^{-1})
0.191	11.2	53.3	265	423	2.13
0.204	10.7	51.9	248	423	1.96
0.273	10.7	51.8	245	425	1.67
0.381	11.2	50.4	245	427	1.48
0.667	11.2	52.6	226	426	1.60
0.918	12.1	52.2	227	419	1.57
1.200	11.7	51.9	210	420	1.64

[a] M, moisture. [b] V_f, final volatile matter released. [c] T_{in}, initial pyrolysis temperature. [d] T_m, maximum rate temperature. [e] R_m, maximum rate of mass loss.

primary pyrolysis stage. From previous kinetic studies of the pyrolysis of brown coal [34], the primary pyrolysis stage is proposed as chemical decomposition, whereas the secondary pyrolysis stage is dominated by mass and heat transfer processes. Hence, the cation catalytic effect can only be predominantly associated with the primary pyrolysis stage.

Effect of cation concentration

The effect of cation concentration on the pyrolysis of coal is further investigated, using $CuAc_2$ coals containing different Cu^{2+} concentrations. The results are shown in Tables 5 and 6. As the Cu^{2+} content in the coal increases, the initial temperature of pyrolysis T_{in} and the maximum rate of devolatilization R_m decrease. The weighted mean activation energy E_m decreases rapidly with increasing Cu^{2+} content; however, when the Cu^{2+} content is 0.38 mmol g^{-1} dry coal, further increases in Cu^{2+} content have little effect, as shown in Fig. 3. This suggests that the optimum Cu^{2+} content corresponds to 0.38 mmol g^{-1} dry coal.

Infrared spectra of evolved gases

From the TG–DTG pyrolysis parameters, the cation loading has little effect on the total volatile matter released. In order to understand more about the effect of cations on the pyrolysis of coal, it is necessary to investigate the individual evolved gases during coal pyrolysis. The evolved gases from the pyrolysis of the acid-washed reference coal, raw coal, $CuAc_2$ coal, $PbAc_2$ coal and $FeCl_2$ coal (pH 5) samples were analysed by IR spectroscopy over the range 100–800°C. The IR spectra of evolved gases from the acid-washed reference coal at different temperatures are shown in Fig. 4. From these IR spectra, CO_2, CO, CH_4 and C_2H_6 can be identified

TABLE 6

Kinetic parameters for pyrolysis of Cu^{2+} loaded coal

Cu^{2+} content (mmol per g^{-1} dry coal)	T (°C)	F	E (kJ mol^{-1})	A (s^{-1})	r	E_m (kJ mol^{-1})
0.191	265–449	0.44	80.9	1.09×10^2	0.9971	47.3
	449–789	0.46	25.4	4.92×10^{-3}	0.9981	
0.204	230–460	0.48	64.9	6.12	0.9988	42.2
	460–760	0.42	26.4	6.05×10^{-3}	0.9994	
0.273	220–449	0.46	63.6	5.27	0.9989	40.3
	449–778	0.44	25.1	4.80×10^{-3}	0.9995	
0.381	243–439	0.41	60.7	3.02	0.9966	37.5
	439–813	0.49	25.8	4.85×10^{-3}	0.9990	
0.667	219–488	0.49	57.3	1.57	0.9635	36.6
	488–910	0.43	19.7	1.36×10^{-3}	0.9868	
0.918	210–449	0.48	54.6	1.12	0.9979	36.1
	449–799	0.42	23.4	3.46×10^{-3}	0.9990	
1.200	195–420	0.46	55.4	1.98	0.9921	35.4
	420–747	0.44	22.5	3.94×10^{-3}	0.9983	

by the characteristic peaks at 2350, 2160, 3010 and 2960 cm^{-1}, respectively, and the corresponding absorbances at different temperatures are shown in Figs. 5–8 respectively. These absorbance values were calculated using the "baseline"method [35].

For all the coal samples investigated, below 400°C the evolved gas is mainly CO_2. A small proportion of CO and C_2H_6 is also noted. Most of the CH_4 and C_2H_6 are released in the temperature range 400–600°C. The release of CO occurs mainly above 400°C, even at 800°C, CO release is also noted. The acid-washed reference coal releases more hydrogen-containing gases, such as CH_4 and C_2H_6, compared with other coals investigated, due to its lower cation content. The presence of cations such as Cu^{2+} and Pb^{2+} has a significant influence on the release of CO_2 from coals. As shown in

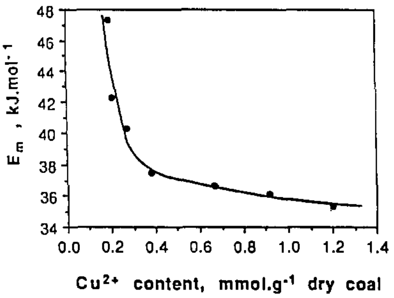

Fig. 3. Effect of Cu^{2+} content on E_m for the $CuAc_2$ coal.

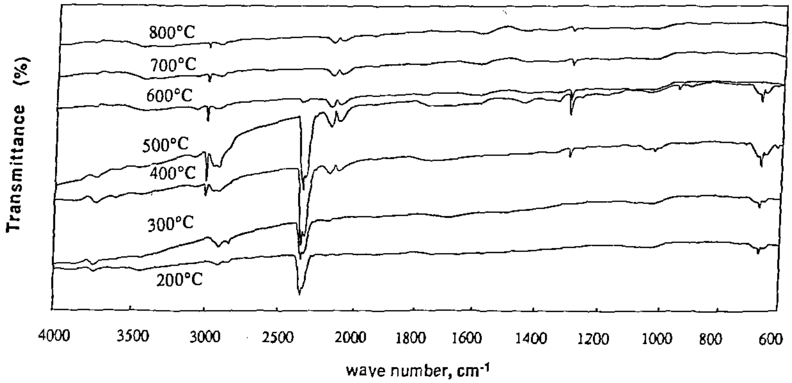

Fig. 4. Infrared spectra of the evolved gases from the acid-washed reference coal at different pyrolysis temperatures.

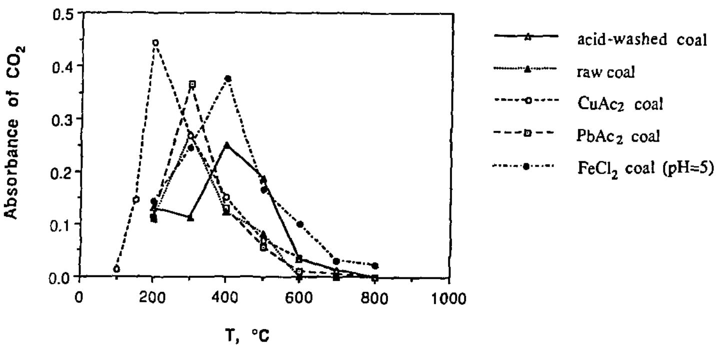

Fig. 5. Effect of cations on the evolution of CO_2 in the coal pyrolysis process.

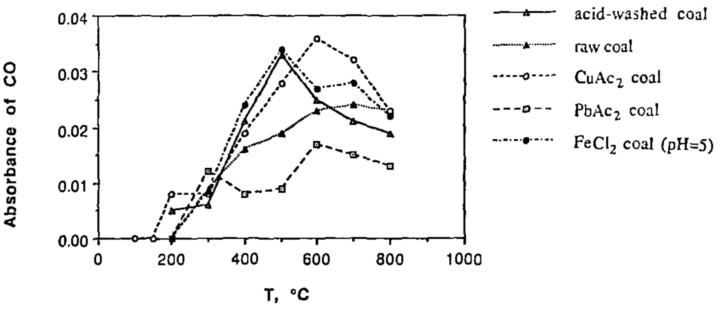

Fig. 6. Effect of cations on the evolution of CO in the coal pyrolysis process.

Fig. 5, for the acid-washed reference coal, the maximum release of CO_2 occurs at about 400°C. Raw coal has a relatively lower maximum temperature of CO_2 release but similar intensity, compared with the acid-washed reference coal. The $CuAc_2$ and $PbAc_2$ coals release more CO_2 and have lower temperatures of maximum CO_2 release than the acid-washed refer-

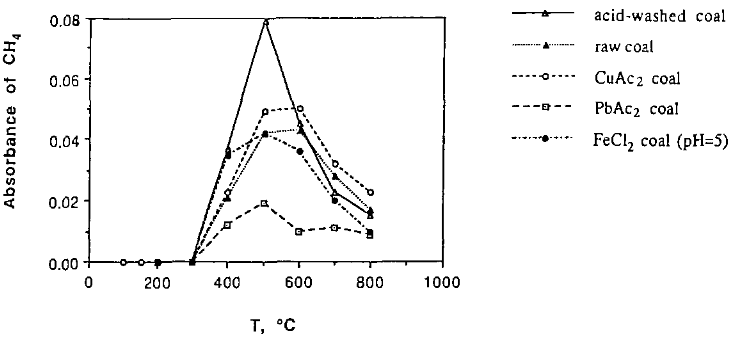

Fig. 7. Effect of cations on the evolution of CH_4 in the coal pyrolysis process.

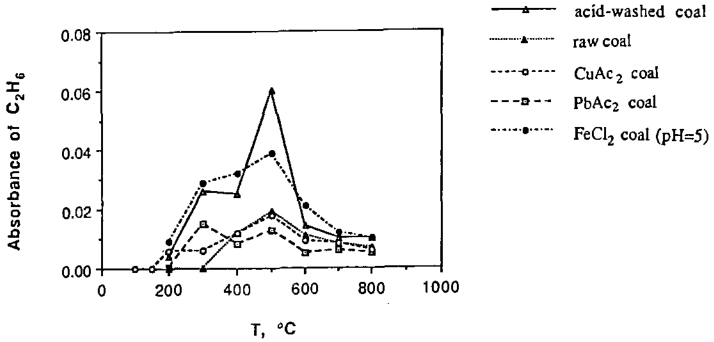

Fig. 8. Effect of cations on the evolution of C_2H_6 in the coal pyrolysis process.

ence coal. For the $CuAc_2$ coal, the release of CO_2 shifts to a significantly lower temperature range with maximum release at 200°C. The $FeCl_2$ coal (pH 5) also releases more CO_2 in a lower temperature range than the acid-washed reference coal; however, the temperature of maximum CO_2 release is approximately that of the acid-washed reference coal. The results obtained by Schafer [8,10] have shown that cation-loaded coals evolved more CO_2 during pyrolysis than the acid-washed reference coals and that the CO_2 originates not only from carboxyl groups but also from other oxygen-containing groups in the coal. Hence, cation exchange of carboxyl group sites alters the mechanism of decomposition of these functional groups during the pyrolysis process.

REFERENCES

1 H.N.S. Schafer, Fuel, 49 (1970) 271.
2 C.J. Lafferty and J.D. Lambert, Metal removal from aqueous solutions by Victorian brown coal and derived products, Res. Rep. 87/2, Coal Corporation of Victoria, Australia, 1987.
3 C.J. Lafferty, M.D. Hobday and G.J. Perry, Proc. 3rd Aust. Coal Sci. Conf., Adelaide, Australia, 1988, A3:1.

4 C.J. Lafferty and M.D. Hobday, Fuel, 69 (1990) 78.
5 A.D. Stuart, Proc. Aust. Coal Sci. Conf., Churchill, Victoria, Australia, 1984, p. 239.
6 A.D. Stuart, Fuel, 65 (1986) 1003.
7 G.V. Cullen and N.G. Siviour, Water Res., 16 (1982) 1357.
8 H.N.S. Schafer, Fuel, 58 (1979) 667.
9 H.N.S. Schafer, Fuel, 58 (1979) 673.
10 H.N.S. Schafer, Fuel, 59 (1980) 295.
11 R.J. Tyler and H.N.S. Schafer, Fuel, 59 (1980) 487.
12 M.E. Morgan and R.G. Jenkins, Fuel, 65 (1986) 757.
13 M.E. Morgan and R.G. Jenkins, Fuel, 65 (1986) 764.
14 M.E. Morgan and R.G. Jenkins, Role of exchangeable cations in the rapid pyrolysis of lignites, in H.H. Schobert (Ed.), The Chemistry of Low-Rank Coals, American Chemical Society, Washington D.C., U.S.A., 1986, p. 213.
15 B.A. Morgan and A.W. Scaroni, Cationic effects during lignite pyrolysis and combustion, in H.H. Schobert (Ed.), The Chemistry of Low-Rank Coals, American Chemical Society, Washington D.C., U.S.A., 1986, p. 255.
16 R.B. Reuther and R.G. Jenkins, Am. Chem. Soc., Div. Fuel Chem., 34 (1989) 1124.
17 J.B. Murray, Fuel, 57 (1978) 605.
18 C. Rai and D.Q. Tran, Fuel, 58 (1979) 603.
19 M.A. Serageldin and W.P. Pan, Am. Chem. Soc., Div. Fuel Chem., 29 (1984) 112.
20 T.K. Pong and I.J. Harris, J. Inst. Energy, 9 (1984) 383.
21 D.E. Mainwaring and G.B. Christie, Proc. 2nd Coal Res. Conf., Wellington, New Zealand 1987, Paper R18.1.
22 H.R. Brown and R.A. Durie, Fuel, 40 (1961) 207.
23 R. Wagner and H.J. Muhlen, Fuel, 68 (1989) 251.
24 M.J. Aho, J.L. Tummavouri and J.P. Hamalainen, Fuel, 69 (1990) 639.
25 R.P. Cavalieri and W.J. Thomson, Fuel, 69 (1990) 334.
26 D.E. Rogers, Fuel, 63 (1984) 1610.
27 T.D. Hengel and P.L. Walker, Jr., Catalysis of lignite char gasification by exchangeable calcium and magnesium, in H.H. Schobert (Ed.), The Chemistry of Low-Rank Coals, American Chemical Society, Washington D.C., U.S.A., 1986, p. 267.
28 S.J. Yuh and E.E. Wolf, Fuel, 63 (1984) 1604.
29 J. Huang and Q. Lin, J. Dalian Inst. Technol., 26 (1987) 39.
30 R.A. Durie and H.N.S. Schafer, Proceedings ANZAAS Conf., Hobart, Tasmania, Australia, 1965 p. 1.
31 S. Ma, J.O. Hill and S. Heng, J. Therm. Anal., 35 (1989) 977.
32 S. Ma, G. Huang and J.O. Hill, Thermochim. Acta, 184 (1991) 233.
33 J. Sestak and G. Berggren, Thermochim. Acta, 3 (1971) 1.
34 S. Ma, J.O. Hill and S. Heng, J. Therm. Anal., (1991), in press.
35 W.J. Potts, Jr., Chemical Infrared Spectroscopy, Vol. 1, Wiley, New York, 1963, p. 165.