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Citation:

Exploratory research in alternative raw material sources and reformulation for industrial soda-lime-silica glass batches

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Abstract

For energy saving and CO_2 emissions reduction, in addition to extending the range of suitable raw material sources for glass manufacture, compositional reformulation and alternative raw materials have been studied in the context of industrial container and float-type soda-lime-silica glasses. Lithium, potassium and boron were applied to modify benchmark glass compositions. Reformulation impacts on key glass properties including the viscosity-temperature relationship, thermal expansion, liquidus temperature, forming behaviour and colour. Compared to the benchmark glass, representative of commercial soda-lime-silica glasses, melting temperatures (taken as temperatures corresponding to log (viscosity/dPa·s) = 2) of reformulated glasses are reduced by 11 - 55 ^{o}C. Investigation of four industrial by-products (seashell waste, eggshell waste, biomass ash and rice husk ash), and their potential suitability as alternative glass batch raw materials, was also conducted. Seashell waste and biomass ash were successfully introduced into representative green glass formulations.

Keywords: decarbonization; alternative raw material; reformulation; viscosity; glass

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1. Introduction

Historically, the sources and proportions of raw materials for soda-lime-silica (SLS) glass batches have evolved over a period of many years, and for a variety of reasons [1]. In ancient times, limited by geography, communication links and glass making knowledge, plant ashes, steatite, sand and natron were applied by the Egyptians and Romans in glass making [2]. Soda-lime-silica glass compositions have evolved over the intervening centuries, and current glass manufacturing practice uses a combination of man-made and mined raw materials with minimal variability in composition, with glass compositions largely unchanged for the past 50 years [1][3]. For flat, container and pressed glasses, a series of average compositional investigations between 1980 and 2000 were presented by Smrček [4][5][6]. This includes commercial glasses from Germany, France, Great Britain, Italy, Russia, USA and others (32 countries in total), thus presenting a truly global assessment.

As an energy-intensive industry, global commercial glass manufacture is a key sector that consumes 220TWh/yr of energy and emits 50-60MT/yr of CO_2. In the UK, the sector produces more than 3 MT of glass per year and emits 2.2 MT of CO_2, using 4.5 TWh of energy at a (current) cost of more than £75M [7]. The UK and other countries are legally obliged to deliver the Paris Agreement through its domestic climate framework [7]. This framework sets a target to reduce greenhouse gas emissions by at least 80% by 2050, against 1990 levels, which places a great burden of responsibility on energy-intensive manufacturing sectors including the glass sector. To help coordinate and support achievement of this goal from a UK perspective, the

Glass Decarbonisation Roadmap 2050 was published in 2015 [8]. According to this plan, batch reformulation was highlighted as one key mechanism to help enable the glass industry to reduce its energy consumption and CO_2 emissions. Low cost, environmentally-friendly, energy-saving, emissions-reducing and increased-recycling are now all major driving forces for exploration of commercial soda-lime-silica glass batch reformulation and alternative raw materials that could help to economically achieve this.

Any changes to glass making raw materials balances using new raw materials including but not restricted to those studied here, will require the availability of substantial tonnages (e.g. in the UK at 10% of batch mass to produce 3MT / year of glass would require up to ~300kT / year of the new raw material to be available at sufficiently low cost). This raw material would also need to be available in a sufficiently consistent form, both chemically and physically. The present, initial study focussed on investigating the potential of candidate raw materials for further development. Whilst outside our scope here, establishing the reproducibility and consistency of any new raw material, in addition to demonstrating its performance in glassmaking at scales larger than a laboratory and establishing a robust supply chain, will all be key requirements to develop and advance the raw material into the marketplace.

Previously, researchers have carried out many studies of the use opportunities for industrial wastes and by-products, with one aim being expanding the sources of raw materials for a range of high-volume manufactured products including glass

[9][10][11][12]. For example, as one of the most important agricultural products in the Far East since ancient times, rice paddies produce almost 100MT of rice husk per year [13][14]. Rice husk ash (RHA) is the product of incineration of this rice husk. In some regions, rice husk is used as a fuel for parboiling paddy in rice mills, whereas in other areas it is field-burnt as a local fuel [15]. Most of the evaporable components of rice husk are slowly lost during burning and the primary residues are thus rich in silicates [15]. Instead of being discarded as waste, rice husk ashes can potentially be used as raw materials for a number of products, as typically such wastes consist of ~95% SiO_2 and ~3% alkali / alkaline earth oxides, if carbonaceous content is discounted [14]. In the United States, rice production generated about 39.3 MT of food waste (15.1% of total municipal solid waste) in 2015 [16].

Due to wide cultivation and high consumption of bananas and corn in the United States, Cornejo *et al.* [9] researched the possibility that recycled banana peels and corn husks could serve as a valuable and sustainable raw material resource for glass manufacture. In particular, the high K_2O contents of ashes from combustion of banana peels (up to 67.6%) and corn husk (up to 20.2%) was considered beneficial for glass manufacture owing to the high cost of man-made alkali sources and the beneficial effects of alkalis in decreasing high temperature viscosity of silicate glasses.

Eggshell waste is a general food waste produced worldwide. In the UK, egg and egg-derivative consumption generates over 100kT of residual shells, which, if untreated, may pose a health threat as a result of microbial action. Cree *et al.* [17] investigated calcined eggshell powder at different temperatures for potential industrial

applications. Eggshells are rich in $CaCO_3$: 96-97% by mass of eggshell is calcium carbonate with 3-4% organic matter. Tite *et al.* [2] reported many soda-rich and mixed-alkali ashes from the combustion of different plant species, which may have potential applications in glass manufacture. Indeed, plant-based ashes were used as alkali sources in antiquity, for example by some Roman glass makers [18]; and later, in the Middle Ages, for glass manufacture in Europe as the so-called "forest glasses" [18]. Broad and detailed compositional data on different plant ashes from the Near East (Syria, Iraq, Iran, Levant) and Western Europe (Sicily, Venice, England, France) were also reviewed by Tite *et al.* [2].

Following the impending scarcity of fossil fuels and their increased price in recent years, as well as environmental concerns relating to CO_2 emissions, there is renewed interest in the use of biomass as a fuel sources for electrical power generation. In 2010, the European Climate Foundation estimated that across Europe the primary production of heat and power from biomass could double to 2000 TWh by 2020. Dodson *et al.* [19] studied the elemental and mineralogical compositions of ashes from the commercial combustion of miscanthus at Ely Power Station (UK), and their use for the formation of structured silicas. In total 7.2 wt% of the initial fuel remained as ash, with 86 wt% of this ash deposited as bottom ash and 14 wt% as fly ash. The process of energy generation by combustion of biomass is considered to have important environmental advantages compared with fossil fuel-based electricity generation [20]. However, it also has disadvantages, in that it still emits large volumes of CO_2 and generates large volumes of ash that can affect the conversion process,

reducing the efficiency of combustion systems, increasing costs for boiler cleaning and maintenance and hindering wider utilization of biomass materials as fuels [20]. The increasing volumes of biomass ash generated globally, as a consequence of the increasing use of biomass to generate energy, supports recycling and reuse to reduce landfill burden and costs, and mitigate negative environmental impacts [21]. However, relatively few studies have yet considered biomass ashes as raw materials in other manufacturing applications, and fewer still in the context of glass manufacture.

The use of any new raw material in glass manufacture, if proven suitable, may not only reduce dependency on man-made or mined carbonates (e.g. sodium carbonate and limestone, respectively), but it could also enable chemical reformulation of the final glass composition. The impact of such reformulation may be to enable lower furnace operating temperatures, leading to reduced energy consumption, lower raw material-derived and fuel-derived CO_2 emissions, and also reduced thermal NO_x emissions [1]. However, the current forms of commercial soda-lime-silica glass batches are stable because they strike a balance between oft-competing factors including raw materials availability, cost, furnace lifetime, melting and fining characteristics, glass durability and glass quality, among other factors [3]. Above all glass production, as a highly mature technical process, has many sophisticated details and strict process parameters that must be maintained in order to ensure problem-free continuous operation in glass manufacturing plants. Changing or modifying such parameters is never performed lightly, as it can have negative impacts on production if the effects and resulting impacts on production are

not first thoroughly developed, tested and demonstrated. Previous reviews and research in this area have been published on the (re)formulation of container glasses [3], commercial fibre and E-glass [22] and float glass [1].

The viscosity-temperature (η-T) relationship is fundamentally important to sodium-lime-silica glass manufacture. It is determined by the chemical composition of the glass and impacts on melting, forming, softening, working and annealing temperatures. Several models exist for η-T behavior of sodium-lime-silica glass systems, and a common approach uses the Vogel-Fulcher-Tammann (VFT) equation which describes the viscosity of Newtonian fluids [1]. Lakatos *et al.* [23][24][25] developed a model to accurately estimate the η-T relationship within the variation of glass compositions considered relevant at that time (1970's) to commercial soda-lime-silica glasses. The Mauro–Yue–Ellison–Gupta–Allan (MYEGA) model for equilibrium viscosity was derived in 2009 [26] and shown to provide certain advantages compared to the previous VFT viscosity expressions in terms of both fitting accuracy and the predictive capabilities at low temperature, however, there are to date limited published composition-related parameters. Other notable models include those developed by Fluegel [27], Hrma [28] and Priven [29]. Arrhenius models were developed by Hrma [28] for glass viscosity within the processing temperature range for six types of commercial glasses; and Fluegel [27] developed a viscosity model for predicting the complete viscosity curve using a global statistical approach and more than 2200 composition-viscosity data for silicate glasses collected from over 50 years of scientific literature. For container, and particularly for float

glass manufacture, an important issue may arise if glass is subject for a sufficient length of time to temperatures that produce crystallization. To minimize the likelihood of unacceptable levels of crystal nucleation and growth during conditioning, forming and post-processing, it is commonly accepted that the liquidus temperature (T_{Liq}) should typically be 10-20°C below the working point (T_w: for container glass, T_w is the temperature at viscosity $\log(\eta/ dPa \cdot s) = 4$) [1]. For modern container and float glasses, T_{Liq} is typically 980-1050°C [1][30]. The parameter ΔT_{FL}, the difference in temperature between the forming temperature (T_F) and the liquidus temperature (T_{Liq}), is an important criterion in the development and manufacture of all SLS glass formulations. This criterion has been used successfully in the reformulation of container glass [1] [3] [31] and fiberglass [1] compositions.

Specific to the ingredients of soda-lime-silica glass compositions, some oxides generate attention for their effectiveness in reducing the melt viscosity and therefore the temperatures required to melt, homogenize, condition and form the glass. Compared to sodium oxide (Na_2O), some authors have suggested that molar replacement by potassium oxide (K_2O) may have the dual effects of increasing the glass melt viscosity at high temperatures (e.g. melting temperature, $\log (\eta / dPa \cdot s) = 2$) and reduce viscosities at lower temperatures (e.g. near the glass transition temperature, $\log (\eta / dPa \cdot s) = 13$) [1][32], providing a "longer" glass. Potassium strongly decreases surface energy [32]. It can reduce the surface energy of lithium silicate glass from 317×10^{-3} N/m to 212×10^{-3} N/m by introducing 33wt% K_2O) [23][32][33], but it is more volatile than Na_2O [1]. Boron oxide (B_2O_3) is among the most effective melting

accelerants and fluxes when added to soda-lime-silica glasses at levels of up to a few weight percent [1][4][5][6]. Important studies of the effects of B_2O_3 in soda-lime-silica glass [34][35] have demonstrated that B_2O_3 reduces glass melt surface energy, viscosity, and liquidus temperature [5][6]. Whilst health and safety considerations make boron compounds and raw materials more difficult to handle than other glass raw materials, boron remains a key component in the manufacture of borosilicate glasses and, as noted above, strong precedent exists for its application in other forms of glassmaking [1, 3, 4-6]. Typical boron-bearing compounds used in glassmaking include man-made borax pentahydrate and decahydrate ($Na_2B_4O_7.5H_2O$ and $Na_2B_4O_7.10H_2O$) or boric acid (H_3BO_3); and also naturally-occurring minerals such as Colemanite ($Ca_2B_6O_{11}.5H_2O$) or Ulexite ($NaCaB_5O_6(OH)_6.5H_2O$). Boric oxide (B_2O_3) has rarely been used as a glassmaking raw material due to its hygroscopic nature and relatively high toxicity. Although expensive, lithia (Li_2O) is the strongest oxide melting flux and accelerant for soda-lime-silica glass and small additions of only 2.1wt% Li_2O [32]) produce large decreases in melt viscosity. Tang and Frischat [36] studied soda-lime-silica container glasses with molar substitution of Li_2O for Na_2O, introducing Li_2O contents of 0.09–0.43 wt%. Chemical durability was also substantially improved upon addition of only 0.18 wt% Li_2O. This improvement may be attributable to the so-called "mixed alkali effect" and to the high field strength of Li^+ by comparison with Na^+, which strengthens the glass network. The decreases in furnace temperature made possible by the addition of Li_2O also provided a decrease in refractory corrosion rates. The addition of 0.26 wt% Li_2O led to a decrease in

refractory corrosion rate from 2.35×10^{-2} to $\sim1.40\times10^{-2}$ mm h^{-1} at a constant viscosity of log (η / dPa·s) = 2.24), as shown by Tang and Frischat [36]. In the present study we have combined the effects of chemical modification of soda-lime-silica glass compositions with the effects of introducing new, sustainable raw materials derived from industrial by-products, with the aim of reducing the environmental impact of glass manufacture.

In this study, four by-products from industrial processes were obtained and characterized in this research: biomass ash from a biomass power station; eggshell waste; seashell waste and rice husk ash. As shown in literature for biomass ashes [37][38][39], eggshells [40][17], seashells [41] and rice husk ashes [39], the feedstock and subsequent treatment/s of these materials (e.g. combustion / heat treatment) can significantly impact on the chemical components that are available post-process - i.e. the source and process of the waste influences its' chemical composition. As noted earlier, this initial study aimed to investigate the potential of candidate raw materials for further development and it is recognised that further work would be required to establish consistency and suitability of any such materials before they could be commercialised as glass making raw materials. However, strong precedence exists for such an approach, as demonstrated by the now-worldwide use of blast furnace slag (metallurgical industry by-product) as a glassmaking raw material since the 1970's [1].

A growing number of power stations (UK and worldwide) are using biomass fuel sources to generate electricity. These sources include wood pellets, waste wood (of

various grades), wheat straw, miscanthus, poultry litter and meat and bone meal [42]. Biomass plants generate >2MT / year of waste ash in the UK alone; a small percentage is used in higher value products such as fertilisers, however, the majority is either used in low grade products (aggregates and construction product fillers), or is sent to landfill. Each power station typically uses one type of waste stream. There is likely to be some variability in the nature of the feedstock over time (e.g. due to seasonal variations in weather, different soil types etc.). Biomass ashes are typically rich in valuable alkali and alkaline-earth metals (K, Na, Ca, Mg) and other components depending upon the plant and processes used.

Egg and egg-derivative consumption generates ca. 180kT / year of residual shells in the UK, which pose an environmental pollution as a result of microbial action. An important ingredient of eggshells is calcium carbonate which can be potentially used in various material applications [17]. Eggshell waste primarily contains magnesium, calcium carbonate (limestone), and protein. The calcium oxide obtained from calcined eggshells can be potentially used in various applications including glassmaking [9][17]. Eggshells were considered as a substitute for limestone for use in the production of both clear and green SLS glass in this study.

Growth of global mussel and other seashell farming industries has increased the amounts of shell waste, and there have been a number of studies on developing new applications for seashell waste. Given that seashells are a calcium-rich material, they can represent an alternative source for calcium carbonate. A detailed report on UK shellfish by-products was compiled in 2006 [43].

Rice husk (RH), an agricultural waste, is abundantly available in rice producing countries. In recent years, many rice mills in rice producing countries have started using RH for energy production for mill operations and household lighting in rural regions. Burning of RH produces rice husk ash (RHA). RHA has been widely used in various industrial applications such as processing of steel, cement, refractory and silicon industries [37][38][39]. Suitability of RHA for a particular process partly depends on the chemical composition of the ash, predominantly its silica content. RHA is not readily available in the UK, which is not a rice-producing nation. However, its use in lab-scale production of coloured glass has been previously reported [9]. Hence, from a scientific perspective, RHA was considered an interesting material for use in the production of glass and was considered in this study.

2. Experimental Procedures

Four by-products were sourced from UK and international industrial processes and characterized in this research: biomass ash from a UK biomass power station; UK eggshell waste; UK seashell waste and rice husk ash from the Far East. The biomass ash was derived from mixed wood fuel; the eggshell waste had been processed to remove the protein; the seashell waste was from mixed shell sources; and the RHA had been combusted prior to receipt. All as-received samples were ground in an agate mortar in preparation for XRD and other analyses. As-received wastes were used in glassmaking. Fused beads were created by mixing finely powdered (<75μm) samples with lithium tetraborate flux at a flux/sample ratio of 5:1 and then melted at

$900^{o}C$-$1000^{o}C$ in a platinum crucible the poured to form fused beads for XRF measurement.

Industrial glassmaking raw materials and cullet were provided by a UK glass manufacturer as follows: white silica sand (colourless container glass and float glass), brown silica sand (green container glass), soda ash Na_2CO_3, limestone $CaCO_3$, dolomite $MgCO_3.CaCO_3$, salt cake Na_2SO_4, chromium oxide Cr_2O_3 (used in green glasses only), Calumite blast furnace slag (used in container glasses only) and iron silicate (used in green glasses only). Additionally, the aforementioned four waste by-products were used and also some glass batches contained commercial glassmaking grade spodumene (lithium aluminosilicate) or colemanite (calcium borate), and / or analytical grade (>99.9% purity) potassium carbonate (K_2CO_3) in order to introduce Li_2O, B_2O_3 or K_2O, respectively, into the resulting glasses. Raw materials were dried at $110°C$ for 24 hours prior to weighing and mixing. For all glass samples, raw materials were weighed using a 3 decimal place balance to create batches to produce a theoretical 1300.000g glass. Batches were thoroughly mixed for several minutes using a Turbula mixer and were then placed in recrystallized Al_2O_3 crucibles. Crucibles were heated in a standard electric furnace at a heating rate of $5^{o}C/min$ from room temperature to a temperature of $1450°C$. Glass melts were not stirred or agitated during melting, however, the (relatively) large size of the laboratory-scale melts provided enhanced mixing and homogenisation by comparison with smaller (e.g. 100g) laboratory-scale glass melts, as observed in terms of levels of glass homogeneity. After 4 hours at $1450\ ^{o}C$, the crucibles were removed from the

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furnace and fibres were drawn from each melt for Littleton softening point measurement according to ASTM C338-93. After fibre drawing, the crucibles were immediately placed back into the furnace and the remaining glass was briefly reheated to 1450 ^{o}C prior to pouring into a preheated steel mould, and then placed in an annealing furnace at 520°C for 1h to relieve internal stresses. Glasses were then cooled slowly to room temperature.

Three benchmark glasses were prepared in this research, one each for colourless container glass (CC_B), float glass (F_B) and green container glass (GC_B). To improve the energy efficiency of glass manufacture through optimising mixtures of feed materials, a series of compositional reformulations was applied to the colourless container (CC series) and float (F series) glasses, aimed at reducing the high-temperature viscosity in addition to substitution of some virgin (mined or man-made) raw materials with biomass ashes. For the green container (GC series) glasses, a series of alternative glass batch raw materials, consisting of by-products (seashell waste, eggshell waste, biomass ash and rice husk ash), were reviewed and blended with other batch ingredients for melting and analysis. The two most promising wastes were taken forward into melting trials with partial replacement of raw materials in GC_B glass batch without a deliberate variation in final glass composition: GC_B_SS (with 12.99 wt% seashell waste), and GC_B_WA (with 1.77 wt% biomass ash). All glass batches are presented in Table 2. All raw materials and resulting glasses were characterized using XRF and XRD. The high-temperature viscosity, liquidus temperature and other physical properties of all glasses were

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measured and / or modelled. Finally, selected CC and GC series glasses were measured by UV-Vis spectra to assess colour and redox.

The Society of Glass Technology provides a series of Certified Reference Material (CRM) glasses for compositional analysis of commercial SLS type glasses. However, as discussed by Smrček [4][5][6], commercial glass compositions continue to evolve with time and also vary slightly between different manufacturers. A brief survey of current UK container and float glass compositions was carried out to establish representative benchmark compositions against which reformulated candidate glasses could be assessed. The survey revealed differences in compositions both between colourless and coloured (green) container glass systems and float glass formulations; there was also variation in composition within each type of glass, as expected between different manufacturers. A number of commercial glass compositions for each glass type were acquired and analysed by XRF; and the averaged results are presented here in order to provide a representative glass composition for each glass type (see Table 3). All reformulated glass compositions are also listed in Table 3. These were compared against the benchmark colourless container (CC series) and float (F series) glasses. For green container (GC series) glass, the addition of four different alternative raw materials (biomass ash, eggshell waste, seashell waste and rice husk ash) was studied.

For the reformulated glasses, the furnace temperature for melting each glass was changed, in accordance with the revised melting temperature predicted by the Lakatos model in Table 5. For example, the 'CC_R6' glass had a melting point (i.e.

temperature corresponding to a log (viscosity / dPa·s) of 2.000) that was 7°C lower than the benchmark CC_B glass, so for this glass the furnace temperature was set to 1443°C.

X-ray diffraction (XRD) was carried out on finely-powdered samples from all studied by-products and glasses using a Panalytical X'Pert Pro X-Ray Diffractometer. Measurements were taken from diffraction angles (2θ) between 10° and 90° at a rate of 0.02°2θ per second. Phase identification was performed using Jade software and ICDD powder diffraction files (International Center for Diffraction Data).

The four studied by-products and all glasses were analysed using X-ray fluorescence (XRF) spectroscopy (wavelength dispersive Philips PW2440 sequential X-ray fluorescence spectrometer) and results are presented in Table 1, 2 and 4. Uncertainties associated with these measurements are conservatively estimated to be ±2% of measured concentrations. Optical absorption spectra were measured using a Varian 50Scan UV-Visible-near-IR spectrophotometer over the wavelength range 300-1100 nm. The repeatability of measured absorbance data was confirmed by measuring each sample three times.

Liquidus temperature (T_{liq}) was measured using a temperature gradient furnace. Pieces of sample glass were placed in a platinum boat and held for 24 h in the furnace, with a known temperature gradient measured for each sample with a calibrated thermocouple. Liquidus temperature was measured by observing the sample using a polarised light microscope and deriving the corresponding temperature above which no crystals were present.

Thermal expansion coefficient, dilatometric softening point (T_d) and glass transition temperature (T_g) measurements were obtained from dilatometric analysis of bulk samples and are given in Table 5. A calibrated Netzch DIL-402PC dilatometer connected to a computer was used for these measurements, with a heating rate of 10 ^{o}C / minute.

Measured densities of all glasses are shown in Table 5. Densities were measured by the Archimedes method using distilled water as the suspension medium. Densities were calculated using:

$$\rho = [\frac{W_A}{W_A - W_W}]\delta_w$$

where ρ= density in g cm^{-3}; W_A= weight in air; W_W= weight in water and δ_W = water density with temperature correction.

Key viscosity points including melting point, working point, softening point and annealing point, were modelled using the Lakatos and Fluegel models and are listed in Table 5. The relative machine speed (RMS), working range index (WRI) and devitrification index [1][3] were also calculated for each glass and are included in Table 5. Relative machine speed (RMS) is a term widely used in glass manufacturing, and is defined as the relative average speed at which articles can be produced using a particular glass composition. Compositional changes have previously been used to modify RMS [1]:

$$RMS = \frac{S - 450}{(S - A) + 80}$$

where S = softening point / °C, defined as log (η / dPa·s) = 7.65 and A = Annealing Point / °C, defined as log (η / dPa·s) = 13.0. Working range index (WRI) is defined as the temperature difference in temperature between the softening point S and the annealing point A [32]. WRI is used as an indicator of the working range and should not be confused with the actual working range. For most commercial soda-lime-silica container glasses, WRI > 160°C [44]:

$$WRI = (S - A)$$

The devitrification index (D) has previously been used to estimate the likelihood of devitrification problems [44]. A positive value of D indicates relative freedom from devitrification while a negative value of D indicates increasing likelihood of devitrification, particularly if the glass is fed to the forming machine at relatively low temperatures or high viscosities, for example, during the manufacture of large articles [1]:

$$D = WRI - 160°C$$

where WRI = working range index, as defined above. Values of D vary; however, +15 is now common in the global container glass industry [1].

3. Results

The normalized XRF analyses for four samples industrial by-products (seashell waste, eggshell waste, rice husk ash and biomass ash) are given in Table 1. More than 98wt % of the oxide composition of seashell waste and eggshell waste is analysed to

be CaO, although XRD confirms this is in fact present in the form of $CaCO_3$ (XRF does not detect carbon). For rice husk ash, more than 95wt % of the oxide composition is SiO_2, and biomass ash can be considered a source of Al_2O_3, SiO_2 and CaO, amongst several other oxides. Toxic or undesirable elements such as Pb or Cl are present at such small levels so as to be below the limits of detection for the XRF programme used. The content of Fe is also very low in seashell waste and rice husk ash. By comparison, the Fe content of the biomass ash sample is somewhat higher.

To improve understanding of the waste materials and how they might perform as raw materials in the glass melting process, samples of each waste were analysed using X-ray diffraction in order to identify the nature of crystalline phases and the degree of crystallinity present within the waste. For phase identification, a summary of the results is shown in Figure. 1.

It can be seen that both the eggshell and seashell wastes have a high degree of crystallinity and that the calcium is present in the form of $CaCO_3$; this suggests that these materials seem likely to have similar (although not necessarily identical) effects on the glass melting characteristics as limestone. The majority of the biomass ash and nearly all of the rice husk ash is in the amorphous phase, with some level of crystalline phases including quartz and mullite also identified. The presence of high levels of amorphous content suggests that these materials may form liquid phases more readily than the crystalline materials they partially replace during glass melting, and thus may require less energy to melt (owing to the absence of latent heats of melting associated with changes of state, combined with no decomposition reactions

to drive) compared with the standard raw materials such as silica sand, soda ash or limestone. This could conceivably enable specific energy consumption (SEC) savings through reducing the time the raw materials need to spend in the furnace in order to fully dissolve sand grains and completely form the liquid phase [45][46].

Table 4 shows the compositions of all benchmark and modified / reformulated glasses, analysed by XRF. As expected, the GC series glass compositions show little variation with partial replacement of raw materials. For the CC and F series glasses, the variation of final glass composition is consistent with that of the nominal compositional design. The XRF results indicate that any contamination of the glasses from dissolution of the Al_2O_3 crucibles in which they were melted, is small to negligible. This was evidenced by a lack of clear corrosion "fluxline" attack on the crucibles post-melting，and supported by the low surface area (crucible) to volume (glass melt) ratio for these large 1.3kg glass melts. It is also important to note that the Li_2O and B_2O_3 contents of the glasses could not be analysed by XRF, and hence we have assumed zero losses due to volatilisation during melting. Whilst there is some evidence that relatively small amounts of alkali and boron species can indeed be evolved in gaseous forms during glass melting (e.g. see [1] and references therein), again we believe that the low surface area (crucible) to volume (glass melt) ratio for these large 1.3kg glass melts can reasonably be expected to reduce such volatilisation to very low levels, under the melting regime used here. However, the possibility of low levels of Li and B losses cannot be discounted entirely.

Table 5 shows the measured and modelled properties of the glasses produced. It

is important to note that all viscosity models will give an overall view of trends in viscosity, but only measured values can be guaranteed to be absolutely accurate. For example, as shown in Table 5, measured mid-point glass transition temperatures, T_g, for each glass are generally higher than the corresponding modelled value (TLog13, or the temperature corresponding to log (η / dPa·s) = 13). Although the measured mid-point T_g values are typically ca. 20 ^{o}C greater than corresponding modelled T_g values, the overall trends in T_g are mirrored. All glass samples have been confirmed by XRD to be X-ray amorphous, with no detectable levels of crystallinity. Measured glass densities exhibited values close to 2.50 g/cm^3, and small variations above and below this value can be attributed to the effects of variations in glass composition. Glass transition temperature, dilatometric softening point and coefficient of thermal expansion exhibit modest variations between glass samples. To display the composition modification impacts on the glass viscosity-temperature relationship, the η-T curves for each glass in CC series were plotted in Figure 3. UV-Visible-near-IR spectra of glass samples are presented in Figure 2. As shown in Figure 2 (a), the absorption spectra of samples CC_B, CC_R1 and CC_R6 are closely similar, indicating equally similar colouration and redox properties (e.g. $Fe^{2+}/\Sigma Fe$ ratios). In Figure 2 (b), the absorption spectra of the green GC series glasses, produced with varying types of additions, are presented. The intensities of the absorption bands centred at 450 nm and 660–700 nm in samples GC_B and GC_B_SS are lower than those of sample GC_B_WA, and the broad absorption band centred at 1050 nm is present in all three samples.

4. Discussion

4.1 Glass composition reformulation

As discussed in the previous section, the purpose of glass compositional reformulation here was to reduce the melting temperature of SLS glass by comparison with the benchmark compositions. The action of alkaline and alkaline earth elements on SLS glass melts is well understood [1] and it is possible to predict their effects on the η-T properties of the final glass melt [23][24][25].

For colourless glass CC_R6, a fraction of the MgO was substituted by K_2O. Addition of MgO to commercial container and float-type glasses in the SLS system can enable reductions in T_{liq} and crystallization rate [1]. This is the principal reason why float glass typically has a considerably higher MgO and lower CaO content than container glass. As MgO replaces CaO on a weight % basis in SLS glasses, the melt viscosity increases at high temperatures close to the melting temperature [1][47], whilst it tends to decrease melt viscosity at lower temperatures closer to T_g [23]. Additions of MgO tend to decrease the activation energy for viscous flow and provide a 'longer' glass. For potassium additions, the field strength of K^+ is lower than that of Na^+. K_2O decreases viscosity at high and lower temperature,[47][48] but not as drastic as Na_2O, also providing a 'longer' glass. It can strongly decrease surface tension and is more volatile than Na_2O [47]. Meanwhile, K_2O, as an alkali metal, is more capable of providing non-bridging oxygens and depolymerising the Si-O-Si network than CaO, as an alkaline earth metal. To reduce the melting temperature of glass without negatively affecting the features or shape of the η-T curve, a limited amount of K_2O

was added to replace MgO. As shown by the modelled viscosity for glass CC_R6 in

Table 5, the viscosity of glass CC_R6 is lower than that of the benchmark glass CC_B

at each point by 17 ^{o}C to 7 ^{o}C, which indicates that viscosity decreases overall as the

composition was modified from glass CC_B to glass CC_R6, but with small changes

in the overall profile of the η-T curve. From measured properties, the T_{liq}, T_d, T_g and

Littleton softening point of glass CC_R6 are lower than those of, but not greatly

different from, the benchmark glass CC_B. The thermal expansion coefficient of glass

CC_R6 is also, somewhat surprisingly, not significantly higher than that of glass

CC_B upon substitution of MgO by K_2O. The temperature difference between the

forming temperature and the liquidus temperature of glass CC_R6, ΔT_{FL}, is -11°C.

For container glass, liquidus temperature is generally 10-20°C below the working

point (TLog4, where log(η/ dPa·s) = 4), and hence the likelihood of crystallization

during forming is kept to a minimum [3]. Compositional changes may be sufficient to

produce a negative value of ΔT_{FL}, increasing the risk of devitrification problems

during forming. Whether this problem occurs during glass production depends on how

long time the glass stays within, or how quickly the glass passes through, this

temperature range during conditioning and forming, which reflect the structure and

pull rate of the furnace and forming operations. Some of the present authors have

received anecdotal evidence that some manufacturers can operate with negative ΔT_{FL}

quite safely in the UK [3] and China. This may partly explain why the specific

process parameters between different manufacturers and even different furnaces and

forming operations can be different from one another, with each having good reasons

based on experience, but all still processing container glasses satisfactorily for that particular furnace and glass composition, conditioning and forming operation. Whilst flexibility in production clearly exists, nevertheless the ΔT_{FL} parameter remains an excellent guide and reference point for risk analysis (and mitigation) in glass manufacture. The RMS, WRI and DI of glass CC_R6 are all in the appropriate range. However, the thermal expansion coefficient is the highest among those four different glasses.

Lithium ions, like potassium ions, have a similar effect on reducing the viscosity of molten glass; therefore, direct substitution of sodium ions by either lithium or potassium can provide alternative routes to reducing the melting point. Previous research [49] has indicated that SLS glass batches containing Li_2CO_3 reacted at lower temperatures and more completely before melting compared with Li_2CO_3-free batches. Secondly, unlike the alkalis Na^+ and K^+, Li^+ tends to increase the surface energy [50]. For glass melts containing Li^+, the surface energy increases more noticeably when the temperature is decreased. Container glasses containing Li_2O set more quickly in a mold without viscosity changes for Li_2O increasing the surface energy and its temperature dependence. A small amount of Li_2O could give a noticeable surface energy variation that may benefit the glass forming controlling process [50]. Lithia (Li_2O) is a strong melting flux and accelerant for SLS glass and small additions produce large decreases in melt viscosity. In Tang and Frischat's [36] research, chemical durability of SLS glass was substantially improved upon addition of only 0.18 wt% Li_2O. This improvement was attributed to the mixed alkali effect and to the

high field strength of Li^+ by comparison with Na^+, which strengthens the glass network.

For colourless container glass CC_R1, 0.3 wt. % Li_2O was introduced in addition to increasing K_2O content from 0.33 wt. % to 0.65 wt. % to substitute for SiO_2. From the property modelling results, the overall CC-R1 viscosity curve shifts to lower temperature compared to the benchmark glass CC_B. The value of ΔT_{FL} is 37^oC, which is strongly positive; T_d and T_g are lower than those of glass CC_B. However, the thermal expansion coefficient is higher than that of the benchmark glass (CC_B). The RMS, WRI and DI of glass CC_R1 are all in the appropriate range.

For glass CC_I4, reformulation included introduction of 1 wt. % B_2O_3 to substitute for a proportion of the MgO. This was combined with substituting a proportion of the Na_2O by CaO. It is known that B_2O_3 enables melting acceleration in SLS glass melts at low addition levels [51]. The peak period for incorporating small amount of B_2O_3 for UK and USA container glass manufacturers was from the 1920s to 1930s [1][3][51]. Nowadays, B_2O_3 has generally been removed from most Western container glass batches for it needs to be imported (e.g. Turkey), and is therefore costly, and its potential H&S issue in bottle glass manufacture. Previous research indicated the benefits of adding low levels of B_2O_3 and borate raw materials, such as reduced melting and refining times, decreased liquidus temperatures, and reduced crystallization rates [1][51]. All of these conclusions can be explained from a glass chemistry perspective [47][48]. B_2O_3 can exist in oxide glasses as $[BO_3]$ triangles or $[BO_4]$ tetrahedra, the interconversion of $[BO_3]$ and $[BO_4]$ units with each other under

different conditions could affect several glass properties, an effect named the 'boron anomaly'. At high temperatures and low contents in silicate glasses, boron usually exists as [BO$_3$] trigonal units, and reduce the high temperature viscosity and melting temperature [47][48]. However, B^{3+} can also form [BO$_4$] tetrahedral by acquiring charge balance from, for example, alkali cations, and can thereby join the (boro)silicate network increasing glass melt viscosities at lower temperatures, and enhancing the chemical durability of the glass. Additions of B$_2$O$_3$ can also decrease the surface energy of glass melts [1]. Calcium ions, Ca^{2+}, introduces non-bridging oxygens and depolymerizes the silicate network and thus can reduce high temperature viscosity of silicate melts [48]. Typically, CaO in container glass compositions is higher than CaO contents float glass, one reason being in order to 'shorten' the glass η-T profile to meet glass article forming process requirements. In typical boro-silicate glasses, the CaO contents are kept to a minimum or to reduce the tendency for devitrification [47]. However, the amount of B$_2$O$_3$ added to the SLS glasses studied here is very low (ca. 1 wt. %), thus there was no need to substitute part of Na$_2$O with CaO in glass CC_I4 to further reduce melting temperature, enhance chemical durability or counter the effects of B$_2$O$_3$ in "shortening" the η-T profile. From the modelled viscosity of glass CC_I4 in Table 5, the temperatures at viscosity (TLog2, TLog3 and TLog4) are all lower than that of the benchmark glass, CC_B. Above TLog6, the temperatures are almost the same as for glass CC_B. Measured T$_d$ and T$_g$ are almost the same as for glass CC_B. However, the ΔT$_{FL}$ of glass CC_I4 is -31°C. It is the lowest among these 4 colourless container glasses studied, which indicate an

increased risk of devitrification issues arising during forming.

As an important sub-sector of the glass industry, float glass was also included in this study. Compared to container glass compositions, the CaO/MgO ratio of float glass is lower, in order to achieve 'longer' glass to adapt to the float glass forming process, combined with the beneficial effects on liquidus temperature and crystallisation rates noted earlier. Based on a typical commercial UK float glass composition in the benchmark glass, F_B, it was decided to substitute 3 wt.% SiO_2 by a combination of CaO, MgO and Na_2O (glass F_R4). The melting temperature (TLog2) of glass F_R4 was decreased from 1471^oC to 1416^oC. From the modelling results, the overall η-T curve for glass F_R4 shifts towards lower temperatures compare to glass F_B. The measured liquidus temperature of glass F_R4 increased from 914^oC to 972^oC, but the measured T_d and T_g temperatures decreased. Although the ΔT_{FL} of glass F_R4 is positive, it decreases from $+123 \, ^oC$ for glass F_B to $+36 \, ^oC$ for glass F_R4. The thermal expansion coefficient of glass F_R4 was slightly increased due to increases in the alkali and alkali earth contents. The WRI and DI decreased but remain in an appropriate range.

4.2 Alternative glass raw materials/waste streams and impact on glass properties

4.2.1 Selected alternative raw materials/waste streams

There is a great potential for both agri-food and industrial waste streams to be recycled as effective and sustainable resources for the raw materials used to produce glass and the valorisation of waste in the manufacture of glass has been previously

considered [2][52]. The mineral content and chemical composition of waste streams are key factors determining the potential feasibility and extent of use of such by-products in an economical and energy-efficient manner for the manufacture of glass at industrial scale.

Following the impending scarcity of fossil fuels and their increased price, as well as environmental concerns has led to renewed interest in the use of biomass for power generation, with the additional promise of employment in rural economies. There are a growing number of biomass power stations within the UK using biomass sources to generate electricity, including the large Drax power station in the north of England which supplies 7-8% of all UK electricity. There are wide range of biomass fuels that are used in biomass power generation, including wood pellets, waste wood (of various grades), wheat straw, miscanthus, poultry litter and meat and bone meal. Biomass power plants generate between 1.5-2MT of waste ash each year [53]. Each power plant will typically only use one type, or at most 2-3 types, of waste stream. Ashes from different plants may thus differ significantly. There may also be some variability in the nature of the fuel feedstock over time (e.g. due to seasonal variations in weather, different suppliers or different soil types). A number of UK biomass ash generators were identified and ash samples were collected for analysis in this research. It was found that the surveyed UK biomass ashes are rich in useful (for glass manufacture) alkali and alkali-earth metals (K, Na, Ca, Mg) and contain widely varying levels of other components depending upon the plant and processes used. A typical UK biomass ash was studied as a potential alternative raw material for glass

manufacturing in this research, and further studies on biomass ashes as potential glassmaking raw materials are in progress [42].

Seashells have been historically used within concrete to make a specific type of building material called "Tabby". The material was mainly used during the late 1800's in coastal areas. Tabby is made from equal parts of lime, water, sand, oyster shells, and ash [54]. Seashells were also historically present in many of the sand sources used for Roman glassmaking, and were thus at least partly responsible for the CaO contents of the resulting glasses [55]. More recently, given the fast growth of the mussel and other seashell farming industries around the world, and the subsequent increased amounts of seashell waste, there have been several studies into developing new applications for seashell wastes. Given that seashells are a relatively pure, calcium-rich material, they can represent an alternative source for calcium carbonate for potential application in the pharmaceutical, agricultural, construction and / or paper industries. A detailed report on the potential applications of shellfish by-products was compiled by ADAS UK in 2006 [43]. Wastes arising from the UK seafood industry are widely dispersed, largely around the coastline of the UK, with no particular region dominant and no organised collection / recycling system. The largest quantities are produced in South West Scotland, Eastern England, Northern Ireland, Central Scotland and South West England. Although the average disposal cost per tonne varied somewhat between areas, the typical cost was £40 - £45 per tonne of waste. Use of seashell-based by-products in SLS glass production would not constitute a high-value application but it would be an effective, resource-efficient

re-use option for the increasing volumes of this waste stream. Therefore, in this study, seashells supplied by an UK commercial supplier were used to replace limestone in the representative SLS glass batches.

Egg and egg derivative consumption generate a great volume (>100 kT / year in the UK alone) of residual shells. An important ingredient of eggshells is calcium carbonate which can be potentially used in various applications as a source of calcium oxide or calcite. Eggshell wastes primarily contain magnesium and calcium carbonates, and protein [56][57]. The calcium oxide obtained from calcined eggshells could be potentially used in various applications such as in the starting materials for dielectrics such as $CaSiO_3$, $CaTiO_3$, $CaAl_2O_4$, and also in gypsum ($CaSO_4$) or as bio-catalysts [58]. Given the purity of eggshell powder obtained for this study (the heavy metal content was extremely low); eggshells were considered as a substitute for limestone for use in the production of both clear and green container glass, in this study.

Rice husk (RH), an agricultural waste, is abundantly available in rice producing countries including China, India, Brazil, US, and throughout South East Asia. Rice husk ash (RHA) has been widely considered for its potential applications in industrial applications such as processing of steel, cement and refractory industries [59]. RHA is not, at present, readily available in the UK and therefore must be imported. However, its potential use in the production of coloured glass has been previously reported [13]. Hence, from a scientific perspective, RHA was considered an interesting material for use in the production of clear container glass in this study.

4.2.2 Alternative raw materials impact on green container glass melting

According to the XRD and XRF analysis results of the obtained waste materials, the composition and degree of crystallinity present within each waste are presented. For seashell and eggshell wastes, more than 98 wt. % are calcium oxide. These could therefore be quite pure sources of CaO, with low levels of iron; the main crystalline phases present are identified as calcite and aragonite respectively. For rice husk ash, 98 wt.% is SiO_2 (mostly amorphous). This material could thus provide the potential for a pure, lower energy consumption, alternative SiO_2 source for glass manufacture. The composition of biomass ash is relatively complex and it is thus more challenging to be recycled as glass raw materials. From the XRF results, RHA also contains chloride and phosphate which are not currently present in commercial SLS glass compositions. Chloride can be volatile and can increase corrosion of furnace refractories. Its emissions are also limited by emissions regulations. Uncontrolled phosphate in SLS glass can lead to phase separation and crystallization during melting process, if present at levels above approximately 1.5 weight % [60] .The 9.5 wt. % Fe_2O_3 present in this RHA sample will impart a green / blue glass colour; the 1.07 wt. % TiO_2 will slightly decrease melt viscosity whilst the 18.17 wt. % of Al_2O_3 will substantially increase the melt viscosity. From XRD analysis, the presence of the high temperature phase, mullite, could potentially cause defects in final glass products unless it is present as very small crystallites that can rapidly dissolve in the glass melt. Another issue may be the presence of residual carbon, which was not detected by

XRF. Arising from incomplete combustion of the fuel, there may be carbon-containing residues in biomass ashes which can impact on the redox status of the melting glass.

Based on a typical GC_B green glass composition, seashell (GC_B_SS) and biomass ash (GC_B_WA) were added without significant variation of final glass composition. As shown in Table 4, the heavy metal contents of glasses made with the waste-derived raw materials were not substantially greater than the benchmark glass. The P_2O_5, Cl and TiO_2 present in biomass ash were diluted and not present at significant levels in glasses GC_B_WA and GC_ B. The viscosity of the green GC series of glasses was also modelled based on the XRF results. The η-T curve of glass GC_B_SS is close to that of the benchmark glass, GC_B. However, the viscosity of glass GC_B_WA increased for the compositional variation due to the introduction of the biomass ash. The ΔT_{fl} of glass GC_B_WA also decreased from +35 to -9 ^{O}C, which indicates an increased risk of devitrification problems during conditioning or forming.

As new raw materials, seashell and biomass ash have characteristic effects on final glass quality. The alternative raw materials can have a moderately reducing effect on redox conditions during melting due to organic residual protein in seashell and unburned residual carbon in biomass ash. This reductive carbon affects the partial pressure of oxygen ($p O_2$) in and above the glass melt in the furnace and can, in some circumstances, potentially lead to problems with final glass colour and refining. Most importantly, glass colour will be affected, as the Fe^{2+}/Fe^{3+} ratio varies with $p O_2$ [61]

and under strongly reducing conditions the well-known Fe^{3+}-S^{2-} amber chromophore can form [62][63][64]. Under less reducing conditions than those required to form full amber colour, an olive-green colour can form [63][64]. Such colours may be undesirable if the aim is to manufacture a green glass. On the other hand, such behaviour may actually prove beneficial in amber glass production, although this was outside the scope of the present study.

The UV-Vis spectra for the colourless container (CC series) and green container (GC series) glasses are presented in Figure 2. The spectra indicate that the reformulated CC glass composition is almost the same, in terms of optical transmission properties, as the benchmark glass. A weak optical absorption band centred at 380 nm appears in all three spectra, which can be attributed to the $^6A_1(S)\rightarrow$ $^4E(D)$ transition of tetrahedrally coordinated Fe^{3+} cations [45]. Theoretically, network modifiers in silicate glass can produce a significant shift of the UV edge to longer wavelengths [65]. However, the impurities and colourants in glass produce considerably greater impacts on UV edge position. For example, Fe^{3+} and Fe^{2+} both produce very strong oxygen-metal charge-transfer (OMCT) bands centred in the deep UV. These have tails which reach into visible regions, thus UV edge positions and profiles in commercial silicate glasses tend to be dominated by the effects of iron impurities (clear container and float glass) and both iron and chromium impurities (green container glass).

For some transition metal ions UV-Vis absorption spectra can not only characterize the colour properties of glass, but also help to assess the redox state of

different glasses from the relative intensity of spectral components. In Figure 2 (b), as a practical commercial green container glass, GC_B shows a typically UV-Vis absorption spectrum. It is well known that glass redox status can be estimated through the Fe^{2+}/Fe^{3+} or $Fe^{2+}/\Sigma Fe$ ratio [66][67]. The optical absorption band centred at 380 nm is attributable to the $^6A_1(S) \rightarrow {}^4E(D)$ transition of tetrahedrally coordinated Fe^{3+} cations [65][67]; A broad optical absorption band cantered at a wavelength of slightly higher than 1000 nm is attributable to the $^5A_2(S) \rightarrow {}^5E(D)$ transition of octahedrally coordinated Fe^{2+} cations [65][67]. For the small amount of Cr that does exist in glass, Cr^{3+} exhibits a distinctive absorption spectrum with a strong, split, broad band centred at 660–700 nm attributable to the $A_{2g}(F) \rightarrow {}^4E_{2g}(F)$ transition; and another band with similar intensity occurring at ~450 nm, attributable to the $A_{2g}(F) \rightarrow {}^4E_{1g}(F)$ transition [68]. For glass GC_B_SS, the strength of the ~1000 nm absorption band is greater than for the benchmark glass, GC_B, which indicates increasing $Fe^{2+}/\Sigma Fe$ ratio. The absorption band at ca. 450nm moves towards shorter wavelengths and can be attributed to the appearance of a new absorption band centred around 410 nm, which has been attributed to tetrahedrally-coordinated Fe^{3+} ions surrounded by three O^{2-} ions and one S^{2-} ion [69]. This combined presence of Fe^{3+} and S^{2-}, which can occur in silicate melts prepared under reducing conditions. ($pO_2 < {\sim}10^{-6}$ bar) [70][71] gives rise to the well-known 'amber' chromophore. For glass GC_B_WA, the intensity of absorption at 410 – 450 nm increases and moves towards shorter wavelengths compared to the benchmark glass, GC_B.

The redox status of the green container GC series glasses that contained the

studied waste streams are thus shown to be melted under more reducing conditions than the baseline glass. Combining with the characterization results and discussion of seashell and biomass ash wastes discussed previously, it is clear that these impure, carbon containing, alternative materials do have impact on the redox status of SLS green glass. As an exploratory study, this issue has been fully demonstrated and discussed. However, it is also clear that such effects can be mitigated, and also suggest potential applications for these wastes in amber glass manufacture. Moreover, this result may serve as a guide to help biomass power plants "tailor" their by-products to minimise carbon contents through process control, thereby valorising their by-products to generate additional revenue whilst enabling more widespread applications for the products of their processes.

5. Conclusions

Exploratory reformulation research based on representative industrial colourless container and float soda-lime-silica glasses was delivered with the aim of modifying properties to enable energy-saving, CO_2-reducing glass manufacture. Four different reformulation methods (including partially replacing SiO_2 with other alkali and/or alkali earth oxides; or introducing new oxides Li_2O and B_2O_3) were applied. Compared to the benchmark glasses, melting temperatures (the temperatures corresponding to log $(\eta / dPa \cdot s) = 2$) of reformulated glasses were reduced by up to 55^oC. Reformulation impacts on multiple properties of glass, including viscosity-temperature relationship, thermal expansion, forming performance and

colour. These effects are non-negligible and need delicate balance. A general waste investigation and review studied the introduction of four different wastes (seashell waste, eggshell waste, biomass ash and rice husk ash), into glass manufacture. Samples of each waste were identified and characterized. Seashell and biomass ash were exploratorily introduced into a representative green container glass as alternative raw materials. Both additions impacted on the colour and redox status of the glasses, highlighting both the need to control carbon content in such ashes; and the potential opportunities to use such wastes in amber glass manufacture.

Acknowledgements

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Figure caption

Figure 1:   XRD patterns for (a) Eggshell waste, (b) Seashell waste, (c) Biomass ash, (d) Rice husk ash.

Figure 2 a) UV-Vis spectra for base and reformulated green container (GC series) glasses; b) base and introduced waste stream green glasses.

Figure 3 Fitted viscosity curves of CC group glasses by Lakatos' viscosity modelling results in Table 5.

Table caption

Table 1. Analysed (XRF) oxide composition (weight %) of studied waste materials.

Table 2. Glass batch recipes for each glass type (weight %)

Table 3. Nominal benchmark glass compositions (weight %) for each glass type.

Table 4. XRF-analysed compositions (weight %) of benchmark and modified / reformulated glasses.

Table 5. Results from viscosity modelling and characterization of glasses (viscosity in dPa·s)

Table 1. Analysed (XRF) oxide composition (weight %) of studied waste materials.

Wt%	Seashell	Eggshell	Biomass Ash	Rice Husk Ash
SiO_2	0.34	0.00	39.13	95.05
Al_2O_3	0.15	0.00	18.17	0.00
Na_2O	0.54	0.31	1.46	0.19
K_2O	0.00	0.12	8.87	1.15
CaO	98.30	98.43	14.55	0.97
MgO	0.04	0.52	2.41	0.84
TiO_2	0.00	0.00	1.07	0.00
Fe_2O_3	0.00	0.00	9.60	0.15
SO_3	0.11	0.20	2.09	0.16
P_2O_5	0.03	0.24	1.29	1.25
Cl	0.06	0.11	0.17	0.00
Others	0.43	0.07	1.19	0.24
SUM	100.00*	100.00*	100.00*	100.00*

*XRF analysis does not include any C or H present in these materials, e.g. carbonate or water.

Table 2. Glass batch recipes for each glass type (weight %)

Wt %	Colourless Container Glass Benchmark	Reformulated Colourless Container Glass Batches			Green Container Glass and Waste Blended Glass Batches			Float Glass Benchmark	Reformulated Float Glass Batch
	CC_B	CC_I4	CC_R6	CC_R1	GC_B	GC_B_SS	GC_B_WA	F_B	F_R4
Brown Sand	-	-	-	-	61.18	61.23	61.13	-	-
White Sand	58.92	57.13	55.92	56.87	-	-	-	59.56	55.64
Soda Ash	18.63	18.93	19.40	19.79	18.26	18.18	18.12	18.91	19.72
Limestone	13.33	16.09	17.62	17.72	12.90	-	13.93	8.59	5.97
Eggshell Waste	-	-	-	-	-	-	-		
Seashell Waste	-	-	-	-	-	12.99	-	-	-
Nepheline Syenite	2.80	2.81	2.81		-	-	-	1.02	1.06
Saltcake	0.37	0.37	0.37	0.39	0.27	0.22	0.17	0.35	0.34
Dolomite	3.32	-	-	-	2.85	2.85	3.70	11.57	17.27
Colemanite	-	2.07	-	-	-	-	-	-	-
Biomass Ash	-	-	-	-	-	-	1.77	-	-
Iron Silicate	-	-	-	-	0.43	0.40	-	-	-
Calumite	2.63	2.60	2.60	0.98	4.08	4.10	1.15	-	-
Spodumene	-	-	-	3.47	-	-	-	-	-
Cr_2O_3	-	-	-	-	0.03	0.03	0.03	-	-
K_2CO_3	-	-	1.28	0.78	-	-	-	-	-
SUM	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 3. Nominal benchmark glass compositions (weight %) for each glass type.

Wt %	Colourless Container Glass Benchmark	Reformulated Colourless Container Glass Batches			Green Container Glass andWaste Blended Glass Batches	Float Glass Benchmark	Reformulated Float Glass Batch
	CC_B	CC_I4	CC_R6	CC_R1	GC_B (SS and WA)	F_B	F_R4
SiO_2	72.00	70.00	69.00	71.00	71.00	72.06	68.92
Al_2O_3	1.50	2.00	1.50	1.00	2.00	0.70	0.70
Fe_2O_3	0.05	0.05	0.05	0.05	0.50	0.00	0.08
CaO	11.25	12.00	13.00	12.25	11.25	10.10	10.70
MgO	1.15	0.65	0.70	0.15	1.15	3.00	4.56
Na_2O	13.30	13.55	14.00	14.00	13.30	13.60	14.50
K_2O	0.50	0.50	1.50	0.80	0.60	0.30	0.30
SO_3	0.25	0.25	0.25	0.25	0.17	0.24	0.24
Cr_2O_3	0.00	0.00	0.00	0.00	0.03	0.00	0.00
P_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B_2O_3	0.00	1.00	0.00	0.00	0.00	0.00	0.00
Li_2O	0.00	0.00	0.00	0.50	0.00	0.00	0.00
SUM	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 4. XRF-analysed compositions (weight %) of benchmark and modified/reformulated glasses.

wt %	CC_B	CC_I4	CC_R6	CC_R1	GC_B	GC_B_SS	GC_B_WA	F_B	F_R4
SiO_2	73.14	72.89	72.43	71.96	72.02	71.84	72.69	73.96	70.99
Al_2O_3	1.34	1.34	1.37	1.36	2.23	2.21	2.23	0.44	0.45
Fe_2O_3	0.03	0.03	0.03	0.02	0.47	0.48	0.35	0.04	0.05
CaO	10.79	11.05	11.12	11.50	10.36	10.77	10.06	9.19	9.73
MgO	1.05	0.35	0.30	0.15	1.08	1.07	1.04	2.62	3.90
Na_2O	13.14	12.80	13.21	13.79	12.70	12.50	12.38	13.48	14.47
K_2O	0.33	0.32	1.33	0.65	0.97	0.97	1.09	0.13	0.15
TiO_2	0.05	0.05	0.05	0.03	0.09	0.09	0.08	0.02	0.02
SO_3	0.13	0.16	0.15	0.23	0.05	0.04	0.04	0.22	0.22
Cr_2O_3	0.00	0.00	0.00	0.00	0.03	0.03	0.03	0.00	0.00
Pb (ppm)	9.3	10.5	9.3	21.8	15.3	13.6	15.0	9.9	8.8
Cd (ppm)	1.6	5.0	4.3	4.1	4.2	5.7	3.3	1.6	2.7
Li_2O	0.00	0.00	0.00	0.30†	0.00	0.00	0.00	0.00	0.00
B_2O_3	0.00	1.01†	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SUM	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

† Lithium and boron contents were not analysed and the percentages shown are based on theoretical contents from batch calculations.

Table 5. Results from viscosity modelling and characterization of glasses (viscosity in dPa·s)

			CC_B	CC_I4	CC_R6	CC_R1	GC_B	GC_B_SS	GC_B_WA	F_B	F_R4
Modelled Properties	Viscosity (°C) calculated by Lakatos model	TLog2	1463	1452	1446	1413	1475	1470	1492	1471	1416
		TLog3	1190	1177	1175	1146	1198	1197	1211	1192	1152
		TLog4	1035	1025	1023	998	1041	1041	1051	1037	1008
		TLog6	806	809	796	775	813	814	818	805	788
		TLog7.6	743	741	735	716	744	747	749	739	724
		TLog13	563	560	556	545	564	566	566	556	552
	Relative Machine Speed		1.125	1.116	1.102	1.061	1.132	1.139	1.136	1.1	1.086
	Working Range Index (°C)		181	181	178	170	180	180	183	182	172
	Devitrification Index (°C)		21	21	18	10	20	20	23	22	12
	Viscosity (°C) calculated by Fluegel model	TLog2	1459	1440	1444	1436	1467	1465	1479	1458	1416
		TLog3	1200	1191	1188	1183	1205	1204	1215	1200	1166
		TLog4	1034	1030	1024	1020	1037	1037	1045	1033	1005
		TLog6	834	834	825	824	835	836	840	829	809
		TLog7.6	736	738	729	729	736	738	739	729	714
		TLog13	564	569	561	562	563	566	564	552	546
Measured Properties	XRD		amorphous	amorphous	amorphous	amorphous	amorphous	amorphous	amorphous	amorphous	amorphous
	$\rho \pm 0.005$/g cm^{-3}		2.496	2.517	2.516	2.511	2.515	2.511	2.497	2.491	2.508
	a x 10^{-6} / °C ±2/°C		7.63	7.77	8.44	8.02	7.83	7.99	7.75	7.7	7.85
	T_{liq} (°C) ±10/°C		995	1057	1034	961	1006	984	1060	914	972
	T_d (°C) ±2/°C		650	644	630	627	636	644	635	632	628
	T_g (°C) ±2/°C		598	596	583	573	582	586	586	582	577
	Littleton softening point ±5/°C		750	760	740	725	745	750	745	745	730
	ΔT_{fl} /°C (calculated from T_{liq} and T_f)		41	-31	-11	37	35	57	-9	123	36