The fate of ash in gasifiers of various flow regimes

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Abstract—The reliability and performance of gasifiers depends heavily on the fate of ash. Ash fusion temperature (AFT) tests have been devised to quickly and easily predict ash slugging/fouling in combustion and gasification systems. However, these tests are subjective and do not account for the individual fuel particle chemistry. The fate of ash in fixed-bed, fluid-bed and entrained-flow gasifiers is discussed with particular issues relating to the conditions in each type of gasifier. In some gasification regimes, transformation of ash into liquid slag should be avoided to prevent agglomeration and blockage. In other gasification regimes, formation of liquid slag with low viscosity is required. Strategies utilizing scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDX), x-ray diffraction (XRD), slag viscosity measurements and FactSage modeling to predict the behaviour of ash are presented. FactSage modeling is a fast and easy technique, but does not apply to non-equilibrium systems. A case study of a western Canada lignite ash is given. Based on preliminary FactSage modeling and viscosity measurement results with this ash, suggested operating temperatures are given for each gasification regime.

INTRODUCTION

Gasification is a chemical reaction by which a carbonaceous fuel is partially oxidized to form synthesis gas, a mixture of gases mainly comprised of CO and H₂. The carbonaceous fuel may be coal, petroleum coke, natural gas, biomass, waste. Synthesis gas is used as an intermediate building block for the formation of chemical products (e.g. methanol and ammonia), liquid fuel production via Fischer-Tropsch synthesis, synthetic natural gas production, hydrogen production and electricity generation. A single gasification plant may utilize various fuels while aiming to use synthesis gas for a variety of applications. The fuels used for gasification are often divided into four components: fixed carbon, volatiles, moisture and ash. The first three components react, via partial oxidation to form synthesis gas. The ash component of the fuel will be in solid or liquid state, depending on the reaction temperatures, and must be removed from the gasifier. Commercial gasifiers operate in one of three regimes; fixed bed (also called moving-bed, Figure 1), fluidized-bed (Figure 2), or entrained-flow (Figure 3).
Figure 1. Fixed-bed gasifier with temperature profile.¹

Figure 2. Fluidized-bed gasifier with temperature profile.¹

Figure 3. Entrained-flow gasifier with temperature profile.¹
In fixed-bed gasifiers, a bed of solid fuel slowly moves downward by gravity as it reacts with a blast (steam, oxygen and/or air) which may be flowing counter- or co-currently to the bed movement. The bed has sequential zones, from top to bottom, of drying and devolatilization, gasification, and combustion. The hottest zone is the combustion zone which typically reaches 1300°C in dry ash gasifiers and 1500-1800°C in slagging gasifiers. In fluidized-bed gasifiers, the blast is used to fluidize the fuel bed resulting in very good heat and mass transfer. These gasifiers are generally limited to temperatures below the ash softening temperature since agglomeration of the ash will disrupt fluidization. They typically operate at 800-1050°C. In entrained-flow gasifiers, the fuel is entrained by the blast and has a very short residence time, in the order of a few seconds. High temperatures are required to ensure good fuel conversion, and to convert the ash to slag which sticks to the walls and flows out the bottom of the gasifier. They typically operate at 1200-1600°C.

In all types of gasifiers the ash thermal properties are important to operability. ASTM D1857 is a standard method to determine ash fusion temperatures (AFTs): the initial deformation temperature, softening temperature, hemispherical temperature and fluid temperature. These are used to assess the melting and slagging properties of a given ash. Hence, they are used to predict the likelihood of agglomeration in fixed-bed dry-bottom and fluidized-bed gasifiers, or proper slagging in fixed-bed slagging or entrained-flow gasifiers. The AFT test is widely employed, inexpensive and can be automated. However, it is also subjective, has poor reproducibility, does not indicate when melting begins and does not subject ash to the same time-temperature history encountered in gasification processes. Furthermore, ash in fuel is highly heterogeneous (Figure 4) and different ash particles will have very different behaviour during gasification. Since AFT tests are applied to lumps of ash, specific particle chemistry is not captured.

![Image of particle maps obtained using QEMSCAN, showing modes of mineral occurrence and degree of mineral liberation in finely crushed feed coal particles.](4)

The purpose of the present study is to review alternatives to the AFT test for predicting mineral matter behaviour in gasification processes. One such method is FactSage modeling. FactSage software predicts equilibrium solid-liquid-gas phases and compositions based on Gibbs free energy minimization. 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. For all predictions in this study, the FactSage 6.2 Equilib module was utilized with the FACT53 and FToxid databases.

In the following, techniques used to predict mineral matter behaviour in fixed-bed, fluidized-bed and entrained-flow gasifiers are reviewed. Then, as a case study, some techniques
are applied to a western Canada lignite ash to assess its suitability for the various gasification regimes.

**FIXED-BED GASIFICATION**

Some agglomeration of ash particles may be desired to modify porosity of the ash bed for adequate steam and oxygen flow and distribution, whereas excessive slagging inside the gasifier can cause channel burning, pressure drop problems or unstable operation. To avoid excessive slagging, additional steam or less oxygen can be used to reduce the temperature in the gasifier. However, such measures of action can greatly reduce process efficiency. Another option is to add minerals to the feed which will increase the ash fusion temperature in the gasifier. Van Dyk and Waanders explored this option with SiO2, Al2O3 and TiO2-based minerals.

X-ray diffraction (XRD) analysis of a fixed-bed gasification ash shows that it contains quartz (SiO2), mullite (Al6Si2O13), anorthite (CaAl2Si2O8), cristobalite (SiO2), diopside (CaMgSi2O6) and amorphous glass. Scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDX) of ash agglomerates from a commercial fixed-bed gasifier reveal minimally altered mineral matter fragments, bonded together by slag-like material containing anorthite, mullite, iron oxide and pyrrhotite particles. Matjie et al. propose that during gasification, mineral matter may fuse, melt and partially crystallise on cooling to form a number of new phases associated with a glass component. The glass formation is most likely due to impure calcereous sediments which have a low fusion temperature, or mineral matter associated with coal which forms calcium-rich and iron-rich glasses.

Many techniques are used to assess the suitability of a fuel, based on its ash properties, for fixed-bed gasification. Van Dyk et al. used ash fusion temperatures, computer-controlled SEM (CCSEM), high-temperature XRD (HT-XRD) and FactSage predictions to study mineral transformations of a typical fixed-bed dry-bottom gasification coal. They concluded that the major source of the liquid phase components which lead to bonding of ash particles are included minerals from carbon-rich particles. Hence, not only is the mineral composition important, but also the associations between various minerals and organic components. In another study, Van Dyk et al. applied a slag viscosity model to the liquid portion of ash, as predicted by FactSage, to predict the strength of deposits with a given ash. Liquids with viscosities above 300 Pa·s would form weak deposits, and below 300 Pa·s would form strong deposits. Hence, ash with high CaO content will form low viscosity slag leading to strong deposits.

Van Dyk et al. used HT-XRD to observe coal ash phase transitions as it is heated from 500 to 1400°C. Between 600 and 650°C, kaolinite (Al2Si2O5(OH)4) transformed into mullite (Al6Si2O13). At 500-900°C, calcite (CaCO3) and dolomite (MgCO3) decomposed, allowing the formation of anhydrite (CaSO4). Around 1000°C, anorthite (CaAl2Si2O8) and gehlenite (Ca2Al2SiO7) were formed. A FactSage counter-current fixed-bed gasifer model was developed. The model treated the gasifier as three distinct zones; drying and devolatilization, gasification, and combustion. Findings from HT-XRD and FactSage modeling were in agreement. It was noted that feldspar minerals, such as anorthite, have low ash fusion temperatures and cause the most slag-liquid formation. An improved version of the FactSage gasifier model was presented by Van Dyk and Waanders.

**FLUIDIZED-BED GASIFICATION**

Marinov et al. studied ash agglomeration during fluidized gasification of high sulphur lignite. Feed lignite ash and pilot gasifier ash samples were analysed. Feed ash and a gasifier slag samples were found to have very similar compositions, yet the slag sample softening temperature (980°C) is much lower than the feed ash softening temperature (1195°C). This was attributed to the different mineral forms in each sample. β-pyrrhotite (FeS) and wüstite (FeO) were detected by XRD in the slag sample. The authors note that the FeS-FeO eutectic, with a melting point of 924°C, led to the formation of liquid which other particles can stick to. These other particles react with the liquid to form hard agglomerates in the gasifier.
Li et al. performed pilot scale fluidized-bed gasification tests using Xiaolongtan coal as feed. After operating at 900-1000°C for 24 h, the gasification was halted due to slag accumulation problems. Li et al. then heated and quenched Xiaolongtan ash samples in a muffle furnace at various temperatures with a 50/50 H₂/CO₂ gas atmosphere. Quenched samples were analysed by scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD). At 700°C, quartz (SiO₂), illite (KAl₂(OH)₂AlSi₃O₁₀), anhydrate (CaSO₄) and magnesium ferrous oxide ((MgO)₀.₇₇(FeO)₀.₂₃) were present. At 950°C, illite and magnesium ferrous oxide are no longer present, while oldhamite (CaS), anorthite (CaOAl₂O₄(SiO₂)₂), hedenbergite (CaOFeO(SiO₂)₂) and hercynite (FeAl₂O₄) are formed. It was proposed that the mechanism of slag formation was by the generation of glassy materials, the formation of partial melting entities, the substitution of iron in liquid aluminate or aluminosilicate by calcium, and the mergence of individual particles. Hence the formation of Fe-Si-Al and Ca-Si-Al phases lead to agglomerations in the gasifier. It was hypothesized that by reducing the operating temperature of the gasifier, formation of key phases could be avoided. A later pilot gasifier test was done with a temperature range of 850-930°C. No slag was produced during a continuous 100 h run time. In the current study, FactSage calculations were made using the ash analysis of Xiaolongtan as input, in the temperature range of 600-1000°C, to determine whether Li et al.’s experimental quenching results could be predicted (Figure 5). 100 g of ash and 1000 g of gaseous atmosphere, 50/50 H₂/CO₂, were used for the calculations. Although Ca-Al-Si and Fe-Al-Si solutions (Mellilite, AWollastonite, AClinopyroxene) and compounds (grossularite, anorthite) are predicted by FactSage, their forms and temperatures of formation are very different from the phases observed in Li et al.’s experiments. Since the quenched samples were held at the target temperature for only 10 min, they may be far from equilibrium state. This could explain the differences with FactSage predictions which do not consider kinetic effects.
Nel et al. compared the sintering and compressive strength tendencies of a model coal mineral mixture in inert and oxidizing atmospheres, focusing on heating from 25 to 1000°C. Compressive strength tests, simultaneous thermogravimetric and differential thermal analysis, scanning electron microscopy and x-ray diffraction were used to analyse the sample at various temperatures. In the current study, FactSage calculations were made for the same mineral mixture in the temperature range of 500-1000°C to determine whether the experimental results in air and N₂ could be predicted (Figure 6 and Figure 7, respectively). The mineral mixture consists of 25% kaolin (Al₂Si₂(OH)₄), 20% quartz (SiO₂), 20% pyrite (FeS₂), 15% calcite (CaCO₃), 8% iron carbonate (FeCO₃), 8% hydromagnesite (MgCO₃) and 4% anatase (TiO₂), by weight percentages. 100 g of mineral mixture and 1000 g of gaseous atmosphere were used for the calculations.

Nel et al. noted that the major crystalline phases in the mineral mixture sintered in air at 500-1000°C are quartz (SiO₂), hematite (Fe₂O₃), anhydrite (CaSO₄), anatase (TiO₂), and magnesium sulphate (MgSO₄) (only 500-800°C). According to the FactSage calculations, SiO₂ is present as quartz(l), which is probably α-quartz, from 500-625°C. It is present as quartz(h), which is probably β-quartz, from 625-850°C. From 850-1000°C, SiO₂ is present as tridymite(h). These transformations are consistent with Ni et al.’s observations with pure SiO₂. Also, according to the FactSage predictions, Fe₂O₃ and TiO₂ are predominant, but mostly as corundum and rutile, respectively. MgSO₄ is predominant up to 700°C. Anhydrite CaSO₄ is stable up to 950°C. Nel et al. mention sulphur released during the decomposition of pyrite in air is oxidized to SOₓ, which is captured by CaO to form CaSO₄. The CaSO₄ decomposes to lime and SOₓ above 900°C and the resultant lime can react with minerals. In contrast, Nel et al. observed that in N₂, pyrite will not decompose and oxidize to form SOₓ. SOₓ is therefore not available to react with CaO and MgO. CaO and MgO can then more readily react with aluminosilicates. This phenomenon in N₂ is predicted by FactSage, with FeS and anorthite predominant for the entire temperature range.

Nel et al. observed an increase and decrease in mechanical strength of the mineral mixture pellets sintered in air, at temperatures which correspond to the formation and decomposition of CaSO₄, respectively. These changes in mechanical strength were not observed with the pellets sintered in N₂. The formation and decomposition in air and not N₂ can be demonstrated by FactSage predictions. However, there are some discrepancies between the phases and temperatures of transitions observed experimentally by Nel et al., and the predictions by FactSage. These may be attributed to kinetic factors which are not accounted for in FactSage predictions.
Figure 6. FactSage phase predictions for a mineral mixture in air: a) solutions; b) Si-containing compounds; c) Si-free compounds.
Figure 7. FactSage phase predictions for a mineral mixture in N₂: a) solutions; b) Si-containing compounds; c) Si-free compounds.
ENTRAINED-FLOW GASIFICATION

The majority of the successful high throughput coal gasifiers developed in the past 60 years are of the entrained-flow slagging type. The fate of mineral matter in this type of gasifier can take one of two directions. The first is entrainment by the gas phase where the ash leaves the gasifier as fly ash. In this case, it must be removed by some particle removal process prior to downstream processing of the gas. Alternatively, the ash may stick to the gasifier walls, flow down and exit the bottom as a highly viscous slag. This process has many implications as the slag can greatly affect heat transfer in the system, corrode/protect the refractory lining of the gasifier, and even plug the gasifier thus halting its operation. Hence to determine the performance and profitability of a slagging gasifier, it is important to know the slagging properties of the intended fuel. As a rule of thumb, slag viscosity should not exceed 25 Pa⋅s at the slag tapping temperature. If the slag is too viscous, corrective action is required. This may include increasing the gasifier operating temperature, oxygen injection at the slag tap, or ceasing operation. Alternatively, a fluxing agent such as limestone or dolomite may be added, and/or the fuel may be blended with another fuel. Blending fuels may also be necessary if there are issues with fuel availability, flame stability or ash content.

Like any fluid, slag rheology is a function of its molecular structure and dynamics. Slag usually has SiO$_2$ as its main component and can thus be categorized as a silicate melt for which the random network model is often used to describe its rheology. According to this model, silicate melt components can be classified into three categories; network formers, network modifiers and amphoterics. Network formers (e.g., Si$^{4+}$ and Ge$^{4+}$) stabilize the network and therefore increase viscosity. Network modifiers (e.g., Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Fe$^{3+}$, Cr$^{3+}$, V$^{5+}$, Ba$^{2+}$ and Sr$^{2+}$) disrupt the network and therefore decrease viscosity. Amphoterics (e.g., Al$^{3+}$, Fe$^{3+}$, B$^{3+}$ and Zn$^{2+}$) can act either as network formers or modifiers. Although these general tendencies often hold true, the actual phenomena is more complex leading to discrepancies between this description and measured viscosities.

Slag viscosity also has a strong dependence on temperature. At elevated temperatures, slag acts as a Newtonian fluid and its viscosity usually decreases logarithmically with increasing temperature. At lower temperatures, crystallization or the separation of immiscible liquids may occur causing a dramatic increase in viscosity and non-Newtonian behaviour.

Most models developed to predict the viscosity are only applicable to limited slag compositions and conditions. If inappropriately applied, they may provide predictions which are in error by several orders of magnitude. Many studies provide slag viscosity data to assess whether a certain fuel can be used for entrained-flow gasification.

CanmetENERGY’s entrained-flow gasifier (Figure 8) provides the rare opportunity to observe phenomena at pilot scale conditions. The gasifier has an internal diameter of 0.254 m and height of 3.66 m. It can be operated at pressures up to 1500 kPa and temperatures up to 1700°C. The gasifier may be dry-fed (up to 20 kg/h) or slurry-fed (up to 60 kg/h). A protocol to observe and quantify slagging during gasification is under development. A custom designed probe will be used to collect fly ash and slag samples.
A western Canada lignite has been selected as a case study for the assessment of a fuel’s suitability, based on ash properties, for various gasification regimes. Preliminary results, including FactSage modeling and slag viscosity measurements, are presented below. HT-XRD analysis of an ash sample and XRD analysis of quenched slag samples will be completed later to study phase transformations upon heating and cooling, respectively.

The composition of the western Canada lignite ash is presented in Table 1. The listed composition excludes components which represent less than 0.5 wt% of the ash. FactSage predictions are with 100 g of this ash and 1000 g of synthesis gas (2.5 wt% H₂, 70 wt% CO, 22 wt% CO₂ and 5.5 wt% H₂O). The composition of the synthesis gas was selected to fall within typical ranges given in a US DOE report. Predicted masses of phases of interest are shown in Figure 9. For viscosity measurements, an artificial ash was prepared by mixing laboratory or analytical grade Al₂O₃, CaO, Fe₂O₃, K₂CO₃, MgO, Na₂CO₃, SiO₂ and TiO₂ powders. Proportions were based on the composition listed in Table 1. However, sulphur was not included since it devolatilizes once the sample has been heated to its maximum temperature prior to viscosity measurements. The setup and technique for slag viscosity measurements are given elsewhere. Viscosity results are presented in Figure 10.

Table 1. Composition of a western Canada lignite ash

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Composition (wt %)</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>38.65</td>
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<tr>
<td>Al₂O₃</td>
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<tr>
<td>Fe₂O₃</td>
<td>5.70</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.71</td>
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<tr>
<td>CaO</td>
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<tr>
<td>MgO</td>
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<td>Na₂O</td>
<td>6.54</td>
</tr>
<tr>
<td>SO₃</td>
<td>14.50</td>
</tr>
</tbody>
</table>
Figure 9. FactSage phase predictions for a western Canada lignite ash in synthesis gas: a) solutions; b) compounds.

Figure 10. Viscosity curve for a western Canada lignite ash.
According to the FactSage results, Ca-rich and Na-rich phases undergo various transformations before reacting with Si to form a slag phase at 925°C. FeS is present up to 1075°C, at which point it decomposes and iron enters the slag phase. Above 1175°C, only liquid slag is present. The relatively high calcium and sodium contents of this ash induce slagging at a fairly low temperature. According to these results, fixed-bed dry-bottom gasifiers and fluidized-bed gasifiers using this lignite should be operated at less than 925°C to avoid slagging. Fixed-bed slagging gasifiers and entrained-flow gasifiers using this lignite should be operated above 1275°C to produce fully molten slag with a viscosity below 25 Pa s. FactSage predictions should be verified by HT-XRD analysis of an ash sample and XRD analysis of quenched slag samples.

CONCLUSIONS

For proper operation of a gasifier, behaviour of the fuel’s ash component is critical. Techniques to predict mineral matter behaviour in fixed-bed, fluidized-bed and entrained-flow gasifiers are reviewed. These techniques include AFT tests, SEM, EDX, XRD, viscosity measurements and FactSage modeling. AFT tests are useful, but also subjective and only indicate bulk ash properties. SEM is a powerful, yet qualitative, tool. EDX and XRD should be used when possible. FactSage modeling is an easy and quick method to predict mineral matter transformations, but it is not always effective at temperatures below the ash melting point due to kinetic effects it does not account for. In such cases, predictions should be verified by EDX or XRD experiments. Viscosity measurements are crucial to predict mineral behaviour in slagging gasifiers. FactSage modeling and viscosity measurements for a western Canada lignite ash are presented. Preliminary results suggest that, based on its predicted ash behaviour, this fuel requires a temperature below 925°C for fixed-bed dry-bottom and fluidized-bed gasification. For fixed-bed slagging or entrained-flow gasification, the operating temperature should be kept above 1275°C.

REFERENCES


6. van Dyk, J. C. & Waanders, F. B. Manipulation of gasification coal feed in order to increase the ash fusion temperature of the coal enabling the gasifiers to operate at higher temperatures. Fuel 86, 2728-2735 (2007).


10. van Dyk, J. C. & Waanders, F. B. *An improved thermodynamic FactSage simulation to simulate mineral matter transformation during a fixed bed counter-current gasification process, validated with HT-XRD* (Twenty Fifth International Pittsburgh Coal Conference, Pittsburgh, USA, 2008).


