



Release of alkali metal, sulphur and chlorine species during high-temperature gasification and co-gasification of hard coal, refinery residue, and petroleum coke



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HIGHLIGHTS

- Release mechanisms of Na-, K-, S-, and Cl-species for co-gasification of coal and petcoke.
- Effect of the mode of occurrence of fuel constituents on the release.
- Dilution effect explains release trends of NaCl and HCl for all fuel blends.
- Dilution effect explains release of H₂S and COS for blends of hard coal/petroleum coke, but not for hard coal/refinery residue.

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ABSTRACT

Basic investigations using three different fuels as well as fuel blends have been performed in an atmospheric tube furnace at 1500 °C under gasification like conditions. Molecular Beam Mass Spectrometry has been used for on-line analysis of the hot product gas. Main vapour species were H₂S, HCl, KOH, NaCl, COS, and KCl. After quantification of the data the release behaviour was correlated to the fuel composition. The released amount of HCl, NaCl, H₂S and COS of the blends hard coal/petroleum coke can be predicted by calculation. This can be explained by simple dilution effect. The released amount of HCl and NaCl of the blends hard coal/refinery residue can be predicted by calculation, but the released amount of H₂S and COS cannot be predicted.

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1. Introduction

The interest in alternative fuels for power plants is increasing worldwide. Petroleum coke is a competitive, high grade alternative fuel with high caloric value which can be fired alone or blended in coal driven power plants [1,2]. A promising, high efficient utilisation process for petroleum coke is the integrated gasification combined cycle process (IGCC).

The direct use of the raw gasifier syngas requires gas clean-up to prevent downstream parts of the gasifier from several problems, e.g. poisoning of catalysts, inactivation of membranes, fouling and corrosion. An increased plant efficiency and a decreased amount of harmful species, e.g. Na, K, S, and Cl species, can be achieved through hot fuel gas cleaning [3]. This innovative clean-up technique requires a comprehensive knowledge of the release

characteristics of inorganic coal constituents. Previous work provided enhanced knowledge of the effect of key process parameters and of the chemical constitution of coal and biomass on the release of inorganic species from gasification and combustion [4–11]. The release behaviour of petroleum coke was not investigated so far. Furthermore, the results of previous works cannot be used to predict the release of petroleum coke, because the fuel characteristics of petroleum coke are very different from those of coal and biomass, e.g. elemental composition, type of bonding of inorganic matter, and volatile behaviour of the organic and inorganic matter. In general, petroleum coke has a low volatiles content, a low ash content and contains a high amount of sulphur and trace metals [2].

Petroleum coke is a by-product of oil refining processes and commonly produced by thermal treatment of refinery residue [1,2]. Refinery residue was included in this study, because its systematic investigation leads to a more comprehensive understanding of the fate of inorganic species released during thermal utilisation of petroleum coke.

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The objective of this work was to study the influence of the fuel composition on the release of different trace elements during gasification and co-gasification of petroleum coke, refinery residue and hard coal. Molecular Beam Mass Spectrometry was used for direct analysis of the hot gas. Qualitative and quantitative data of the release of inorganic trace elements were provided. The results show the fate of the inorganic species in correlation to the processing step (refinery residue and petroleum coke) as well as process conditions (high-temperature gasification).

2. Experimental

2.1. Fuel preparation and analysis

The fuels under investigation originate from Germany. Samples from hard coal, petroleum coke, and refinery residue were taken and prepared for analysis. The hard coal was deep mined in the Ruhr Valley. Petroleum coke is the carbonisation product of high-boiling hydrocarbons which is commonly produced from residues of petroleum processing, e.g. refinery residue. The refinery residue is a high boiling, mainly solid, waxy material. The samples were dried and ground in a mill and sieved if procurable. The particle size of interest was <100 μm . Hard coal/petroleum coke and hard coal/refinery residue blends with the weight ratios 25/75, 50/50, and 75/25 were mechanically mixed. After this treatment the fuels were stored under dry conditions at room temperature in hermetically sealed plastic bottles. The proximate and chemical analysis of the pure fuels was performed using standard methods. The chemical analysis of the pure fuels was done by the Central Division of chemical analysis of the Forschungszentrum Jülich. The results of the analysis are given in Table 1. The hard coal has the highest content of chlorine, sodium, and potassium as well as aluminium, silicon, iron, calcium, and magnesium. The latter elements are mainly non-volatile. It has been shown recently that 58.9% of the total sulphur content of the German hard coal is bound in organic form [4]. The bulk of chlorine and sodium is leachable in water and ammonium acetate and therefore, highly volatile [5]. Potassium is

mainly bound to aluminosilicates [5]. The petroleum coke shows high sulphur content with 6.89 wt.%, but it is strongly depleted in aluminium, calcium, magnesium, and potassium. The amount of silicon, iron, sodium, and chlorine is higher than for the refinery residue, but still several times lower than for the hard coal. The main part of the sulphur of the petroleum coke is likely bound to aromatic structures, because of the release of highly volatile sulphur and transformation of sulphur to the coke matrix (S_{aromatic} and $S_{\text{aliphatic}}$) during the production process of the petroleum coke. The refinery residue is strongly depleted in nearly all ash forming elements, chlorine, and the alkali metals sodium and potassium, but it has the second highest sulphur content with 1.93 wt.%. Furthermore, the Fe/S and Ca/S molar ratio is very low. Therefore, sulphur must be mainly covalent bound to the organic matrix. The amount of phosphorus is comparably low for all four fuels. In sum, the composition and the mode of occurrence of the elements of the fuels samples differ significantly.

2.2. Experimental setup

The following description of the experimental setup including the high temperature furnace reactor and the Molecular Beam Mass Spectrometer (MBMS) is based on detailed recent publications [6–8]. The experimental setup is depicted in Fig. 1. A more detailed description of the experimental setup has been recently given [6,9–11]. The batch gasification experiments were carried out in an electrical heated furnace. The hot gaseous products were detected online by a Molecular Beam Mass Spectrometer. The experiments were carried out in a high density alumina tube to prevent reactions of the tube walls with the released species. All parts of the reactor downstream the reaction zone were kept at temperature above the condensation point of the Na-, K-, Cl, and S-species of interest. The temperature in the reaction zone was kept at 1500 °C. The end of the alumina reactor was coupled to the orifice of the MBMS device to sample the high temperature gasification products. A typical measurement run consisted of the following steps. At the start of the experiment a platinum sample boat loaded with 100 mg fuel was positioned into the air cooled end of the heated flow channel to prevent the sample from heating and reactions to take place. After this a gas flow of 2.88 Nl/min He and 0.12 Nl/min O₂ corresponding to 96 vol% He and 4 vol% O₂ was fed into the reactor to simulate a gasification like environment. The latter has been shown recently [10,11]. Then a background spectrum was recorded for 20 s. Afterwards the sample boat was carried within 2–3 s into the hot reaction zone (1500 °C). The fuel sample is heated up with about 300–350 K/s. The gaseous products of the gasification experiments were carried away by the gas stream, flowed to the end of the reactor and were finally analysed by MBMS. As shown in Fig. 1, the MBMS consists of three differentially pumped chambers. Gases enter the first chamber through a 0.3 mm diameter orifice. Due to the pressure difference between the corundum reactor ($p = 1.013 \text{ bar}$) and the first chamber ($p = 4 \times 10^{-2} \text{ mbar}$), the gases undergo a supersonic free jet expansion with strong cooling of the gas significantly below room temperature in microseconds. About 10 orifice diameters downstream from the orifice the expansion has attained free molecular flow. Interaction of the molecules of the product gas with residual gas molecules in the vacuum chambers is inhibited by the high vacuum of the chamber system and the big distance between the molecules in the so-called molecular beam. The core of the free jet expansion is extracted by a conical skimmer of 1 mm diameter and directed into the third chamber. There, a hot filament emits electrons with an electron energy of 50 eV and an emission current of 1 mA. Every 10^{-4} – 10^{-3} molecule is ionized by electron impact. After passing the deflector, the ions are filtered in a quadrupole mass analyzer and detected by an off-axis electron multiplier.

Table 1
Results of the proximate and ultimate fuel analysis.

	Hard coal	Petroleum coke	Refinery residue
<i>Proximate analysis (wt.%)</i>			
Water (as rec.)	7.23	1.02	–
Ash (dry)	8.37	0.39	<0.01
<i>Chemical analysis (wt.%)</i>			
C	80.3	85.1	81.9
H	4.72	3.79	10.5
O	4.95	1.62	5.01
N	1.65	1.29	0.304
P	0.025	<0.005	<0.01
S	0.77	6.89	1.93
Cl	0.156	0.015	<0.001
K	0.16	0.0014	<0.004
Na	0.088	0.015	<0.004
Ca	0.43	0.006	<0.004
Mg	0.2	0.0018	<0.004
Fe	0.55	0.045	0.034
Al	0.91	0.006	0.006
Si	1.6	0.018	<0.001
<i>Elemental ratio (molar basis)</i>			
Fe/S	0.41	0.004	0.01
(Ca + Mg)/S	0.79	0.001	<0.004
Na/Cl	0.87	1.54	n.c.
K/Cl	0.93	0.08	n.c.
(Na + K)/Si	0.50	335.92	n.c.
Al/Si	0.59	0.35	>6.25

n.c.: Not calculable.

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