Fuel 158 (2015) 72–80

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

The temperature-dependent release of volatile inorganic species from Victorian brown coals and German lignites under CO_2 and H_2O gasification conditions

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HIGHLIGHTS

- The Na, Cl and S species released during gasification of low rank coal are reported.
- A release mechanism including the role and influence of CO_2 and steam is proposed.
- The 2-phase mechanism is similar but distinct under CO_2 and steam atmospheres.
- The release of volatile Na and Cl species essentially independent of gas atmosphere.
- The S species release mechanism depends directly on CO_2 and steam concentration.

ARTICLE INFO

Article history:
Received 28 October 2014
Received in revised form 2 April 2015
Accepted 28 April 2015
Available online 8 May 2015

Keywords:
Brown coal
Lignite
Gasification
Volatile inorganics

ABSTRACT

To promote the use of abundant low rank coal resources, and to assist with the design, development and optimisation of hot gas cleaning and downstream processes, it is necessary to understand the release mechanisms of volatile inorganic species from low rank coals under high temperature gasification conditions. Although a significant amount of work has been reported under combustion and oxygen lean gasification conditions, these studies do not sufficiently explain the role of the gasification reagents CO_2 and H_2O in the mechanisms. Therefore, gasification experiments under 20% CO_2 and 20% H_2O in He were conducted at 1100 °C, 1200 °C and 1400 °C for two Victorian brown coals and four Rhenish lignites. Hot gas analysis was conducted by online molecular beam mass spectrometry to determine the intensity, relative quantity and timing of the release of volatile species of interest. Two overlapping phases were clearly observed from the results – devolatilisation and char gasification. Major species detected were $^{23}Na^+$, $^{34}H_2S^+$, $^{35}Cl^+$, $^{36}HCl^+$, $^{39}K^+/^{39}NaO^+$, $^{58}NaCl^+$, $^{60}COS^+/^{60}NaCl^+$, and $^{64}SO_2^+$. The release during devolatilisation was essentially independent of the bulk gas atmosphere and constituted the majority of Na and Cl species. The release of S-species occurred predominantly during gasification under both CO_2 and H_2O atmospheres by similar but distinct mechanisms, and was directly affected by the absence, presence and concentration of the gasification reagents.

1. Introduction

Coal accounted for over half of the increase in global energy use over the past decade and is predicted to play a major role in all future projection scenarios to 2035 [1]. It is therefore important to continue the development of cost-effective, environmentally responsible coal processes, such as high efficiency gasification, for the conversion of this abundant resource to power and products. In particular, low rank coals are of interest for use in advanced coal-to-product gasification technologies for countries with significant reserves, such as Australia and Germany.

Low rank coals, as well as those of higher rank, often contain significant amounts of inorganic species including Na, Cl and S. During gasification and other high temperature processes, these species undergo decomposition and reaction, resulting in a complex mixture of volatile inorganic products known to cause slagging and fouling deposits, corrosion and pollution problems [2]. It is therefore important to design, develop and optimise high temperature gas cleaning systems, downstream conversion processes,

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http://dx.doi.org/10.1016/j.fuel.2015.04.071
0016-2361/

and environmental controls to enhance the overall gasification process efficiency. A comprehensive knowledge of the mechanisms of release and subsequent interactions between volatile inorganic species, including the role of the gasification reagents, is therefore required to facilitate the prediction of detrimental gas-phase components based on parent coal properties.

Investigations into the modes of occurrence and release of volatile inorganics at high temperatures have historically been conducted using a variety of modelling and experimental methods [3,4]. Recently, online mass spectrometric techniques [5–8] have predominantly been used to measure in situ decomposition and reaction products from high temperature gasification and combustion processes. In particular, molecular beam mass spectrometry (MBMS) yields time dependent, online, simultaneous data pertaining to the release of volatile inorganic species under high temperature conditions of industrial interest [9].

Recent investigations in the area of the release of volatile inorganic species from low rank coals under gasification conditions have focused on the effects of temperature, pressure, oxygen partial pressure and steam addition [6,10–14]. However, the influence of different bulk gas atmospheres on the release mechanisms is still unknown. This study therefore uses the online MBMS technique to investigate the influence of temperature and bulk gas atmosphere on the in situ reaction products from high temperature gasification of two Victorian brown coals and four Rhenish lignites. In particular, a greater understanding of the role of the primary gasification reagents, CO_2 and H_2O, in the release and reaction mechanisms of the volatile Na-, Cl- and S-species under entrained flow conditions is sought. The results of this study are further compared with previous results obtained under O_2 and O_2/steam atmospheres [10,11,13] where appropriate.

2. Materials and methods

2.1. Fuel preparation

Run-of-mine samples of four Rhenish lignites (HKN-S+, HKN-S−, HKS and HKT) were supplied by RWE Power and two Victorian brown coals (Loy Yang – LY and Morwell – MOR) were supplied by the Loy Yang and Hazelwood Power Stations, respectively. Coals from these two regions were chosen due to their similarities in age (tertiary) and rank (low). The samples were air dried and pulverised in a mill. The Rhenish coals were sieved to a particle size range of <100 μm and the Victorian coals to 90–106 μm. All samples were thereafter preserved at room temperature under dry conditions.

Of particular interest in this investigation was the difference in the inorganic composition of the coals, specifically regarding Na, K, S, Cl, Al, Si, and Ca. These elements and various compounds thereof, typically found in low rank coals, are known either for their volatile nature or for their influence on the volatilisation of other inherent or derived inorganic species released during the thermal treatment of coals. The chemical composition of the coals under investigation is given in Table 1. Chemical analysis was performed by the central division of analytical chemistry (ZCH) of the Forschungszentrum Jülich. The standard methods used and variance of analytical results are detailed elsewhere [6].

The chemical analysis of the Loy Yang sample showed anomalously high ash content – almost 8% on a dry basis (Table 1). Based on similar samples reported in recent literature, Loy Yang coal is expected to have an ash content in the range of 0.5–1.6% on a dry basis. Uncharacteristically high aluminium and silicon were also measured in the current sample in comparison to previously reported values for Loy Yang coal [7,15,16] and the presence of large amounts of silica was confirmed by XRD. These features are likely an artefact of sampling, such as extraneous sand or clay from the interseam or overburden. The additional silica content may influence the release mechanism of sodium as discussed in previous work [14].

Table 1
Results of the chemical analysis of the coals under investigation.

	HKN-S−	HKN-S+	HKS	HKT	LY	MOR
Proximate analysis of the coals (mass %)						
Moisture (air dried)	20.02	19.76	20.45	10.27	11.16	14.92
Ash (dry basis)	3.58	4.23	6.59	13.20	7.99	3.59
Volatiles (dry basis)	51.43	53.17	52.45	55.24	48.25	49.31
Chemical composition (dry basis, mass %)						
C	65.8	65.8	62.0	57.3	50.1	60.7
H	4.81	4.98	4.89	4.18	4.3	5.35
N	0.78	0.84	0.69	0.75	0.445	0.52
S	0.205	0.508	0.365	0.478	0.207	0.041
Cl	0.01	0.03	0.02	0.01	0.092	0.039
Al	0.024	0.025	0.099	1.2	0.204	0.019
Fe	0.18	0.22	0.40	0.20	0.209	0.185
Ca	0.79	0.90	1.2	1.1	0.133	0.417
Mg	0.30	0.34	0.43	0.39	0.114	0.194
K	0.016	0.016	0.018	0.069	0.014	0.010
Na	0.19	0.19	0.42	0.22	0.101	0.056
Si	0.009	0.020	0.60	2.7	7.180	0.052
Elemental Ratios (molar basis)						
Na/Cl	28.88	11.33	27.48	31.05	1.68	2.21
Na/K	20.48	19.68	38.29	5.56	12.40	9.51
Ca/S	3.08	1.42	2.58	1.90	0.52	8.16
Na/Ca	0.42	0.36	0.62	0.34	1.32	0.23

HKx = Rhenish Lignites, Hambach; LY = Loy Yang brown coal, Victoria; MOR = Morwell brown coal, Victoria.

2.2. Experimental setup

The release of Na-, S-, and Cl-containing species during steam gasification was investigated under conditions analogous to those experienced by coal particles during industrial entrained flow gasification. The fixed-bed, batch configuration with continuous gas flow was deliberately chosen. In contrast, under continuous feed conditions the final product gas mixture would mask detection of the intermediate products, which is necessary for elucidation of the release mechanisms. Experiments were performed in a sealed horizontal reactor under controlled atmospheres of 20% CO_2 in He or 20% H_2O in He at temperatures of 1100 °C, 1200 °C and 1400 °C. Thermal cracking of organics tar species occurs in the reactor [11]. All parts of the reactor downstream of the reaction zone were maintained at temperatures above the condensation point of the species of interest, and the MBMS was installed downstream for online gas analysis. A simplified schematic of the coupled apparatus is shown in Fig. 1.

The experiments were carried out in a high density alumina tube to prevent reaction of the tube walls with the released inorganic species. A total gas flow of 4.0 L/min comprising 20 vol.% CO_2 in He or 20 vol.% H_2O in He was maintained in the reactor. A background spectrum was recorded for 20 s and a platinum boat loaded with 100 ± 2 mg of prepared coal (dry basis) was rapidly inserted into the hot zone of the furnace. The sample was heated to the prescribed experimental temperature and the gaseous reaction products flowed to the end of the reactor to be analysed by the coupled MBMS.

Six duplicates of each release measurement were performed with identical sub-samples and the results averaged to determine the experimental variance. The averaged results were analysed qualitatively by examining the released species detected, the shape of the individual release signals, and the relationships between species indicated by the intensity, timing and duration of various