Chemical Engineering Science 175 (2018) 278–285

Contents lists available at ScienceDirect

Chemical Engineering Science

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

A new method of estimating the liquidus temperature of coal ash slag using ash composition

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HIGHLIGHTS

- Liquidus temperature (T_{liq}) is studied by molecular and thermodynamic simulation.
- A correlation between T_{liq} and I_a is proposed and yields predictions with satisfactory results.
- T_{liq} is predicted by linear relation using ash composition for the first time.
- SiO_2/Al_2O_3 ratio, is a key factor on T_{liq} of coal ash.

ARTICLE INFO

Article history:
Received 23 May 2017
Received in revised form 17 September 2017
Accepted 2 October 2017
Available online 4 October 2017

Keywords:
Coal ash slag
Liquidus temperature
Ionic potential
Potential energy

ABSTRACT

The liquidus temperature (T_{liq}) of coal ash is above the temperature at which the last solid phase disappeared. T_{liq} of coal ash slag is widely used to evaluate ash fusion and flow behaviors. The method of determining the liquidus temperature is based on phase equilibrium, the activation energy of viscous flow and chemical composition models. In this work, a linear relation between average molar ionic potential (I_a) and potential energy (P_e) as well as T_{liq} and potential energy is supported by molecular dynamics simulations. We correlated T_{liq} (derived from thermodynamic equilibrium calculation) and the molar ionic potential of the chemical composition. The linear relation between coal ash composition and the T_{liq} is established for the first time, with $T_{liq} = (170.43 - 3.1457 \times I_a) \times S/A + 15.725 \times I_a + 360.78$ (DE < 40 °C). The SiO_2/Al_2O_3 ratio (simplified as S/A, calculated by mass basis), a key factor in T_{liq}, is also introduced into the equation. The relation supplies a convenient method to determine T_{liq} of multicomponent silicates, specifically using the coal ash based ionic potential of chemical composition.

1. Introduction

China has relied heavily on coal due to its lack of oil and natural gas for a long time. This will not change until renewable sources are well developed. The increasing utilization of coal results in several issues of serious environmental concern, including the increased emissions of greenhouse gases and various pollutants. However, coal gasification is regarded as the first step for clean coal utilization, including the integrated gasification combined cycle (IGCC) which has been considered as a promising technology and coal to chemicals (Minchener, 2005; Silakhori et al., 2014). The entrained-flow gasifier is the preferred gasification technique for coal utilization due to its high efficiency and environmental friendliness (Ma et al., 2014). The entrained flow gasifiers operate with feed and blast in co-current flow. The residence time in this process is short (a few second), which means huge treatment capacity. Moreover, the entrained-flow gasifier is operated at a high temperature (>1400 °C) and pressure (20–30 atm), (Buhre et al., 2005) which produces the highest quality synthesis gas because of the low methane content (Higman and Burgt, 2008). Besides, less waste is produced compared to fixed bed and fluidized bed gasifiers. In the entrained gasifier, organic materials nearly 100% transform into syn-gas (Guo et al., 2007), and most minerals in coal exposed to the high-temperature conditions become melting slag

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https://doi.org/10.1016/j.ces.2017.10.002
0009-2509/

Notation

S/A	the ratio of silica to Alumina at mass basis
T_{liq}	liquidus temperature, °C
I_a	ionic potential, nm^{-1}
Pe	potential energy, kcal/mol
T_{PL}	predicted temperature by the empirical equation, °C
Q/R	activation energy, kJ/mol
g_i	the mass fraction of the ith component
x_i	the molar fraction of the ith component
A_i	the *ith* component partial-specific T_{liq}
ΔG_i^f	the free energy of formation of ith component
$\Delta T/x_2$	the slope of the liquidus line
L_f	the heat of the fusion of the pure solvent
T_f	the eutectic temperature
R	gas constant
K	equilibrium constant
A	pre exponential factor
Ea	activation energy
n	the number of components in the melts

Greek letters

α	the constant fitted by the experimental data
β	the constant fitted by the experimental data

(Song et al., 2009). Slag tapping from an entrained-flow gasifier is smooth only when the slag is suitably fluid. Hence, from the perspective of coal chemistry, the fluidity of the slag is the key factor for running the entrained-flow gasifier.

The liquidus temperature (T_{liq}) of coal ash is above the temperature at which the last solid phase disappeared (Jak et al., 1998), which mainly can be classified as aluminosilicates. It is well know that the ash fusion temperatures and slag viscosity are widely used to describe the slag fluidity, however, the measurements of them are complex and the repeatability and veracity are always not good (Seggiani and Pannocchia, 2003). Thus, T_{liq} is applied to predict the ash fusion temperature and temperature of critical viscosity (Jak, 2002; Song et al., 2011). Therefore, a convenient way to determine the liquidus temperature based on the chemical composition is required. Although, some thermodynamic packages were been developed to calculate the compositions of slags including coal ash and these parameters including liquidus temperature, all of them are not free. Hence, the aim of this work is to provide an alternative mathematical tool to calculate T_{liq} in four component slag system without thermodynamic calculations. The main components of coal ash and slag are silicates, aluminosilicates and quartz, which is close to glass and ceramic. Following the tradition in glass research, the chemical composition of coal ash is also expressed in terms of oxides such as SiO_2, Al_2O_3, CaO, Fe_2O_3, MgO, K_2O, Na_2O and so on, these oxides can be divided into acidic oxides (SiO_2 and Al_2O_3) and basic oxides (Fe_2O_3, CaO, K_2O and Na_2O) (Ashizawa et al., 1997). The ash from coal tends to melt at high temperature and forms a homogeneous liquid. The liquidus temperature of coal ash is related to their chemical compositions (Küçükbayrak et al., 1993). The existing method of determining the liquidus temperature of glass is obtained by its phase equilibrium, the activation energy of viscous flow or an empirical equation.

1.1. Phase equilibrium

The procedure of obtaining a phase diagram includes high temperature equilibration of slag, rapid quenching and chemical analysis of the phases. This method is used to study the system of Al_2O_3-CaO-SiO_2 and CaO-SiO_2-Al_2O_3-MgO (Gutt and Russell, 1977; Haccuria et al., 2016). The Thermodynamic modelling of the system Al_2O_3-SiO_2-CaO-FeO-Fe_2O_3 was embedded in the database of FactSage and was applied to characterize coal ash slags and predict the flux requirements (Jak et al., 1998, 2007). FactSage is able to predict T_{liq} from the chemical composition of coal by using the algorithm of minimizing activation energy and obtaining the fraction of every phase (Bale et al., 2009).

1.2. Activation energy

The activation energy of viscous flow to a certain degree reflects the intensity of inter-ionic bonds to be broken to form a homogeneous liquid during heating (Bockris et al., 1955). The second derivative of the curve of activation energy for viscous flow and temperature shows a break, which is the liquidus temperature (Seetharaman et al., 2000). Activation energy increases sharply in the vicinity of the liquidus temperature and remains constant above the liquidus temperature. A discontinuity in the second derivative appears at the liquidus temperature. Thus, the liquidus temperature can be obtained by the following equation in the derivative form and the value of the second derivative changes to zero at the liquidus temperature.

$$\frac{1}{R}\frac{\partial^2 Q}{\partial T^2} = \frac{\partial\left(\frac{\partial \ln \eta}{\partial \frac{1}{T}}\right)}{\partial T^2}, \tag{1}$$

where η is the viscosity of the flow, R is the gas constant, T is temperature and Q/R is the activation energy.

1.3. Empirical equations

The empirical equation basing on chemical composition includes the Kim-Hrma and Jantzen model.

1.3.1. Kim-Hrma model

Kim and Hrma (1994) presented a multi-component expression, which is a first order polynomial expansion of T_{liq} in chemical composition

$$T_{liq} = \alpha + \beta\sum_{i=1}^{n} g_i \tag{2}$$

,where g_i stands for the mass fraction of the *ith* component. α and β are constants fitted by the experimental data and n is the number of selected components (usually n is less than the total number of the components in the melt). When the composition of glasses is within the primary phase field of spinel, this equation could be simplified to:

$$T_{liq} = \sum_{i=1}^{n} A_i g_i \tag{3}$$

In Eq. (3), A_i is the ith component partial-specific T_{liq} and i = Al_2O_3, CaO, Fe_2O_3, SiO_2, and "other" oxides, n is the number of components in the melt. The value of R^2 of this model is 0.64 within glass composition range (Vienna et al., 2001).