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The influence of K_2CO_3 and KCl on H_2 formation during heat treatment of an acid-treated inertinite-rich bituminous coal–char

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Abstract Thermogravimetric-mass spectrometry (TG-MS) studies were conducted in order to investigate the effect of potassium carbonate (K_2CO_3) and potassium chloride (KCl) on the conversion and hydrogen evolution of chars derived from acid-leached South African inertinite-rich bituminous coal. K_2CO_3 and KCl (0.5, 1, 3, 5 potassium ion mass percentages) were loaded to the acid-leached (demineralized) coal samples prior to charring. The resulting 'doped' coal–char samples were subjected to heat treatment in a CO_2 atmosphere up to 1200 °C, and the thermogravimetric curves, as well as the temperature ranges of evolution of hydrogen, were investigated. The results obtained indicate that the temperatures at maximum rate of mass loss (from the DTG curves), as well as the temperatures at maximum rate of hydrogen (H_2) evolution (from the MS curves) are lowered with increasing potassium salt loadings. The relative coal gasification reaction reactivity ($1/T_{max}$) determined from the DTG curves increases with increasing potassium salt loading and increases more for K_2CO_3 than for KCl. The catalytic influence of K_2CO_3 on the CO_2 gasification of the acid-treated coal sample was found to be greater than that of KCl at a loading of 5 % potassium ion mass percentage.

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Introduction

Coal and char gasification has been studied extensively over the past decades and is an alternative technology to produce liquid hydrocarbons (gasification with Fischer–Tropsch synthesis). Catalytic coal gasification has also been studied in order to gain more insight and understanding into the reactivity of coal–char. The use of minerals during coal–char gasification has been shown to lower gasification temperatures and also to overcome the slow reaction of carbon with CO_2 [1]. The addition of some minerals produces more porous coal–chars, thus enhancing char's reactivity with CO_2 [2]. Kinetic models consisting of elementary steps of the overall gasification reaction of carbon with CO_2 have been proposed by many researchers [3–6]. However, these studies have focused predominantly on Northern Hemisphere vitrinite-rich coals and the inertinite-rich Southern African coals need to be investigated.

South African coals have high mineral matter contents, sometimes in excess of 20 % [7, 8]. The most abundant minerals are clays, carbonates, sulphides and quartz. Mineral matter in coal has a significant effect on coal utilization processes such as combustion, coking and gasification [9]. Mineral matter comprises of all inorganic material and elements present in coal as discrete (crystalline and non-crystalline) mineral phases [10] and may occur in coal as minerals, mineraloids and as organically associated inorganic elements [9, 10]. During heat treatment, these minerals may react and are transformed into new mineral phases [9–11]. Some disadvantages of the mineral phases formed during coal processing include:

fouling, slagging, corrosion of equipment and the reduction in the overall rate of coal conversion processes. However, some of the mineral matter may exhibit a catalytic effect on the coal thermal processes [8, 9].

Leaching of the raw coal with hydrochloric acid (HCl) and hydrofluoric (HF) acid has been shown to alleviate the problem of mineral matter associated with coal. Acid leaching removes most of the inorganic constituents (mineral matter) without causing significant changes to the carbonaceous part of coal [12]. Acid leaching of coal to remove mineral matter from the coal sample is used to prepare coal samples for investigations regarding the effect of added minerals or inorganic compounds on the further thermal processing of the carbon part of the coal.

Potassium-containing minerals and salts can act as gasification catalysts for vitrinite-rich coal [10, 13]. However, potassium compounds are also known to react with mineral matter in coal, resulting in catalytically inactive silicates [13, 14].

Although South Africa is the fifth largest coal producer worldwide, there is comparatively little scientific knowledge of its inertinite-rich coals [7, 12, 15, 16]. No literature of thermogravimetric-mass spectrometry (TG-MS) studies on the effect of potassium salt additions on the hydrogen gas composition of gasification products from South African inertinite-rich coal could be found. This paper reports on a study investigating the influence of added potassium carbonate and potassium chloride on the hydrogen gas evolution during the CO_2 reaction with the char derived from an inertinite-rich South African bituminous coal from a Highveld coalfield. To remove the influence of minerals and inorganic compounds present in the coal sample, the coal sample was acid treated to remove these before the potassium salts were added to the coal to prepare the char sample. The thermal behaviour of the acid-treated coal sample and the acid-treated coal samples with added potassium compounds was compared to give a relative indication of the influences of the potassium compounds on the gasification reactivity of the coal.

Experimental

Coal sample and demineralization

A typical Permian-aged South African Highveld inertinite-rich medium rank C bituminous coal was chosen for this study (particle size <75 μm). In order to obtain a coal sample with low mineral matter content, the coal was demineralized using an acid treatment method of HCl and HF [7, 12]. The coal sample (500 g) was leached with 4 dm^3 of a 5 mol dm^{-3} HCl solution for 24 h, and the solution filtered in a polypropylene Buchner funnel under vacuum. The residue was leached with 4 dm^{-3} of a 5 mol dm^{-3} HF solution for 24 h, and the solution was again filtered under vacuum using a Buchner funnel. The resulting residue was again leached with 4 dm^3 of 5 mol dm^{-3} HCl for 24 h, after which the product was filtered under vacuum and washed with large quantities of distilled water until a constant pH was observed. The resulting product was then dried overnight in an oven at 80 °C. All the leaching steps were carried out at room temperature, and the resulting leached coal samples were stored in a desiccator under nitrogen in a dark place until use.

Sample preparation

Potassium carbonate (K_2CO_3) and potassium chloride (KCl) were chosen as the inorganic salt dopants. The salts were dried in an oven overnight at 120 °C prior to all experiments. Catalytic salts were added to the demineralized coal prior to charring. The coals and salts were mixed together using a mortar and pestle and an electric mixer until uniform mixing. Samples with loadings of 0.5, 1, 3 and 5 potassium ion mass percentages for each of the salts were prepared.

Thermogravimetric (TG) analysis

Thermogravimetric (TG) studies of the coal samples were carried out using a TA Instruments' SDT-Q600 thermogravimetric analyser. Approximately 10 mg of sample was used per experiment. The TG chamber was purged with nitrogen (purity >99.9 %) for 10 min to ensure an inert atmosphere, and the temperature was allowed to equilibrate (at room temperature). Char samples were prepared by heating the coal samples to 900 °C at a rate of 10 °C min^{-1} using a nitrogen flow rate of 75 mL min^{-1} followed by holding the temperature for 15 min at 900 °C. The samples were then allowed to cool down (in situ) to room temperature under the nitrogen atmosphere, to prevent the sample from oxidizing. Once the sample had cooled down to room temperature, the nitrogen flow was switched to CO_2 (purity >99.9 %). The temperature and the masses of the resulting samples were allowed to stabilize, and after stabilizing, the sample was heated under CO_2 flow to 1200 °C at a rate of 10 °C min^{-1} and a CO_2 flow rate of 20 mL min^{-1}.

The mass loss as a function of temperature was recorded. All samples were subjected to the same experimental conditions, and multiple runs were performed to ensure repeatability. The averaged thermogravimetric curves were used as relative measures to compare the effect of addition of the potassium salts on the thermal behaviour of the coal samples. This method of relative comparison of coal's thermal behaviour is often used in coal science [4, 5, 16].

Mass spectrometry (MS)

A Cirrus mass spectrometer with a dual Faraday and multiplier detector was used. The mass spectrometer was attached to the outgas port of the TG instrument, and the evolved gases were simultaneously detected as the thermogravimetric curves were obtained. The evolved gaseous species from the sample in the TG were fed through the outgas port, via a heated capillary to the mass spectrometer. The hydrogen evolved was detected and recorded from the beginning of the reaction under the CO_2 atmosphere up to a temperature of 1200 °C.

Results and discussion

Coal characterization

The original and acid-leached coal samples were submitted for proximate and ultimate analyses. These analyses were used to determine the effect of acid leaching on the mineral matter content in this coal sample. Proximate and ultimate analyses results are summarized in Table 1 and are consistent with previous findings of an inertinite-rich South African coal [7, 8].

A substantial reduction in the ash content (from 22.6 % to <3 %, dry basis) was observed from the proximate results, indicating that a large proportion of the inorganic matter was removed by sequential leaching of the coal sample.

The leaching method has been reported not to affect the coal molecular structure, except for a slight increase in –COOH content [12]. This increase in –COOH functional groups on the coal surface may be attributed to some oxidation during the acid leaching process.

Effect of catalyst loadings on the coal–char derived from demineralized coal

Thermogravimetric (TG) curves

The TG curves for the K_2CO_3- and KCl-loaded demineralized coal–char samples are presented in Figs. 1 and 2, respectively. No significant mass loss was observed below 600 °C for all the samples. These results are consistent with the fact that carbon gasification (C–CO_2 reactions) only occurs at 700 °C and above [3–5]. Note that all the mass loss curves are reported on a potassium salt-free basis.

The average final remaining unreactive contents of the K_2CO_3 experiments were observed to range between 1 and 9 % (Fig. 1) and that of the KCl-loaded char samples range between 4 and 8 % (Fig. 2). Approximately 3 % of this remaining unreacted part of the coal–char samples is due to the ash yield (as measured using proximate analyses) and the rest is due to <6 % of the coal carbon structure that does not react under these conditions. The results are consistent with the literature and as expected for the heterogeneous nature of the coal molecular structure [7, 15, 16].

Figures 1 and 2 indicate catalytic behaviour by K_2CO_3 and KCl on the CO_2 gasification reactions of the coal–char samples, as the reactions are observed to occur over a smaller temperature range using the same experimental conditions. An increase in rate of conversion (decrease in temperature range of the reaction) of the coal–char with

Table 1 Normalized proximate and ultimate analysis results of raw coal and acid-treated coal

	Coal Moisture-free basis/mass%	Acid-treated coal Moisture-free basis/mass%
Proximate analysis		
% Ash yield	22.6	2.8
% Volatile matter	24.9	26.9
% Fixed carbon	52.5	70.3
Total	**100**	**100**
Ultimate analysis	Moisture- and ash-free basis/mass%	Moisture- and ash-free basis/mass%
% Carbon content	77.1	79.2
% Hydrogen content	4.2	4.0
% Nitrogen content	2.1	2.3
% Oxygen content	15.3	13.5
% Total sulphur	1.3	1.0
Total	**100**	**100**

Bold values indicate the listed temperatures focus specifically on hydrogen generation (MS curves), whereas the maximum temperatures determined from the DTG curves are more generally the combined gasification reactions' maximum rates
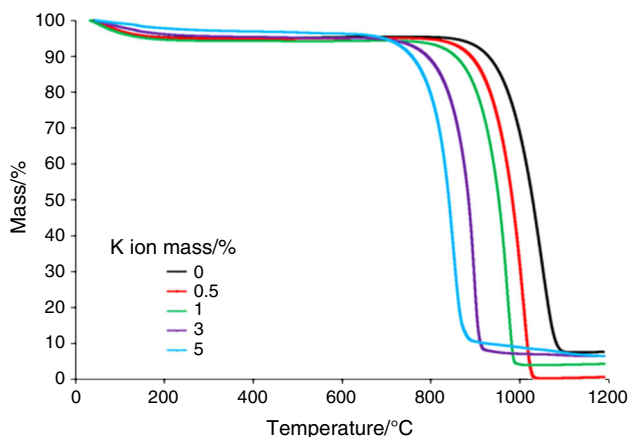
Fig. 1 Thermogravimetric mass loss curves of the char derived from the acid-treated coal with K_2CO_3 loadings during heat treatment in a CO_2 atmosphere
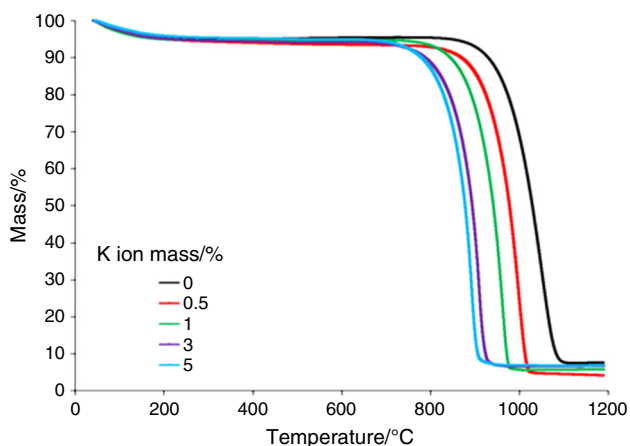

Fig. 2 Thermogravimetric mass loss curves of the char derived from the acid-treated coal with KCl loadings during heat treatment in a CO_2 atmosphere

increasing potassium salt loadings (up to 5 potassium ion mass percentage) was also observed.

Differential thermogravimetric (DTG) curves

The first derivatives of the TG curves, the DTG curves, for the K_2CO_3- and KCl-loaded coal–char samples were obtained to further evaluate the thermal behaviour of these samples. DTG curves of the K_2CO_3- and KCl-loaded demineralized coal–char samples are presented in Figs. 3 and 4, respectively.

The DTG curves enable determination of the 'characteristic' temperatures of interest. These are the temperature at which maximum rate of mass loss (T_{max}) took place (under the specific experimental conditions), as well as the temperature at the initial (T_i) and termination (T_f) of mass
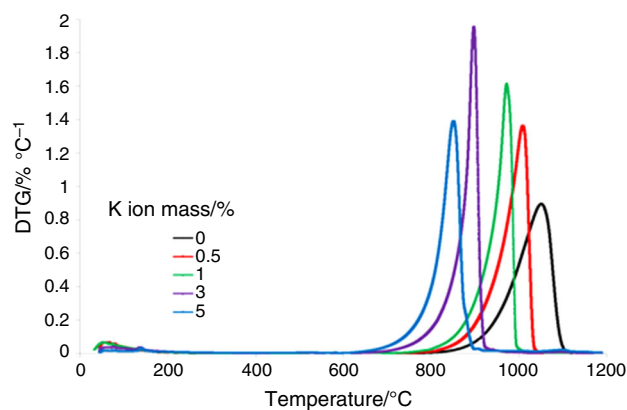

Fig. 3 DTG curves of char derived from the acid-treated coal with K_2CO_3 loadings during heat treatment in CO_2 atmosphere
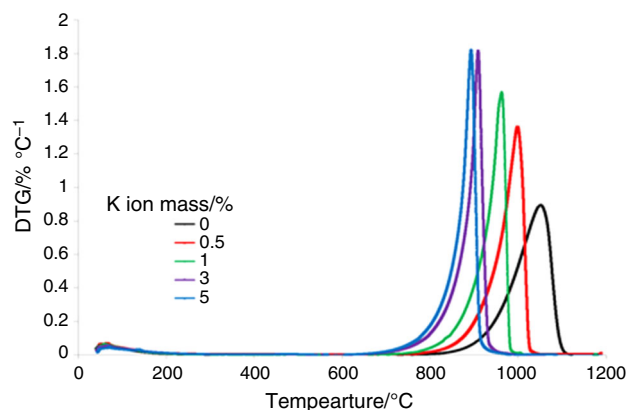

Fig. 4 DTG curves of char derived from the acid-treated coal with KCl loadings during heat treatment in CO_2 atmosphere
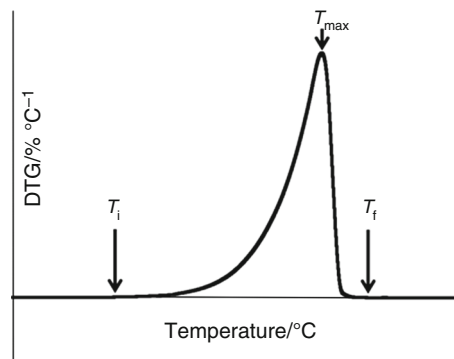

Fig. 5 Illustration of characteristic temperatures on a DTG curve

loss. Figure 5 presents an illustration of how these temperatures were determined.

It was observed that the conversion of the sample with no potassium salt loading occurred over a broader temperature range as opposed to that with catalyst additions (i.e., char conversion of the potassium salt-loaded samples

Table 2 Temperatures at initial (T_i), termination (T_f) and maximum (T_{max}) rate of mass loss/°C

Acid-treated coal with	Loading/potassium ion mass%	T_i	T_f	$\Delta T = (T_f - T_i)$	T_{max}
No additions	0	748	1130	382	1047
K$_2$CO$_3$	0.5	732	1065	333	1006
	1	715	1030	315	970
	3	682	957	275	896
	5	617	945	328	848
KCl	0.5	744	1061	317	997
	1	721	1022	301	961
	3	668	984	316	908
	5	643	971	328	892

occurs over a narrower temperature range). These characteristic temperature values are listed in Table 2.

The DTG curves showed that when the catalyst loading was increased, the temperature at maximum rate of mass loss was also lowered. The relative gasification reactivities ($1/T_{max}$) were calculated from T_{max} on the DTG curves for the different K$_2$CO$_3$- and KCl-loaded samples, and the variation of the relative gasification reactivity with potassium salt loading is presented in Fig. 6. This method of calculating and approximating the relative coal gasification reactivity is used in coal science as a relative measure of determining various additions' and conditions' influence of the gasification process. It was observed that the relative coal gasification reactivity increased with increasing loadings of K$_2$CO$_3$ and KCl, indicative of an increased in rate of the gasification reaction with increased potassium salt loading.

TG results indicated that K$_2$CO$_3$ and KCl (similar potassium loadings) are catalytic active during heat treatments of char derived from the acid-treated coal. The relative gasification reactivities of the coal–char sample with potassium ion mass loadings of 3 and 5 % were higher for the K$_2$CO$_3$-loaded samples than for the KCl-loaded samples, with the highest relative gasification reactivity measured for the 5 % K$_2$CO$_3$ addition. These results and observations indicate that the catalytic effect of K$_2$CO$_3$ is greater than that of KCl on the gasification reactions of the acid-treated inertinite-rich coal.

MS gas evolution profiles

H$_2$ evolution profiles

The hydrogen (H$_2$) evolution profiles of the coal–char samples derived from the acid-treated coal–char samples, with and without potassium salt loadings, are presented in Fig. 7. Qualitative determination of H$_2$ evolution during
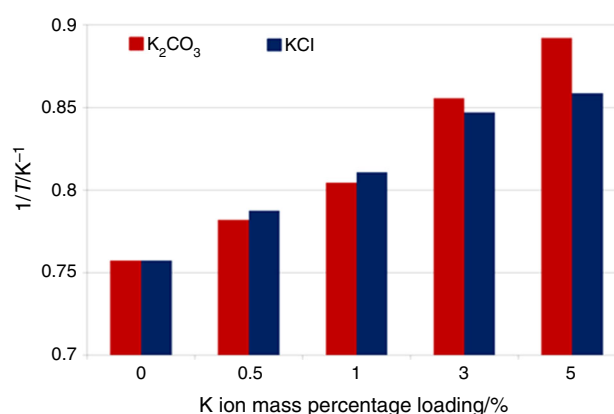

Fig. 6 Relative gasification reactivity ($1/T_{max}$) of the char derived from the acid-leached coal samples with K$_2$CO$_3$ and KCl loadings

the heat treatment of the chars in CO$_2$ atmosphere for the samples with and without K$_2$CO$_3$ and KCl loadings were performed. As H$_2$ is one of the main synthesis gases produced by the coal gasification process, following the evolution thereof during thermal processing of coal in a CO$_2$ atmosphere (partially the gasification process) is used to better understand the influences of various added minerals or salts to the leached and neat coal samples. The H$_2$ identification using the mass spectrometer was based on measuring the key fragment H$_2^+$, corresponding to mass number (m/z) of 2.

Hydrogen evolution during heat treatment of coal–char is associated with different functional groups present on the surface of the carbon matrix in the coal–char [17]. The H$_2$ observed in the gaseous phase is attributed to the abstraction and removal of the hydrogen from the hydrocarbons functional groups due to temperature increase. The remaining parts of the functional groups on the coal carbon matrix's surface then act as carbon active sites for further gasification reactions [18]. As a result, chemisorption of

Fig. 7 Mass spectroscopic spectra of H_2 ($m/z = 2$) of the acid-treated coal with and without potassium ion mass percentage loadings of **a** 0 %, **b** 0.5 %, **c** 1 %, **d** 3 % and **e** 5 % during heating in a CO_2 atmosphere
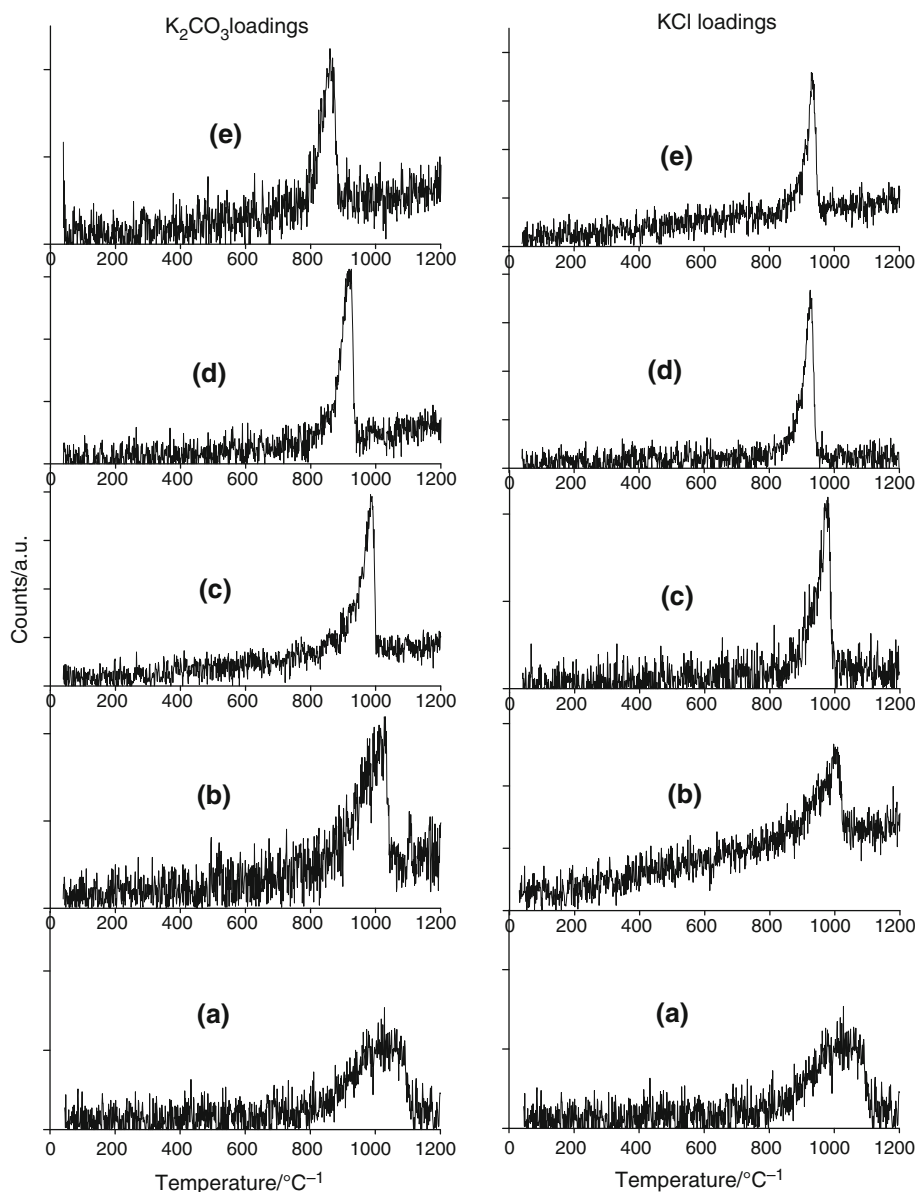
the CO_2 gas molecule takes place at these active sites and these steps are described as the initial stages of coal gasification [19–21]. Removal of the edge hydrogen atoms is proposed to take place at 700–900 °C [18]. Evolution of hydrogen at lower temperatures or an increase in the rate of removal of hydrogen thus indicates that the gasification process also has shifted to lower temperatures.

Hydrogen evolution for all the samples (Fig. 7) began at approximately the same temperature of 800 °C; however, potassium salt addition caused the H_2 evolution to take place over a narrower temperature range than that observed for the sample without any potassium salt loading. As can be seen from Fig. 7, addition of the potassium salts to the leached coal samples shifted the temperature at which the

maximum amount of H_2 is evolved (on the MS curves) to lower temperatures. In Table 3, the temperatures at maximum amounts of hydrogen evolution as measured on the mass spectroscopic curves for hydrogen are listed. These temperatures follow a similar trend than the temperatures (T_{max}) at maximum rate of the gasification reaction as observed on the DTG curves (Figs. 4, 6). An increasing shift to lower temperatures at maximum reaction rates was observed with increasing potassium salt loadings (up to a maximum loading of 5 mass percentages) for both the K_2CO_3- and KCl-loaded samples. This implies that K_2CO_3 and KCl facilitate the evolution of H_2 by speeding/enhancing the rates of the reaction steps and/or mechanisms where H_2 is given off, resulting in faster H_2 formation and

Table 3 Temperatures at maximum rate of mass spectrometric determined H_2 evolution ($T_{\max,H_2}$) of the acid-treated coal–char samples with/without indicated potassium salt loadings/°C

Acid-treated coal with	Loading/potassium ion mass%	$T_{\max,H_2}$
No additions	0	1020
K₂CO₃	0.5	1000
	1	980
	3	900
	5	880
KCl	0.5	1000
	1	980
	3	920
	5	920

release. It is proposed that additions of potassium carbonate and potassium chloride to coal enhance gasification and that these salts thus act as gasification catalysts.

Conclusions

The proximate and ultimate analyses results of the neat coal sample and the acid-treated coal sample indicate that the leaching process successfully reduced the inorganic matter associated with coal, from 23 % to <3 % (dry basis). Thermogravimetric analyses of the prepared coal–char samples with and without the potassium salts indicated that the added salts influenced the CO_2 gasification steps of the process. The relative coal gasification reactivity, measured as $1/T_{\max}$, with $T_{\max}$ the temperature at maximum rate of the reaction as measured on the DTG curves, increased with increasing loadings (up to a maximum of 5 potassium ion mass percentages) of K₂CO₃ and KCl, indicative of an increased in rate of reaction with increased potassium salt loading. The potassium carbonate and potassium chloride salts thus seem to act as catalysts for the coal gasification reactions.

Addition of K₂CO₃, at a potassium ion mass percentage loading of 5 %, has the greatest catalytic effect on the gasification of the inertinite-rich acid-leached coal. K₂CO₃ and KCl additions to the inertinite-rich acid-treated coal cause H_2 evolution to take place over a narrower temperature range than that observed for the samples without potassium salt loading. Industrial coal gasification may thus be catalysed by the addition K₂CO₃ or KCl to the coal feed, and a K₂CO₃ loading of 5 % potassium ion mass percentage is indicated as an option to perform gasification at lower temperatures.

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