Molecular dynamics simulations of the molten CaO-K₂O-SiO₂ system to study viscosity of woody biomass ash slags

C. Ma¹*, N. Skoglund¹, M. Carlborg¹, M. Broström¹

¹. Department of Applied Physics and Electronics, Thermochemical Energy Conversion Laboratory, Umeå University, SE 901 87, Umeå, Sweden

*corresponding author, charlie.ma@umu.se

Abstract

Compositions in the CaO-K₂O-SiO₂ system have been simulated with molecular dynamics in order to elucidate aspects of structural characteristics that correlate to molten slag viscosity. Focus was placed on the structural characteristics of the Si and O atoms, which included pair distribution and coordination number functions, angular relationships, $Q^n$ values, and oxygen types. Principal component analysis was used to reveal correlations between reported viscosity values and attributes of the structural characteristics. The simulations indicated that silicate tetrahedral units were prevalent and angular and atomic mobility attributes between these units correlate with viscosity. Viscosity also tends to increase with increasing shares of $Q^3$ or higher, and tends to decrease with increasing shares of $Q^2$ or lower, as expected.

1. Introduction

Silicate slags often form during thermal conversion processes that use solid fuels and can create problems for operations. For example, their viscosity has a critical role in causing accumulative depositions within furnaces and other thermochemical reactors that can often lead to shutdowns [1]. The slags are characterised by the ordering of Si and O atoms such that SiO₄/silicate tetrahedral units of can exhibit extensive formations of inter-tetrahedral networks that influence viscosity. Accurate knowledge of molten slag viscosities can contribute towards more robust and reliable processes. This may be achieved by attaining an understanding of the structural characteristics of molten slags at the molecular level. Obtaining such information in-situ at high temperature can be difficult, but such characteristics have the possibility of being elucidated via molecular dynamics (MD) simulations [2]. A number of recent studies have already applied this method towards studying slag viscosity. Dai et al.[3] performed MD simulations of coal ash compositions to study the effects that fluxants have upon viscosity. Oxygen atoms were found to have different numbers of Si atoms in close proximity, where free (FO), non-bridging (NBO), bridging (BO), and tricluster (TO) O atoms have 0, 1, 2, and 3, network-forming atoms (e.g., Si) within close proximity, respectively. A stability coefficient based on this distribution was defined to form relations with viscosity values as predicted by thermodynamic modelling. In a similar manner, diffusion coefficients from MD simulations of blast furnace slag by Zhang et al.[4] were applied to the Stokes–Einstein equation to produce viscosity values comparable to those as predicted by thermodynamic modelling. Another example was reported by Xuan et al.[5], who analysed synthetic
coal ashes both experimentally and with MD simulations. They found a logarithmic relationship between the degree of polymerization, as defined by $Q^n$ values, from the MD simulations and their measured viscosity values of the different slag compositions. In these three studies, selective parametrization were necessary and only the latter compared results with experimental values. They do, nonetheless, suggest prospects of good correlations between quantities extracted from MD simulations and slag viscosity. Others have also used MD simulations to study structural features like pair distribution functions and bond/bridging angles between atoms [6-8]. Such common structural characteristics may be closely correlated to the viscosity of slags because they are indicators of atomic mobility in the silicate network. As such, it is the aim of this study to elucidate how quantities that are commonly extracted from MD simulations correlate with experimentally reported viscosity values. To this end, compositions within the CaO-K$_2$O-SiO$_2$ system at various temperatures were simulated. For conciseness, the focus was restricted to the Si and O atoms. Principal component analysis (PCA) was carried out to elucidate correlations between characteristic quantities and measured viscosity values found in the literature [9]. The results further the understanding of molten ash slag viscosity in this system by indicating structural characteristics that are most directly linked.

2. Method

Slag compositions
Six CaO-K$_2$O-SiO$_2$ compositions based on those used by Chen and Zhao [9] in their viscosity measurements were used as inputs in the simulations (Table 1). They are labelled according to their study, from K1 to K6. Up to eight different temperatures were simulated for each composition, giving a total of 39 cases.

<table>
<thead>
<tr>
<th>Label</th>
<th>SiO$_2$ [mol%]</th>
<th>K$_2$O [mol%]</th>
<th>CaO [mol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>70</td>
<td>21.1</td>
<td>8.9</td>
</tr>
<tr>
<td>K2</td>
<td>77.7</td>
<td>15.1</td>
<td>7.2</td>
</tr>
<tr>
<td>K3</td>
<td>52.6</td>
<td>29.5</td>
<td>17.9</td>
</tr>
<tr>
<td>K4</td>
<td>49.8</td>
<td>17</td>
<td>33.2</td>
</tr>
<tr>
<td>K5</td>
<td>70</td>
<td>10.5</td>
<td>19.5</td>
</tr>
<tr>
<td>K6</td>
<td>78.2</td>
<td>7.7</td>
<td>14.2</td>
</tr>
</tbody>
</table>

Tab.1: Slag compositions

Simulation
LAMMPS (Version 8 Feb 2019) [10, 11] was the simulation tool used. The simulation method followed that of Li et al. [12] and is briefly described here. The potential function used as the basis for interatomic forces between atoms $i$ and $j$ separated by distance $r_{ij}$ is based on the Born-Mayer-Huggins function augmented with the Morse potential between cation-anion pairs [12-14]. A constant number of approximately 5000 point ion atoms were simulated at 1 femtoseconds ($10^{-15}$ s) timesteps within constant volumes and temperatures. Slag densities were obtained from the relationship by Lange [15]. Random initial positions and velocities were assigned to atoms before simulations at 5000 K were run for 100000 timesteps (0.1 ns) to relax and randomize the system. The system temperature was then ramped to the specified values at cooling rates no greater than $10^{13}$ K/s, in order to avoid formation of locked-in local structures. The simulation was then run for another $4 \times 10^5$ timesteps before data files for analysis were dumped periodically during an additional $10^6$ timesteps. For each simulation, characteristic structural quantities were extracted from over $10^5$ atoms within the files and averaged using scripts written in R (Table 2). The mean squared displacements of each atomic species was monitored to check that a
liquid phase prevailed. The tilt angle characteristic is as defined by Yuan and Cormack [16].

<table>
<thead>
<tr>
<th>Structural characteristic</th>
<th>Atomic pair/unit</th>
<th>Attribute(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pair distribution functions</td>
<td>Si-O, O-O, Si-Si</td>
<td>Nearest neighbor distance [Å] median, FWHM [Å]</td>
</tr>
<tr>
<td>Angles</td>
<td>O-Si-O, Si-O-Si, Silicate tetrahedral unit tilt</td>
<td>Median [°], Interquartile range [°]</td>
</tr>
<tr>
<td>$Q^n$ values</td>
<td>Si-O</td>
<td>Distribution [%]</td>
</tr>
<tr>
<td>Oxygen types</td>
<td>Si-O</td>
<td>Distribution [%]</td>
</tr>
</tbody>
</table>

Tab.2: Structural characteristics extracted from simulation

Attributes that possibly reflect atomic mobility were also quantified so that their correlations with viscosity could be assessed. SIMCA 16 facilitated the multivariate principal component analysis (PCA).

3. Results and discussion

Pair distribution and coordination number functions

The Si-O pair distribution function (PDF) for each simulation in Fig.1a show the relative atomic density of O atoms that surround Si atoms. They are characterised by a major peak at a radial distance of approximately 1.6 Å, which is a Si-O distance typical for silicate glasses and melts. Based on the valley position after the major peak in the Si-O PDFs, a cutoff radius of 2.4 Å was set as the criterion for Si and O pairs to be considered as coordinated with each other. This value was used to evaluate $Q^n$ values and to classify O atom types. The coordination number (CN) curves in Fig.1b show plateaus when Si atoms are coordinated with four O atoms.

This highlights the stability of these coordinated units as it is a region in which predominately four, and only four, O atoms are located.

Angles

Angles formed by coordinated O-Si-O chains have similar median values (108.2 – 108.7°) for all compositions and temperatures as demonstrated in Fig.2a.
This is close to the tetrahedral angle (109.47°) and, along with the coordination number mentioned previously, indicates the prevalence of silicate tetrahedral units. The interquartile range varies between 11 – 15°, which is lower compared to those of the Si-O-Si and tilt angles. The distribution of Si-O-Si angles, which constitutes the link between silicate tetrahedral units, have median values between 143 – 151° and interquartile ranges of 20 – 25° (Fig.2b). The distribution of tilt angles (Fig.2c) show some variation in the median values (126 – 130°) and the interquartile range is relatively broad (37 – 39°). Taken together, these values indicate the presence of relatively rigid silicate tetrahedral units that are linked in a relatively flexible manner at their O atom vertices.

Fig.3a to 3c shown simulation snapshots of Si atoms with bridges to O atoms coloured according to their $Q^i$ value for each composition (O atoms are omitted for the sake of clarity). This distribution did not vary significantly with temperature but is clearly affected by the differences in composition. The sparsity of K3 and K4 (Fig.3a) and their higher shares of low $Q^i$ values is attributed to their relatively low contents of Si atoms. This restricts the formation of extensive networks with high $Q^i$ values that are exemplified by K2 and K6 (Fig.3c).

**Oxygen types**

The distribution of oxygen types shown in Fig.4 indicates that BOs and NBOs dominated almost completely. The distributions did not show much variation with respect to temperature but the ratio of BO:NBO differed significantly between the compositions. In line with the $Q^i$ values, the share of BOs is greater for compositions with greater Si content.
The scarcity of TOs (below 0.1 % in all cases) is consistent with the stability of the silicate tetrahedral unit; TOs instead tend to be more apparent in systems containing e.g., Al [7].

Fig. 3: Silicate network coloured according to $Q^n$ value: $Q^0 =$ cyan, $Q^1 =$ blue, $Q^2 =$ green, $Q^3 =$ yellow, $Q^4 =$ orange, $Q^5 =$ red. Compositions presented in order of increasing $Q^n$.

Fig. 4: Distribution of oxygen types from the simulations.
**Multivariate analysis**

The PCA score plot of Fig. 5a indicates that the structural characteristics enable the cases to be grouped and aligned according to composition and temperature.

Fig. 5: PCA plots of first two components. Based on a 2-component model, the goodness of fitting and prediction (based on cross-validation) are 83.2 % and 79.3 %, respectively.

The first principal component (PC1, horizontal axis) is largely aligned to the structural characteristics that are due to the differences in composition. From the loading plot of Fig. 5b, these include mainly those pertaining to $Q^k$ values and oxygen types, as well as a few from PDF and angle attributes. The second principal component (PC2, vertical axis) is largely aligned with the structural characteristics that are due to the differences in temperature. These are almost exclusively those pertaining to PDF and angle attributes. This implies that $Q^k$ values and oxygen types are largely independent of temperature, as exemplified for the former in Fig. 4. It is noted that the strong alignment of TO towards PC2 is due to the scaling of variances as part of the PCA, in order to apply equal importance to all variables. The actual share of TOs was well below 0.1 % of all O atoms in all simulations. The loading plot also identifies the structural characteristics that can have strong positive or negative correlations with the reported viscosity values (the variable identified as the purple point with log10([Pa.s]) label in Fig. 5b). The structural characteristics that lie closest (most strongly correlated) are the median Si-O-Si and tilt angles, while those most diametrically opposed (most negatively correlated) are the interquartile ranges of the Si-O-Si angle and Si-Si PDF peak FWHM. These angle and PDF attributes are plotted against viscosity in Fig. 6. The median values of Si-O-Si angles show a proportional relationship with the viscosity, in a range comparable to that of quartz and cristobalite. The negative correlation with the interquartile range implies a greater disorder in the silica network that gives lower viscosity. By contrast, the median values and interquartile ranges of the O-Si-O angles are less correlated to viscosity, and their deeper relation with viscosity is beyond the current scope. Nonetheless, taken together with previous discussion, this implies that silicate tetrahedral units are...
relatively rigid units that are linked to other units in a relatively flexible manner.

![Graph](image1)

**Fig.6: Plots of viscosity against structural characteristic attributes identified in loading plot Fig.5b to be most correlated or negative correlated.**

This is also apparent in the negative correlation of Si-Si FWHM with viscosity. In concordance with the angle variations, the FWHM of the Si-Si peak also implies a more volatile network where the distances between Si atoms are more scattered. $Q^n$ values show less sensitivity to viscosity than the aforementioned structure characteristics, but viscosity tends to increase with increasing shares of $Q^3$ or higher, and tends to decrease with increasing shares of $Q^2$ or lower. Similarly, bridging O atoms tend to be loosely correlated with viscosity, while the inverse is evident in regards to non-bridging and free O atoms. This is expected to be based on the influence that the degree of polymerization has upon viscosity. The O-O PDF attributes of peak location and FWHM do not correlate significantly with viscosity.

4. Conclusion and Outlook

Based on molecular dynamics simulations using a Born-Mayer-Huggins potential function augmented with Morse interactions, the following relations between the structural characteristics of molten $K_2O-CaO-SiO_2$ slags and their viscosity were elucidated:

- Si and O atoms tend to form stable silicate tetrahedral units that polymerize via bridging O atoms
- The median value of the Si-O-Si angle that links silicate tetrahedral units varies between approximately $143^\circ - 151^\circ$ and correlates with reported viscosity values between approximately $0.1 - 6500$ Pa.s. The extent of variation in this angle (i.e., interquartile range) is also negatively correlated to viscosity.
- Correspondingly, the FWHM of the major peak in the PDF of Si-Si pairs is also negatively correlated with the viscosity.
- The silicate tetrahedral units form relatively flexible links between them via O atom network bridges.
- $Q^n$ values show less sensitivity to viscosity than the aforementioned structure characteristics, but viscosity tends to increase with increasing shares of $Q^3$ or higher, and tends to decrease with increasing shares of $Q^2$ or lower.
- Similarly, bridging O atoms tend to be loosely correlated with viscosity, while the inverse was evident in regards to non-bridging and free O atoms.
In future, the structural effects that K and Ca atoms have on the silicate network will be presented, in order to give deeper insights into their effects upon the molten slag viscosity presented herein.

5. Acknowledgements

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6. References

[12] K. Li et al., Chemical Engineering Journal 313 (2017) p1184