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Fate of inorganic matter in entrained-flow slagging gasifiers: Fuel characterization

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ABSTRACT

This study is the first of a three-part research program which involves fuel characterization, testing in a 1 MW_{th} gasifier, and computational fluid dynamics (CFD) modeling for entrained-flow slagging gasification. Focus is on the behaviour of inorganic fuel components since the end goal is to develop a CFD model which includes inorganic matter transformations. Initially, four coals were selected for this program and one limestone was also chosen to act as a fluxing agent. Fuel properties related to ash particle formation, gas-particle transport, particle sticking, slag flow and slag-refractory interaction are provided with prioritization based on their potential application for screening of potential fuels, ensuring proper gasifier operation, gasifier design and/or CFD modeling. The selection of one or multiple experimental and/or modeling techniques is justified and applied to determine each relevant property. Of the four coals tested, one was deemed unsuitable based on initial screening tests. Two of the three remaining coals require fluxing for proper gasifier operation. Design tests showed that alumina is preferred over silicon carbide and alumina–chromia (with 30 wt.% chromia) for use as refractory material with the selected fuels. Characterization for CFD modeling is also discussed with results provided as supplementary data.

1. Introduction

Fuel and product flexibility have always been some of gasification's selling points. More recently, concerns over reducing emissions in industry and the power sector have renewed interest in this technology. In comparison with coal combustion systems, the advantages of coal gasification include high efficiency, suitability for carbon capture, relatively easy removal of sulfur oxides, nitrogen oxides and trace contaminants, and low water consumption [1]. Most of the successful high throughput coal gasifiers developed in the past 60 years are of the entrained-flow slagging type [2]. This study is the first of a three-part research program which involves fuel characterization, testing in a 1 MW_{th} gasifier, and computational fluid dynamics (CFD) modeling for entrained-flow slagging gasification. Here, the focus is on the behaviour of inorganic fuel components as this is still ill-understood even though it can be the determining factor in designing and operating entrained-flow gasifiers [3]. For instance, fouling or plugging of the gasifier by inorganic matter is a major concern. Refractory wear, which is largely dictated by interaction with inorganic matter, leads to poor plant availability. Also, the distribution of potentially toxic inorganic matter in fly ash and slag is an environmental concern. Four coals were selected for this program. One limestone was also selected to act as a fluxing agent to reduce slag viscosity if required for operation with any of the coals. F1 fuel is a lignite coal from Saskatchewan, Canada. F2 fuel is a sub-bituminous coal from Alberta, Canada. F3 fuel is a beneficiated version of F2 with reduced ash content. F4 fuel is another sub-bituminous coal from Alberta, Canada. L1 is a limestone from a Canadian power company. The characterization of the fuels is described in this study. Some bench-scale tests and models which do not relate to inorganic matter transformations are not included. For example, thermogravimetric analysis of the fuels can be used to optimize gasifier performance based on fuel reactivity, but is not directly related to inorganic matter transformations and is therefore not included.

Selection of fuel analyses depends on the intended application of the results: (i) screening of potential fuels; (ii) proper gasifier operation; (iii) gasifier design; and/or (iv) CFD modeling. Unless an accurate CFD model is readily available, fuel screening, gasifier operation and gasifier design will only make use of a subset of the tests required for CFD modeling. A comprehensive CFD model must consider all relevant inorganic matter phenomena, including ash particle formation, gas-particle transport, particle sticking, slag flow and slag-refractory interaction. The properties involved are listed in Table 1 along with their associated phenomena and experimental tests and models used to determine them. The likely applications of each property are given in the last column of Table 1. Since the end goal of this research program is to develop a CFD model which includes inorganic matter transformations, a test or model for each property must be used. In Table 1, underlined experimental and modeling techniques were applied in this study. Although modeling techniques generally require less time and resources,

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Table 1
Fuel properties involved in inorganic matter phenomena.

Property	Phenomena[a]	Experimental	Model	Applications[b]
fuel composition	1	ultimate analysis, proximate analysis, calorimetry	N/A	S, O, D, M
fuel form	1	coal petrography, CCSEM	ultimate/proximate models	M
fuel particle size	1, 2, 3	sieving, laser diffraction, CCSEM	N/A	M
inorganic composition	1, 2, 3, 4, 5	XRF, XRD, CCSEM	N/A	S, O, D, M
inorganic form	1	XRD, HT-XRD	FactSage	M
inorganic particle size	1, 2, 3	CCSEM	N/A	M
fuel-inorganic associations	1	CCSEM, chemical fractionation	N/A	M
ash melting temperatures	3, 4	AFT	composition models, FactSage	S, O, D, M
slag viscosity	3, 4, 5	rheology	composition models	O, D, M
slag-refractory reactivity	4, 5	cup tests, sessile drop	FactSage, numerical diffusion models	D, M
slag interfacial tension	3, 5	sessile drop	composition models	M
inorganic density	1, 2, 3, 4, 5	pycnometry, buoyancy, dilatometer, sessile drop	composition models	M
inorganic heat capacity	1, 4, 5	calorimetry	composition models, FactSage	M
inorganic heat conductivity	1, 4, 5	various techniques with heating and temperature measurements	temperature models, thermal diffusivity models	M
inorganic emissivity	1, 4	FTIR	constant value from literature	M

a) Phenomena are coded as (1) ash particle formation, (2) gas-particle transport, (3) particle sticking, (4) slag flow and (5) slag-refractory interaction.
b) Applications are coded as (S) screening, (O) operation, (D) design and (M) CFD modeling.

experimental techniques are preferred where model accuracies are poor and/or the property is very important for gasifier design and/or operation (e.g. slag viscosity). The reasoning for the selection of each technique or model used is included in the discussion. Properties related to screening were determined first, followed by the properties related to operation, design, and finally CFD modeling. Results pertaining to screening, operation and design are supplied directly in the paper. For brevity's sake, results which only pertain to CFD modeling are provided as supplementary information. However, the methods and importance of all results are discussed with references which demonstrate the use of each property in CFD modeling.

2. Experimental

2.1. FactSage modeling

FactSage software predicts equilibrium solid–liquid–gas phases and compositions based on Gibbs free energy minimization [4]. Gibbs free energy is calculated from optimized models with parameters based on empirical data with various compositions, temperatures and pressures. This information is contained within compound and solution databases which must be carefully selected prior to equilibrium calculations. The FactSage 6.2 *Equilib* module was utilized with the FACT53 and FToxid databases. Oxide components representing less than 1 wt.% for all samples were excluded. Sulphur is not included in the analyses as it is expected to completely devolatilize at the temperatures of interest. All gas and solid compounds were considered. For compounds found in both the FACT53 and FToxid databases, preference was given to the FToxid database to have better thermodynamic consistency with the solution phases data. Pure liquid Fe was also considered. All solution phases were considered. However, only the SLAGA solution was allowed to form multiple immiscible phases. Total pressure was specified at 1 atm and, unless otherwise noted, the activity of O_2 in the gas phase was set to 10^{-9} which is similar to what is typically encountered near the walls in a gasifier [5].

2.2. Slag viscosity measurements

Artificial ashes were prepared by mixing laboratory or analytical grade Al_2O_3, $CaCO_3$, Fe_2O_3, K_2CO_3, $MgCO_3$, Na_2CO_3, SiO_2 and TiO_2 powders. Slag viscosity measurements were performed in a Carbolite 3 liter BLF1700 furnace with a Brookfield RVDV-IIIU rheometer. Both the furnace and the rheometer were connected to a personal computer for external control and data collection. Samples were placed in a molybdenum crucible. The crucible was placed in a custom-built alumina chamber within the furnace for gas atmosphere control and spill protection. A type B thermocouple was inserted into the chamber to monitor the sample temperature. Argon flowed at 0.4 dm^3/min (STP) into the alumina chamber and a graphite sleeve was placed around the molybdenum crucible to consume trace oxygen. Mössbauer spectroscopy of a slag sample after viscosity measurements indicated that the iron components were in the ferrous state, confirming the reducing nature of the experimental conditions. A molybdenum spindle was attached to the rheometer and lowered until it sufficiently penetrated into the slag sample for the purpose of accurate viscosity measurement. It was rotated while measuring the torque required for spindle rotation at a given angular velocity. The operation of the rheometer was validated with the National Institute of Standards and Technology's (NIST, USA) standard reference material 717a. Artificial ash samples were first heated to 1225 °C and left overnight for equilibration. They were then heated to 1525–1600 °C. Measurements were conducted at incremental temperature reduction steps. The cooling step for each set of measurements included a reduction in temperature of 25 °C with a minimum of 25-min to allow the temperature and compositions to equilibrate inside the crucible. At each temperature, viscosity was measured multiple times at various rotational speeds to detect non-Newtonian behaviour [6]. The final measured value was taken at approximately 80–90% of the rheometer's maximum torque.

2.3. Cup tests for slag-refractory reactivity

Approximately 0.5 g of ash was placed on 1200 mm^2 pieces of refractory. The crucible was placed in a custom-built alumina chamber within a Carbolite 3 liter BLF1700 furnace for gas atmosphere control and spill protection. A type B thermocouple was inserted into the chamber to monitor the sample temperature. Argon was fed at 0.4 dm^3/min and small pieces of graphite were placed near the samples to consume any trace oxygen. Mössbauer spectroscopy of a slag sample after testing indicated that all the iron atoms are in the ferrous state, confirming the reducing nature of the experimental conditions. Samples were either heated to 1250 or 1500 °C at approximately 3 °C/min. They were then held at the temperature of interest for 4 h and afterwards, the samples were cooled at approximately 5 °C/min to 1100 °C and then slowly cooled to room temperature. The slag-covered refractory was cross-sectioned using a Buhler ISOMET low-speed saw with a 0.4 mm 15LC wafering blade. The samples were mounted with carbon tape on an aluminum holder. Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) analysis was done using a Hitachi 3400 N VP-SEM with Oxford Instruments Si(Li) Pentafet Plus 10 mm^2 detector. The system was operated at a reduced vacuum of 30 Pa to reduce charging from the uncoated samples. Imaging and analyses were