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Research article

Prediction of ash fusion behavior from coal ash composition for entrained-flow gasification

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ABSTRACT

In entrained-flow gasification, solid fuel is brought in contact with oxygen and steam, yielding slagging conditions at temperatures of 1250–1800 °C. The process temperature cannot be chosen freely but is determined by the melting behavior of the coal ash. By blending different coals and fluxing agents, the ash fusion temperature can be lowered allowing operation at a lower reactor temperature and savings in oxygen. Since ash fusion behavior is not measurable online, it can be beneficial to use a quickly measured coal ash composition and estimate the ash fusion behavior instantly.

In this work, > 300 different coal samples from all over the world were investigated. This includes ash compositions determined from X-ray fluorescence (XRF) analysis and standard ash fusion behavior under reducing and oxidizing conditions. In a systematic approach, the ash components were limited to the most significant ones to optimize calculation time. The software ChemApp was used to calculate thermodynamic equilibrium based on FToxid and FactPS databases. The obtained results involve the temperatures at which 10 to 100% of the ash melt are liquid slag calculated in 10%-pts steps. According to the applied atmosphere, the obtained results have been statistically correlated to the experimentally determined fusion temperatures. In parallel, a neural network approach was tested to accomplish the same task.

It was found that the hemispherical temperature correlates best to a liquid slag fraction of 85.0 wt% under reducing and 80.1 wt% under oxidizing conditions. The thermodynamic model is able to predict the hemispherical temperature under reducing conditions for 32% of the data while exclusion criteria defining the validity range have been formulated.

The neural network model shows in average a higher accuracy of predicting ash fusion behavior from ash composition covering also temperatures of initial deformation and fluidity and appears as a suitable alternative to the thermodynamic calculation if sufficient data are available (i.e. covering the coal ash composition range of interest).

1. Introduction

Entrained-flow gasification is currently the most popular choice among the different coal gasification technologies due to its ability to process a wide variety of coal feeds and its high syngas yield [1]. Entrained-flow gasifiers are usually operated at high temperature conditions, primarily maintained at the cost of oxygen, thus making it an important economic constraint. Hence, predicting the temperature which ensures smooth slag tapping makes operation more robust and reliable. Moreover, the ash fusion behavior is conventionally described by the temperature of initial deformation (IDT), spherical temperature (ST), hemispherical temperature (HT) and ash fluid temperature (FT) [2]. In an industrial framework, these ash fusion temperatures (AFTs) are measured with high frequency replacing costly and time consuming slag viscosity measurements. Hence, the gasifier operation fluctuation range for a certain coal slag is estimated from the difference between the respective AFTs. While the FT represents the minimum temperature for steady operation, the HT can be linked to the temperature of critical viscosity as discussed elsewhere [1,42,43]. Studies show that these AFTs depend on the chemical composition of the ash and the gas atmosphere [3]. The coal ash composition can be controlled by blending different coal types and/or adding fluxing agents making it possible to maintain a suitable window of gasifier operating temperature.

Coal ash is a complex mixture of mineral matters majorly consisting of Al, Ca, Fe and Si, and other minor and trace elements [1]. Many investigations have been carried out to find an empirical or statistical correlation between the AFTs and chemical composition. Winegartner and Rhodes [4] studied correlations based on regression analysis using

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certain slagging indices such as silica value, percent base etc. which was later continued by Seggiani [5], who extended those results for a wider variety of coal ashes and biomass ash. Similar work has been done for some New Zealand coals where multiple and stepwise regression analysis are evaluated in addition to ternary equilibrium phase diagrams [2]. Lloyd et al. conducted a purely statistical analysis to generate correlations using multiple linear regressions [6]. Instead of assuming a mixture of discrete oxides, "cross-terms" are used for the correlation considering the interactions between the ash components [6,7]. Kucukbayrak et al. investigated Turkish lignites using regression analysis, where the relation between ash compositions, based on various slagging indices and the fusion temperature (only HT) is studied [8]. Later, Özbayoglu et al. show that nonlinear correlations give better results by comparing it with the linear counterparts on a case study using Turkish lignites [9]. Coal properties such as Hardgrove grindability index, specific gravity, ash content and mineral matter content are included in the correlations in addition to the ash composition and slagging indices.

As an alternative to focusing on statistical and empirical studies, the interaction between the elements in coal ash are analyzed using equilibrium phase diagrams by Huggins et al. [10]. A qualitative correlation between AFTs and the liquidus temperature is established in that work and it is claimed that the silica-to-alumina ratio is one of the most important parameters governing AFTs [10–12]. Later, Rhinehart and Attar explored the use of thermodynamic approximations, but their model fails to simulate the complex phase equilibrium thermodynamics of slag systems [13]. Further studies have been done using thermodynamic modeling of phase equilibria. Jak shows that AFTs predicted by using thermodynamic calculations are more reliable than empirical or statistical correlations and makes a case for the use of F*A*C*T (a FactSage predecessor) [14]. A similar proprietary software, MTDATA, is employed by Goni et al. to study the combustion performance of coal blends for Chilean coals and indicates that it is very different from the average of the constituting pure coals [15]. FactSage is used in later studies [16].

Recent studies claim improved results for linking thermomechanical analysis (TMA) and liquid slag phase formation calculated by thermodynamic models owing to its better accuracy (± 10 °C) as compared to standard ash fusion temperature tests [17]. Characterization using TMA is based on analyzing shrinkage during different stages of the fusion process. Correlations between the results from TMA and ash fusion tests are established and conclusions are drawn to determine IDT and FT. Another work by the same authors, focuses more on the influence of the SiO_2/Al_2O_3 ratio [18]. Temperatures at different slag liquid fractions are compared with the shrinkage trace and a correlation between the onset temperature of sintering and T_{10}, i.e. temperature at which a liquid slag fraction of 10% is established.

Recently, multivariable regression and adaptive neurofuzzy inference system (ANFIS) was applied by Karimi et al. on over 1000 samples of US coals and presents a nonlinear model for AFT predictions [19]. Other black-box modeling techniques which have been employed to derive correlations between the ash composition and AFTs to yield superior results include support vector machines (SVMs) [20] and artificial neural networks (ANNs). A back propagation neural network model with seven inputs and one hidden layer with four nodes is used by Yin et al. to predict ST [21]. Similar work is done by Miao et al. on Chinese coals, where three models with different numbers of inputs are compared and the one with five inputs is shown to give the best results [22].

In summary, most of the studies make only a qualitative assessment of the AFTs and/or are done using coals of similar origin [23]. Studies which included a diverse database were either not successful or ended up with extremely complex correlations [24]. This is the main reason why most of the later studies focus on a particular coalfield or make use of synthetic ash samples, which is inappropriate since the melting behavior is dictated by the initial phases present. Hence, it is an improvement to develop a model which can accommodate a diverse coal feedstock.

The aim of this study is to devise a robust model based on laboratory ash fusion tests. The resulting model is expected to have an acceptable accuracy in an industrial environment for operation and control of entrained-flow slagging gasifiers with few restrictions on the coal feed types. In this respect, various modeling approaches are investigated, namely a thermodynamic approach using the ChemApp subroutine which implements FactSage calculations, and a purely data driven approach using artificial neural networks.

2. Experimental

2.1. Test method for fusibility of ash

The ash fusion tests performed before 1998, follow the German standard procedure (DIN 51730-1984). The test involves controlled heating of a cylinder shaped ash mould of specific dimensions and recording of the following critical temperatures.

1. Initial deformation temperature (IDT)
2. Hemispherical temperature (HT)
3. Fluid temperature (FT)

A Pt/Pt-Rh thermocouple is used to accurately measure the temperature at different stages of ash fusion. As for the tests performed in later years, DIN 51730-1998 and DIN 51730-2007 are followed, where the softening temperature (ST) is also reported, similar to the one mentioned in ASTM D1857-2010. However, since the majority of the data are recorded without a spherical temperature, it is excluded from this study.

2.1.1. Test atmosphere

The gas atmosphere has a considerable influence on the AFTs, making it necessary to perform the experiment in two distinct test atmospheres, namely oxidizing and reducing. Generally, the reaction or post reaction zone in the gasifier is mainly pertaining to a reducing environment. However, there is an oxidizing environment at the flame zone and the changes in the ash fusion behavior in such conditions need to be determined since in practice all oxidizing stages (i.e. of iron) occur in the slag. The reducing atmosphere test takes place with 55% to 65% CO and balance CO_2. An atmosphere containing mostly air is maintained for the oxidizing atmosphere test. In general, the AFTs in an oxidizing atmosphere test are higher. This can be attributed to the fact that ferrous iron, present in reducing conditions, has more affinity to flux clay minerals than ferric iron, present in oxidizing conditions [1].

2.2. Determination of ash composition

X-Ray fluorescence (XRF) analysis is performed to identify the chemical composition of ash following the German standard (DIN 51729-10). The elemental concentrations of Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, and Fe are measured down to the ppm levels in an ash sample. Due to its simple, quick and accurate nature, XRF is often used in this respect [1].

3. Methodology

3.1. Sample selection

Data for over 350 coal ash samples from Asia, Australia, America and Africa are obtained from an internal database covering all ranks from lignite to anthracite with most samples belonging to the lignite A to high-volatile bituminous coal range. This database provides ash fusion tests and XRF analysis results recorded over a span of five decades. Out of 369 samples available for each reducing and oxidizing atmosphere, only the samples which did not exceed the measurement range