



Ash melting behavior and slag infiltration into alumina refractory simulating co-gasification of coal and biomass



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HIGHLIGHTS

- Ash melting behavior of coal and biomass blends varies strongly from the pure fuels.
- Slag wetting properties on alumina refractory are obviously influenced by blending.
- Slag infiltrates pores and binder matrix, while alumina grains are more resistant.
- Thermochemical modeling may be utilized to describe slag infiltration depth.
- Slags from blends feature higher corrosion potential than those from pure fuels.

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ABSTRACT

In the present study melting behavior of ashes from German brown coal and biomass (wheat straw) as well as from two artificial mixtures of both has been investigated. The four fuel samples were ashed at 450 °C over a period of 26 h. Ash fusion tests and all other measurements have been executed under reducing atmosphere, simulating gasification conditions. The ash melting and wetting properties have been studied for ash cylinders placed onto an alumina refractory at temperatures up to 1600 °C. Optical microscopy and SEM/EDX studies have been performed to analyze the infiltration of slag into the refractory and related progression. For the ash fusion behavior and surface wetting of the refractory clear distinctions from pure ashes have been detected for the blend with 50 wt.% biomass addition due to the formation of eutectics. From optical microscopy and SEM/EDX images of the sections different infiltration properties and mechanisms have been identified. The qualitative infiltration depth and deceleration of slag infiltration by a formation of solid phases have been provided by FactSage™ calculations. In these calculations the contact zone between the two materials has been reconstructed by a stepwise change in the amounts of ash and refractory. The experimental results are very well reflected in this model. Finally, the obtained results suggest low corrosive biomass amounts for co-use in the present gasifier types designed for pure coal.

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1. Introduction

The co-gasification of biomass together with fossil fuels, like coal, intends to reduce the related CO₂ emissions, because of a CO₂ neutral life cycle of biomass [1]. Due to their extensive gas purification, gasification based processes have shown additional environmental advantages compared to combustion ones, i.e. nearly no emissions of sulfur dioxide, heavy metals, and fine dust (PM_{2.5}) [2]. Improvements in the gasification performance of low-grade coals at constant net efficiencies have been attributed

to the biomass addition [1, 3]. From a theoretical point of view biomass addition could be utilized for reduction of ash fusion temperatures. This fact has been accompanied by economic advantages, such as lower consumptions of oxygen, flux additives, and lower thermal stress for the refractory lining. From a practical point of view the reduction of ash fusion temperatures has originated from a higher alkali concentration and has been associated with decreased slag viscosity. Consequently, the corrosion potential of ashes composed of blends from coal and biomass towards metallic and ceramic materials has been found to be raised. In the present study, high-temperature corrosion caused by blends of coal and biomass ashes on ceramic refractories as applied in entrained flow gasifiers has been investigated. Particularly, an admixture of one

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Abbreviations

TOMAC	thermo optical measurement with atmosphere control	HHV	higher heating value
SEM/EDX	scanning electron microscopy with energy dispersive X-ray spectroscopy	LHV	lower heating value
HKN	German brown coal	ar	as received
WS	wheat straw	d	dry
HW--	blended ashes of HKN and WS; '--': biomass fraction by two digits	daf	dry and ash free
AFT	ash fusion temperature	n.d.	not detected
M	moisture	Sinter	sintering temperature
A	ash	DT	deformation temperature
VM	volatile matter	ST	softening temperature
FC	fixed carbon	HT	hemispherical temperature
S _t	total sulfur	FT	flow temperature
		B/A	base to acid ratio

kind of biomass (wheat straw) to a high temperature melting German brown coal (HKN) has been examined. For these samples involving several biomass additions the ash melting behavior has been determined. This has been achieved under simulated gasification conditions (low oxygen partial pressure) in a number of studies, i.e. rather for pure fuels [2,4–10] than for coal samples with gradual biomass addition [11], but without a clear focus on their impact on refractory corrosion. In the present study, a subsequent evaluation and understanding of the slag-related corrosion of an Al₂O₃-based model refractory has been designated as the core purpose of the performed investigation. Finally, it is intended to ascertain a compatible level of biomass addition.

2. Materials and methods

2.1. Materials

2.1.1. Coal, biomass, and their blends

Two kinds of gasification feedstock – a Rhenish brown coal (HKN) and wheat straw pellets (WS) – have been used in this study. HKN is a representative for German low-rank coal. The proximate analysis, ultimate analysis, and the heating values of the raw samples are given in Table 1 (according to the standards DIN 51718–51732 and DIN 51900). Both the raw coal and the biomass samples have been dried at 105 °C until their mass stayed constant. The dried samples have been ground to <2 mm by a cutting mill. Afterwards the samples have been mixed according to the pre-determined biomass ratio. The blended ashes are named by their mass percentage of biomass 10 wt.% (HW10) and 50 wt.% (HW50), which was added before ashing.

Table 1
Proximate analysis, ultimate analysis, and heating values of HKN and WS.

Fuel sample	HKN	WS
<i>Proximate analysis/wt.%</i>		
M (ar)	16.32	6.25
A (d)	4.33	6.88
VM (d)	49.89	75.85
FC (d)	45.78	17.27
<i>Ultimate analysis (daf)/wt.%</i>		
C	67.41	45.87
H	4.42	5.57
N	0.84	0.63
S _t	0.81	0.30
O	22.44	40.84
<i>Heating value/kJ/kg (d)</i>		
HHV	26.10	25.13
LHV	18.14	16.92

2.1.2. Refractory material

For the subsequent refractory tests an alumina refractory ceramic has been produced. It has been consisted of 98 wt.% corundum (Al₂O₃) and 2 wt.% CA-phases (CaO·2Al₂O₃) as binder matrix and has been sintered at 1450 °C. This material has been characterized by an open porosity of 14–15%, which was casted of grains (size < 5 mm) in a cement binding matrix. Ceramic discs of about 50 mm in diameter and 15 mm in height have been used for the tests.

2.2. Methods

2.2.1. Ash preparation

The samples of coal (HKN), the wheat straw (WS), and their mixtures have been ashed at 450 °C under air for 26 h. This ash preparation method according to DIN 51730 is specified for biomasses with more volatile species. Afterwards the resulting ash has been ground to a size ≤ 63 μm.

2.2.2. X-ray fluorescence analysis

The chemical composition of all four ashes has been determined by X-ray fluorescence (XRF) analysis. This has been performed in a Bruker S8 Tiger apparatus equipped with a rhodium radiation source.

2.2.3. Ash fusion tests

The sintering temperature and the four characteristic points of ash fusion – deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT), and flow temperature (FT) – have been estimated in a Leitz heating microscope according to DIN 51730 standard. For this test a cylindrical body with 3 mm in diameter and approximately 3 mm in height has been manufactured from each ash using the ≤63 μm powder. A reducing atmosphere of 65 vol.% CO and 35 vol.% CO₂ has been applied to simulate gasification conditions.

2.2.4. TOMAC measurements

Slag infiltration measurements for the four ashes (HKN, HW10, HW50, and WS) have been performed in reducing atmosphere (5 vol.% H₂ + 95 vol.% Ar) at atmospheric pressure by a thermo-optical measurement system with atmosphere control (abbreviated as TOMAC). An ash amount of about 4 g of the powder (≤63 μm) has been used to produce a cylinder with a diameter of 15 mm and a height of around 10 mm. The tests have been executed in a temperature range of 800–1600 °C with a heating rate of 10 K/min. Cylinder profile photos have been taken every 10 s and the data (width, height, volume, etc.) has been recorded simultaneously during the heating process. The sample has slowly

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