SURFACE TENSION MEASUREMENTS OF MOLTEN COAL ASH SLAGS UNDER OXIDISING AND REDUCING GAS ATMOSPHERE

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ABSTRACT

Detailed knowledge of the surface tension of liquid coal ash slags is important for the design of future coal-fired, CO_2 *- emission-reduced power plants. Those power plant cycles incorporate a gasification step, in which the coals' ashes occur in liquid form. Aiming at the removal of slag particles, ceramic spheres can be introduced into the flow path of the synthesis gas. To characterise the suitability of different black and brown coals for this cleaning technology, surface tension measurements according to the sessile drop method were performed. Exposure of ashes to* O_2 *hardly led to any results as the samples inflated and did not form drops. Varying sulphur content is assumed responsible for this behaviour. In reducing gas atmosphere, the ashes under investigation did form drops so that surface tension and contact angle data could be derived as a function of temperature. The surface tension showed highly negative gradients in the melting temperature regime and slightly rising values up to 1500°C. A correlation between the decrease in surface tension and the way in which the drop forms was found. Gases or inhomogeneities prevailing in the slag led to uneven drop contours and bubble formation at the drops' surfaces. These may have been responsible for the surface tension rise as all three analysis algorithms exhibited difficulties in processing such drop images. In addition, ionic bonding forces in the slag's network are considered to cause the increment of measurement values.*

INTRODUCTION

Motivation Arising from Industrial Application

The necessity of reducing CO_2 emissions requires an increase in efficiency of power plants and their readiness for CO_2 capture and storage (CCS). Integrated Gasification Combined Cycle (IGCC) is able to realise these objectives since it is a highly efficient process and allows separating CO_2 prior to combustion (see [1] and [2]). It incorporates a gasification step into a power plant process consisting of a gas turbine, a heat recovery boiler and a steam turbine. In contrast to common combined cycle plants, IGCCs aim at using coal as fuel. One critical point in this installation is the cleanliness of the gas leaving the coal gasifier and being fed to the gas turbine. Impurities in form of solid or liquid particles as well as gaseous or condensable species may cause damages to equipment downstream of the gasifier, e.g. shift reactor and turbine blades. A schema of the IGCC is shown in Figure 1.

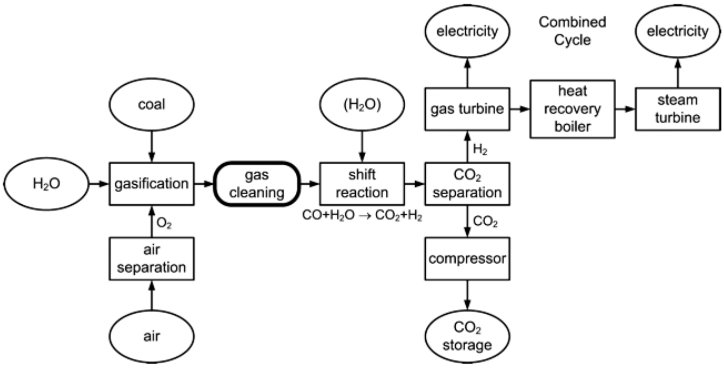

Figure 1: Schematic overview of integrated gasification combined cycle (IGCC)

In order to further augment the performance of IGCCs with entrained flow gasifier, the synthesis gas carrying a load of *molten* ash (slag) particles has to be cleaned at the highest possible temperature directly after gasification. This approach could replace the current water quench installations needed to solidify and to remove slag particles. The envisaged technology aims at depositing the liquid slags on fillings of ceramic spheres that get integrated into the flow path of the synthesis gas. This cleaning technology has already been demonstrated in pressurised coal combustion according to Förster *et al.* [3]. An outline of the proposed design for the gasification process can be seen in Figure 2.

Among other physicochemical properties like viscosity and heat capacity, the slag's surface tension plays a major role in judging the suitability of a coal for the new hot gas cleaning process and therefore limits the choice of fuels. If the relation between a slag's composition and the surface tension is well understood, the use of additives may widen the range of applicable coals.

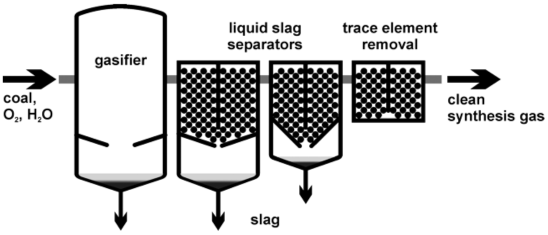

Figure 2: Envisaged gasification technology to remove slag particles

As gas cleaning using ceramic spheres has been proven appropriate in a combustion atmosphere, the difference in behaviour of the slag in a gasification environment should be outlined. Therefore, the ashes under investigation were exposed to O_2 as well as to a gas mixture of 4 vol% H_2 and 96 vol% Ar (ArH_2).

Measurement Fundamentals

The relationship between a liquid's surface contour and its surface tension is expressed by the Young-Laplace Equation (1). In this equation, σ denotes the surface tension, R_1 and R_2 are the principal radii of curvature, $\Delta\rho$ expresses the density difference across the interface (liquid and surrounding gas), g is the gravitational constant and h represents a height coordinate.

$$\sigma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta r \cdot g \cdot h \tag{1}$$

An appropriate surface geometry to apply the Young-Laplace equation to is given by a drop of liquid resting on a plane substrate material (*sessile drop technique*). The principle of energy minimisation leads to the drop contour being sphere-like, so that an assumption of axial symmetry is justified. By taking a digital photo, a computer algorithm can fit the Young-Laplace equation to the drop profile and calculate the surface tension of the corresponding liquid. As small variations in the photographed shape of the drop may cause large discrepancies in the calculated surface tension values, special attention has to be paid to the experimental setup as well as to the image processing algorithm [4].

If the governing equation is properly adapted to the drop contour, the contact angle between liquid and substrate can easily be derived. In contrast to the surface tension – being a characterising material property of the liquid – the contact angle depends upon the substrate material.

METHODOLOGY

Experimental Setup

The ashes under investigation were prepared by exposing different black and brown coals to air at 815°C and 450°C respectively. Aiming at the use of the sessile drop technique, drops of ash slags were generated by melting ash pellets (5 mm in diameter, about 5 mm in height) on different substrate materials in a high temperature furnace at atmospheric pressure. A CCD camera being equipped with a zoom lens was directed into the furnace so that images were recorded in 2°C intervals while heating the sample up to 1500°C at 2°C/min. A light source helped to align the sample inside the furnace at room temperature but could be neglected when the ash started to melt. At those temperatures, the heat radiation was sufficient to provide a clear view of the drop's profile if a welding safety glass was added as optical filter. Figure 3 provides a scheme of the experimental facility.

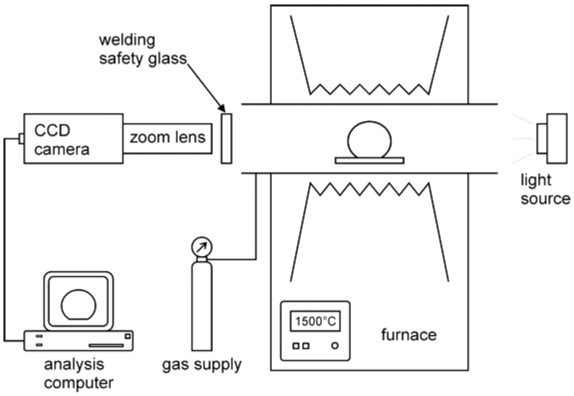

Figure 3: Experimental facility used for surface tension measurements

Analysis Algorithms

All obtained drop images were analysed with the help of three different computer algorithms. Two of those are commercially sold whereas the third one is freely available at [5]. The commercial codes (*SCA20* and *ADSA*) pursue a *classical* approach of numerically integrating the exact Young-Laplace equation prior to the fitting process. Only the non-commercial software package (*LBADSA*) implements an approximation solution of (1) that is adapted to the photographed drop profile by minimising an energy function. Such energy function is also the basis of active contours (snakes, see [6]).

No code outputs a ready-to-use surface tension value, the slag's surface tension σ rather needs to be calculated from the capillary constant *c* or the shape parameter β defined according to Equations (2) and (3). In addition to the nomenclature of Equation (1), *b* denotes the curvature radius at the apex of the drop (axial symmetry). If the density of the surrounding gas is neglected, the slag's density still needs to be known for the surface tension calculation. Up to now, this density was derived by dividing the average sample mass (taken before and after measurement) by the drop volume which is, in turn, one of the algorithms' results.

$$c = \frac{\Delta r \cdot g}{\sigma} \tag{2}$$

$$\beta = \frac{\Delta r \cdot g \cdot b^2}{\sigma} \tag{3}$$

In addition to applying the algorithms to the drop images, the calculation results needed to be checked for physical plausibility. All computer codes showed difficulties in analysing certain drop images which was expressed by negative capillary constants, negative or far too large drop volumes as well as contact angles being orders of magnitudes too high. In some cases, those deficiencies could be traced back to a disturbed drop profile (bubble formation at the surface) whereas the reasons for the software failures were unexplainable in other cases. If physical plausibility was not provided, the algorithm's dataset was fully neglected for the corresponding drop image.

Samples

Table 1 lists the compositions of specimens for which measurement data is given in this article. All *ST-D* samples represent German black coal ashes, *HKR* stands for a German brown coal ash.

Table 1: Ash compositions in equivalent oxides and sulphur (weight percentages)

	ST-D-1	**ST-D-2**	**ST-D-4**	**ST-D-5**	**HKR**
Al_2O_3	26.264	20.028	25.697	23.429	7.558
BaO	0.093	0.212	0.112	0.179	0.223
CaO	2.938	6.996	3.498	3.638	21.828
Fe_2O_3	10.723	9.579	7.578	7.435	11.009
K_2O	2.530	2.168	3.493	3.975	0.253
MgO	2.322	3.980	2.819	2.819	8.789
Mn_2O_3	0.158	0.230	0.124	0.114	0.287
Na_2O	1.038	1.348	0.795	0.997	2.696
SiO_2	43.856	40.433	47.921	49.847	24.602
TiO_2	1.001	0.801	0.951	0.918	0.450
S	1.450	2.230	1.130	1.410	3.910

RESULTS AND DISCUSSION

As the surface tension of NaCl is well documented in [7], this substance was used for reference measurements. Those experiments resulted in a relative measurement error of up to 30% which may be due to the algorithms, the alignment of the sample inside the furnace, the zoom and focus settings and a missing optical distortion correction.

Basically two different drop types were observed when performing surface tension measurements. In a reducing gas atmosphere – where graphite was the substrate material – sphere-like drops comparable to the one in Figure 4a occurred. If (brown coal) ashes were exposed to O_2 on an alloy of platinum and gold (*PtAu5*), images of flat drops could be recorded (see Figure 4b). Cr_2O_3 was also tried as substrate material in oxidising atmosphere but due to its high porosity the slags drained away so that drop formation rarely took place.

Plotting the surface tension of German black coal ash slags (exposed to ArH_2 on graphite) as a function of temperature typically led to large gradients in the melting temperature regime. Nearly constant or slightly rising values in the range of 350 mN/m to 600 mN/m occurred at higher temperatures up to 1500°C. The observation of a surface tension increase as well as the order of magnitude of the measured data is in very good agreement with the findings by Nowok *et al.* [8]. Regarding contact angles, almost constant or gradually decreasing values between 130° and 170° were found. Figure 5 provides the results for the so-called *ST-D-1* German black coal ash. The calculation data of all three algorithms is included in the diagram.

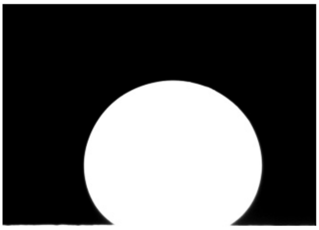

Figure 4a: German black coal ash in ArH_2 on graphite

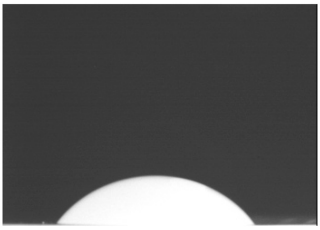

Figure 4b: German brown coal ash in O_2 on PtAu5

In analogy to Figure 5, the findings for three additional German black coal ashes are given in Figures 6 to 8. It should be noted that an exposure of black coal ashes to O_2 only led to inflating sample pellets. Under these circumstances, drop formation (either sphere-like or flat) was hardly ever observed regardless of the substrate material.

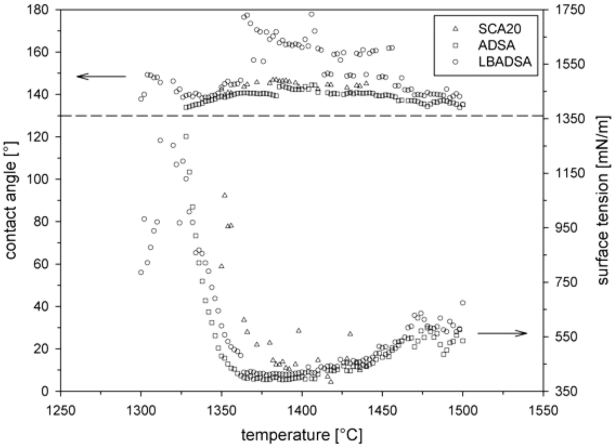

Figure 5: Contact angle and surface tension of ST-D-1 ash in ArH_2 on graphite

In contrast to the results derived from sphere-like drops, Figure 9 gives an example of what contact angle and surface tension data looked like if flat drops were analysed. From Hoorfar and Neumann [4] it is known, that such drop shapes pose problems for algorithms employed in sessile drop measurements. The data points in Figure 9 were gained when a German brown coal ash (*HKR*) was exposed to an oxidising gas atmosphere on the PtAu5 substrate material. Compared to the diagrams 5 to 8, surface tension values scatter a lot (400 mN/m to 950 mN/m) whereas all three algorithms reveal the same decreasing tendency for the contact angle. Because of forming a flat drop, contact angles decline from 60° to 40° and are therefore much lower than for black coal ashes.

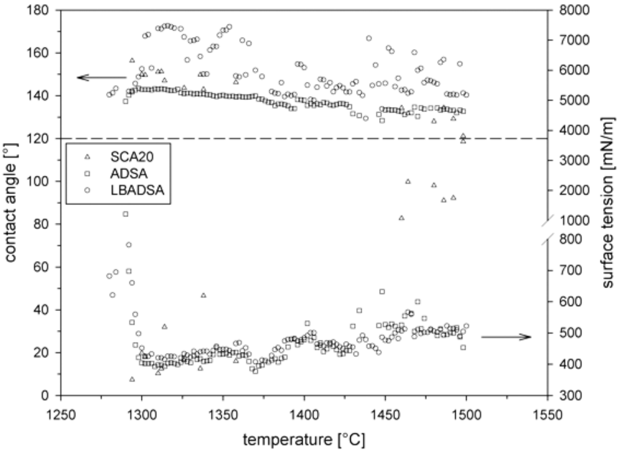

Figure 6: Contact angle and surface tension of ST-D-2 ash in ArH_2 on graphite

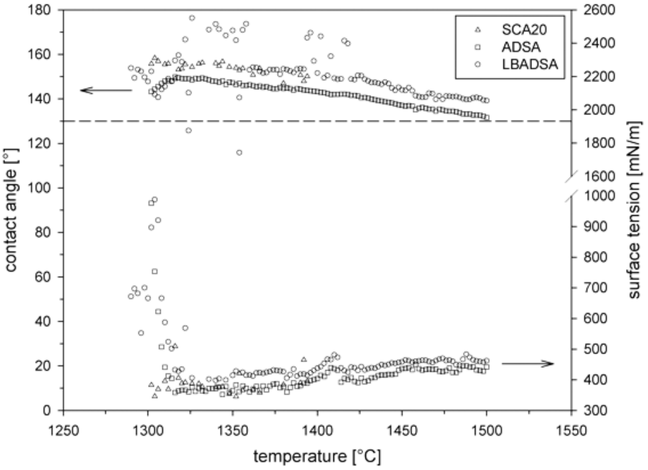

Figure 7: Contact angle and surface tension of ST-D-4 ash in ArH_2 on graphite

With respect to the experiments performed by Nowok *et al.* [8], the decrease of surface tension at low temperatures can be associated with inhomogeneities in the slag. Liquid and solid phases with different chemical compositions may be predominating in the drop throughout the melting temperature interval. It should be noted that Nowok *et al.* only found positive gradients for the surface tension as a function of temperature. The negative gradients given in Figures 5 to 8 must be due to the way the drop is forming from the original ash pellet. As positive gradients were experienced in a few of the current investigations as well, it could be concluded that a rising surface tension at the beginning of drop formation is caused by a growing drop. Such a drop gets more and more sphere-like during heating. If negative gradients occurred, the corresponding images revealed a shrinking ash pellet or drop which slightly flattened in the course of the experiment.

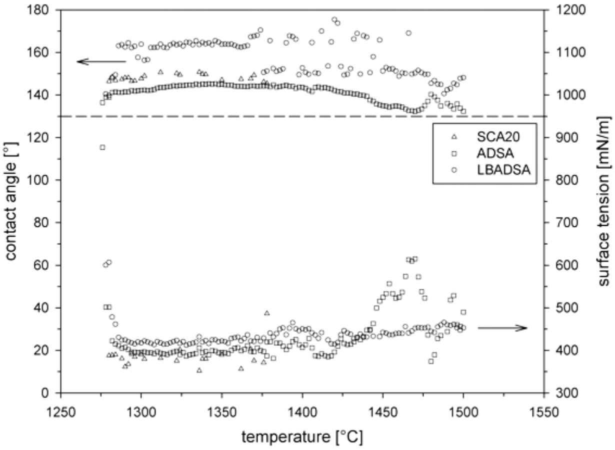

Figure 8: Contact angle and surface tension of ST-D-5 ash in ArH_2 on graphite

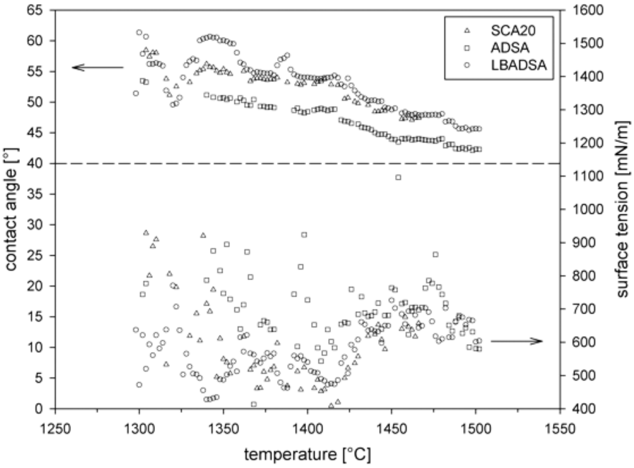

Figure 9: Contact angle and surface tension of HKR ash in O_2 on PtAu5

Contrary to image 4a, black coal drops approaching the last 100°C of the temperature range were often scattered by bubbles at the surface when exposed to ArH_2. Those irregularities led to difficulties for the analysis programs so that the slight increase of surface tension can also be explained by algorithm deficiencies. As no coal ash was pre-melted during sample preparation, gases may still have been dissolved in the slag. According to Mills and Rhine [9], the FeO contained in a slag is thought to react with the graphite substrate in a reducing gas atmosphere. Consequently, CO is formed leading to higher gas content inside the drop that – in turn – increases bubble formation. Even if swellings at the drop profile were not evident, emerging gases may have blown up the drop from inside, resulting in an overestimation of the drop volume by the algorithms. The computed density as well as the surface tension might therefore be underestimated (see Equations (2) and (3)).

With regards to brown coal ashes, corrugated drop profiles were observed when high compressive forces (25 kN) were used to form the sample pellets. Reducing the force to a value of 1 kN yielded much smoother drop contours. This is probably explainable by fewer densely adhering ash clusters that melt inhomogeneously compared to the surrounding grains of looser ash inside the pellet or drop.

If the recorded surface tension rise with temperature is assumed correct, the network-modifying characteristics of Na_2O, K_2O, CaO and MgO cannot be associated directly with a surface tension decrease. Likewise, advancing depolymerisation of the slag seems to be missing. Ionic bonding forces in the slag's modified network could rather cause the increment of surface tension.

The inflation of black coal ash pellets in oxidising atmosphere (involving a lack of measurement data) cannot be explained yet. But a correlation between an ash's sulphur content and its tendency towards inflation in O_2 seems to exist (see Table 1). When comparing the compositions of black coal ashes to the brown coal ash, an obvious difference is the sulphur content. The highest sulphur amount contained in a black coal ash is 2.23 w% whereas the brown coal ash shows a sulphur percentage of 3.91 w%. This observation is in accordance with the brown coal ash forming a (flat) drop in O_2 without any inflation. In addition, melting sulphur-depleted (< 1.824 w%) biomass ashes in air also led to a blowing up of the sample pellet (see [10]).

CONCLUSIONS

It has been shown that surface tension measurements of coal ash slags can be realised using the sessile drop technique. The presented measurement facility in combination with the three employed analysis algorithms is capable of generating surface tension data that is in accordance with literature. Applying three different algorithms to the drop images assures the correctness of the experimental results from a numeric point of view. Nevertheless, the relative error found during reference measurements might be too high to resolve the influences of varying amounts of individual chemical components on the slag's surface tension.

The effects of ionic bonding forces in the slag's network should not be neglected when seeking explanations for a surface tension rise with temperature. Further research has to be done in this field. Low sulphur contents considerably promote an inflation of the sample pellet in oxidising atmosphere. The exact mechanisms leading to drop formation or blowing up of ashes in dependence of the surrounding gas atmosphere must be studied in further experiments.

In order to reduce the measurement error, slags' densities would better be determined using an independent technique. A multiplication of errors can thus be avoided. To further reduce difficulties in the image analysis process, a pre-melting of the ashes should be considered aiming at bubble-free drop contours.

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