Hydrolysis of eutectic compositions in the ZnCl$_2$:KCl:NaCl ternary system and effect of adding ZnO

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ABSTRACT

Molten salt systems have been considered as proper liquefiers, solvents and transfer media due to their transport and thermodynamic properties. Employing molten salts to liquify biomass could be performed to make it pumpable and transfer it more easily through thermochemical conversion processes to e.g. bio-oil. The first challenge for this application is to find a salt with relatively low melting point. It needs to be low enough to avoid producing ash or char and at the same time high enough to liquify biomass. The selected molten salt requires high thermal stability to avoid salt decomposition at high temperatures and make salt recycling possible. Another challenge is minimising the hydrolysis rate of the molten salt in contact with water molecules originated from the biomass, because this can lead to undesired formation of highly corrosive acids. ZnCl$_2$:KCl:NaCl is a promising molten salt with relatively low melting point, high thermal stability and good properties in contact with biomass. The objective of this work is to investigate the properties of the eutectic mixtures of ZnCl$_2$:KCl:NaCl that are of importance for thermochemical conversion of biomass. Four compositions of ZnCl$_2$:KCl:NaCl are investigated, including Salt #1: 60: 20: 20, Salt #2: 59.5: 21.9: 18.6, Salt #3: 52.9: 33.7: 13.4 and Salt #4: 44.3: 41.9:13.8 in mole fraction. Salt #4 is found to exhibit the best properties, with low melting point, the highest thermal stability and the lowest hydrolysis rate. Salt #1 had the highest hydrolysis rate. However, addition of ZnO showed a marked, limiting effect on the hydrolysis, especially at temperatures below 400 °C.

1. Introduction

Molten salts have been used in various applications since the 19th century and their technologies are still under development [1,2]. One of the molten salt usages which has attracted a lot of attention in recent years is their role in the emerging renewable energy applications such as thermochemical conversion of biomass. In the late 20th century, molten salts were employed to develop pyrolysis of biomass in a few studies. The results showed that using molten salts could improve the yield production of for example phenolic compounds [3–5]. This is indicating that the molten salt could have catalytic effects. Another possible advantage is that the heating rate of biomass particles in molten salts is found to be higher than in inert atmosphere [6] or in a fluidized sand bed [7].

Some challenging technical issues are still unresolved, for example feeding the solid biomass into the reaction unit. The complexity of this increases for high pressure reactor such as hydro pyrolysis. Problems such as plugging, clogging, leakages, and uneven flow all lead to low production rate and poor quality. Liquifying biomass before feeding it into the high-pressure pyrolysis reactor can resolve the mentioned

problem. It can facilitate pumping of the biomass and thus give better control of the feeding system.

Molten salts are considered as promising biomass liquefiers since they can maximize the liquid fraction in the fast pyrolysis process downstream. Other advantages of employing molten salts are the solubility of biomass in molten salts [8,9], high thermal conductivity of the molten salt and the possibility of using solar energy to heat and melt the salt. The molten salt is also a heat carrier and a possible catalyst in the follow up hydro-pyrolysis step of the process [3]. Additionally, they have favourable transport properties, i.e. low viscosity which leads to rapid enclosing of the biomass particles [2]. Molten salts can be recycled after removing char and ash.

The salt criteria for biomass liquefaction are in many ways similar to those of high-temperature phase change materials (PCM) for thermal energy storage. Favourable properties of a proper fluid are high heat capacity, high conductivity, low vapor pressure, high boiling point, low viscosity and low cost [10–12]. Moreover, the selected molten salt needs to liquefy the biomass at mild conditions and have a melting point around 200 °C. This temperature is low enough to avoid producing by-products such as ash or char and high enough to liquify biomass. The selected molten salt requires high thermal stability to avoid salt decomposition at high temperatures and make salt recycling possible. It is also important that the salts do not react chemically with constituents from

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the biomass particles and also provide minimum corrosion to metal pipes and containers. Hydrolysis is a possible reaction due to the presence of water in biomass. Water may react with the salts and form highly corrosive gases such as HCl or HF, if chlorides or fluorides are used, respectively. Therefore, the minimum rate of hydrolysis is a considerable issue for this study.

According to the mentioned favourable properties, different groups of molten salts have been considered as possible candidates to liquify biomass:

- Fluorides are thermally stable at high temperatures (>700 °C) [13], but they also have high melting points (>400 °C) [14].
- Carbonate salts are not chemically stable at high temperatures [15].
- Hydroxides show potential for dissolving biomass, but they will form stable carbonates in contact with carbon that need to be regenerated [16].
- Nitrites are not stable and oxidize at temperature higher than 350 °C [12].
- Nitrate mixtures are very common in solar energy systems [17], but they are very oxidizing and will not be stable in direct contact with carbon containing materials such as biomass [18]. Moreover, limited global reserves of nitrate salts is another drawback [19].
- Ionic metal chloride salts have potential due to high boiling points, abundant natural reserves and low cost compared to nitrates and nitrites [10,20]. They have low melting points and high thermal stability limits (>800 °C) [14].

Among all above groups, chlorides have the most essential properties for biomass liquefaction including low melting points and high thermal stability. Although many chlorides have been investigated in the literature for several applications, a eutectic mixture of $ZnCl_2$, NaCl and KCl is one of the most promising candidates for the present purpose. This ternary mixture is non-toxic, non-flammable, has a melting point around 200 °C and is stable at even higher temperatures compared to other ternary mixtures [21]. NaCl and KCl are available in large amounts. They have high heat capacities and low vapor pressures, but too high melting points (>750 °C). However, when a cubic ionic chloride such as NaCl or KCl with a high melting point is mixed with tetrahedral covalent chloride such as $ZnCl_2$ with a lower melting point in a particular proportion, a eutectic mixture is formed with a substantially lower melting point [10,14]. All three single melts ($ZnCl_2$, KCl and NaCl) have high stability even at high temperatures and the ternary salt system has low vapor pressure in temperature range of interest (0.7 atm at 800 °C) which is very promising [10,22]. Low vapor pressure (<1 atm) at high temperature, low melting point (~200 °C), high thermal conductivity, high heat capacity, low corrosion rate and high boiling point have been reported for different compositions of this salt mixture [5,14,23–25]. These results and the promising results in pyrolysis studies and thermal storage studies make $ZnCl_2$:KCl:NaCl as a promising candidate for this study [3–7,10,21,26].

Robelin and Chartrand have reported the thermodynamically modelled phase diagram of $ZnCl_2$:KCl:NaCl [23]. Moreover, the melting points of some compositions of this ternary chloride were investigated experimentally by a few researchers. Nitta et al. reported the eutectic temperature for $ZnCl_2$:KCl:NaCl = 60:20:20 (in mole fraction) to be around 203 °C [26]. Xu et al. carried out Differential Scanning Calorimetry (DSC) on three eutectic compositions of the salt [21]. The theoretical and experimental melting point of four eutectic compositions of the ternary salt reported in literature are given in Table 1. There are some variations for the reported melting points, and these will therefore be verified experimentally in the present study.
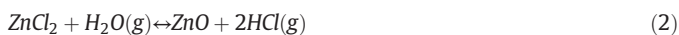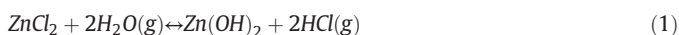
2. Thermodynamic modelling

Although thermodynamic and transport properties of the ternary composition of $ZnCl_2$:KCl:NaCl are investigated in some studies, there

Table 1
Four different $ZnCl_2$:KCl:NaCl compositions and their melting points found in literature.

Salt	Molar composition (mol%)			Melting point (°C)	
	$ZnCl_2$	KCl	NaCl	Theoretical	Experimental
#1	60	20	20	–	203 (26)
#2	59.5	21.9	18.6	213 (23)	198.7 (21)
#3	52.9	33.7	13.4	204 (23)	210.3 (21)
#4	44.3	41.9	13.8	229 (23)	199.4 (21)

are no studies regarding hydrolysis in the case of presence of moisture. Moisture is one of the most common detrimental impurities in molten chlorides [1] since chlorides such as $ZnCl_2$ are strongly hygroscopic. Although this salt is normally kept at high temperatures to avoid absorbing moisture, small amounts of water may induce hydrolysis of the salt. It can react with the chlorine anion and lead to the formation of HCl, which is a highly corrosive gas [14,27]. In the case where a chloride molten salt is in contact with water containing feedstock such as lignocellulosic biomass, this may aggravate the corrosion rate of process equipment [28].

The hydrolysis reactions for the single salts $ZnCl_2$, KCl and NaCl are described by Eqs. (1)–(4) [18]. The Gibbs free energy of the reactions (simulated with HSC Chemistry), are well above zero up to 1000 °C as depicted in Fig. 1. It means that hydrolysis is not thermodynamically favoured at relevant process temperatures. However, all reactions are in equilibrium and the hydrolysing halides form gaseous compounds. The formed compounds will be constantly removed from the system and decrease the vapor pressure and it will tend to drive the reactions towards HCl production [29].

$$ZnCl_2 + 2H_2O(g) \leftrightarrow Zn(OH)_2 + 2HCl(g) \tag{1}$$

$$ZnCl_2 + H_2O(g) \leftrightarrow ZnO + 2HCl(g) \tag{2}$$

$$NaCl + H_2O(g) \leftrightarrow NaOH + HCl(g) \tag{3}$$

$$KCl + H_2O(g) \leftrightarrow KOH + HCl(g) \tag{4}$$

In order to reduce the hydrolysis rate of molten salts, the effect of adding a metal oxide was recently investigated. Olsen et al. reported that adding CaO to molten $CaCl_2$:CaF lowers the tendency for hydrolysis [29]. For the present study ZnO is considered as a potential oxide to reduce the hydrolysis rate. According to Eq. (5) and Fig. 1, ZnO can theoretically react with the produced HCl and hence reduce the levels of HCl in the exit gas [2].
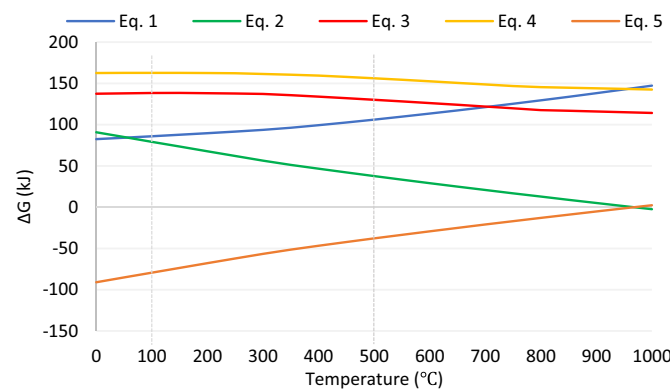
$$ZnO + 2HCl(g) \leftrightarrow ZnCl_2 + H_2O(g) \tag{5}$$

Fig. 1. Gibbs free energy of hydrolysis reactions of $ZnCl_2$, NaCl, KCl (Eqs. (1)–(4)) and the reaction of ZnO with HCl (Eq. (5)) in the range of 0 to 1000 °C. The relevant range of temperature for biomass liquefaction is 100–500 °C.

In addition to hydrolysis reaction, direct oxidation reaction of $ZnCl_2$ can also form ZnO and release chlorine [30,31]. In this case, dissolved oxygen in the biomass may react with molten $ZnCl_2$ and play a role of hydrolysis inhibitor by forming ZnO.

3. Experimental details

Four different compositions of $ZnCl_2$:KCl:NaCl as described in Table 1 have been studied. Experiments to measure melting points, thermal stability and hydrolysis were performed. Afterwards, the hydrolysis process has been studied and the effect of ZnO on hydrolysis rate has been investigated.

3.1. Materials and setup

It was necessary to pre dry the chemicals in order to remove residual crystal water due to the hygroscopic nature of the salts (especially $ZnCl_2$). $ZnCl_2$ (VWR, 98.3%), KCl (Sigma, ≥99.5%), NaCl (Sigma, ≥99.8%) and ZnO (Alfa Aesar, 99%), were dried and kept in a muffle furnace at 200 °C for at least 24 h in separate and closed beakers.

In all experiments, dried salts were mixed and prepared in a nickel crucible. The reactor setup containing the nickel crucible was heated in a vertical electrical tube furnace with radiation shields at the bottom part to minimize the heat loss. LabView 8.2 (National Instrument) was used to monitor and record the measurements. Ar gas was passed through the furnace from the bottom to provide inert atmosphere during the experiments. A type S thermocouple was immersed in the salt for monitoring and recording the salt temperature profile during all experiments. All experiments were carried out at ambient pressure. Since hydropyrolysis of biomass is carried out in high pressure units, it is not possible to conduct such experiments with the existing experimental setup.

Although the mentioned requirements and conditions are common for all experiments, the measurement methods and set up details vary for melting point, thermal stability and hydrolysis, and these are further are described in following sections.

3.2. Melting point experiments

The melting point of the selected molten salt is one of the main issues since the idea is to perform the liquefaction step at mild conditions (~200 °C, atmospheric pressure). To verify the reported melting points from the literature, the melting points were measured experimentally by using the cooling curve method [32]. 120 g of dry salt mixture was placed inside a nickel crucible (with the height of 5.7 cm and the inner diameter of 6.1 cm) and heated up to 250 °C in a vertical electrical resistance furnace to ensure complete melting. The crucible was equipped with radiation shields above to minimize heat loss (see Fig. 2). A mechanical nickel stirrer (40 rpm) was used to mix the molten salt for at least one hour to ensure a homogenous mixture. Then the salt mixture was cooled down slowly at a rate of 0.3 or 0.5 °C/min. In some cases, 0.1–0.15 g of a solid salt crystal ($ZnCl_2$:KCl:NaCl) was fed through a seeding pipe right before the solidification occurred. This was performed in order to reduce undercooling. The melting point experiments were repeated several times by heating up the solidified salt and cooling down again for each composition.

3.3. Thermal stability experiments

Thermogravimetric analysis (TGA) was performed to compare the thermal stability of all four compositions as a function of temperature up to 500 °C. For this purpose, 235 g of dried salt mixture was placed in a tubular nickel crucible with the height of 17 cm and the inner diameter of 5.1 cm. The mixture was compressed as much as possible in order to remove the trapped air and minimize the possible experimental errors, as suggested by Xu et al. [21]. A weight scale which was
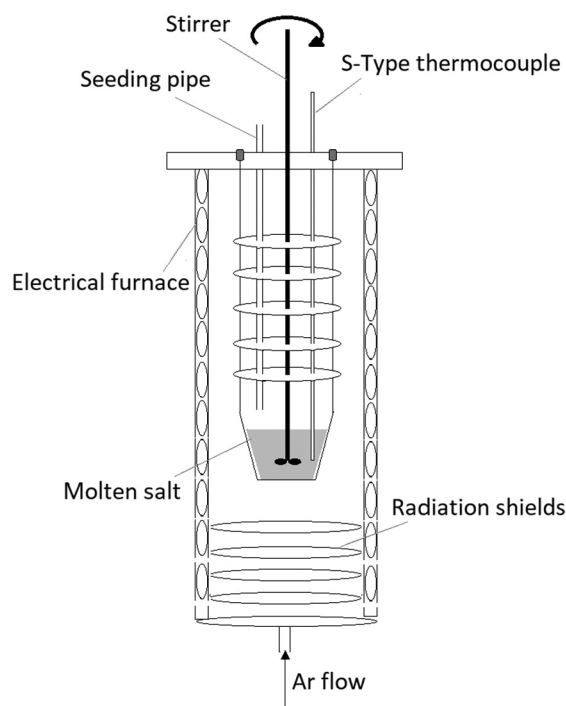

Fig. 2. Schematic representation of the experimental setup for determination of melting points. The sample is placed in a nickel crucible and undergoes controlled cooling under constant stirring. The experiments were performed under inert atmosphere (Ar).

connected to a computer was located above the furnace and the crucible containing the salt was hanged from the weight scale to record the weight change continuously during the experiment (see Fig. 3). The salt mixture was heated up to 500 °C at a heating rate of
10 °C/min.

3.4. Hydrolysis experiments

The possible side reactions of the four $ZnCl_2$:KCl:NaCl mixtures were investigated with emphasize on hydrolysis reactions. Hydrolysis reactions could give HCl formation, which is a highly corrosive and undesirable gas.

In order to test whether the hydrolysis reactions occur, a series of hydrolysis experiments were performed in the setup depicted in Fig. 4. 235 g of dried salt mixture was prepared in a nickel crucible similar to the TGA experiment crucible described in Section 3.2. It was placed inside a sealed stainless-steel vessel. The salt mixture was heated up to 230 °C under inert atmosphere (Ar flow). To ensure homogenous melts and to ensure that all initial crystal water was removed, N_2 was bubbled through the molten salt for at least 12 h at the rate of 0.2 Nl/min while monitoring the gas composition escaping from the system. Experiments were not started before no HCl was detected.

The hydrolysis experiments started from 250 °C. H_2O (g) was added by bubbling 0.4 Nl/min N_2 through a closed, water filled vessel placed on a hot plate with temperature control. The water temperature was kept at a constant value of 46 °C, to ensure a water partial pressure of 10 kPa (10 vol%) [33]. Heated gas lines (around 170 °C) which include PTFE (Teflon) tubes covered by heating elements, were employed throughout the whole system to avoid vapor condensing. The gas consisting of N_2 and water vapor was then added to the molten salt. This was performed by bubbling one centimetre above the bottom of the molten salt by an immersed nickel tube as a part of the sealed vessel. Thus, the gas will flow to the top of the molten salt bath and then being released to the volume above the salt and leave the vessel from the top through the stainless-steel exhausting tube. The exit gas was passed through a high voltage electrostatic filter (3–6 kV) to remove possible
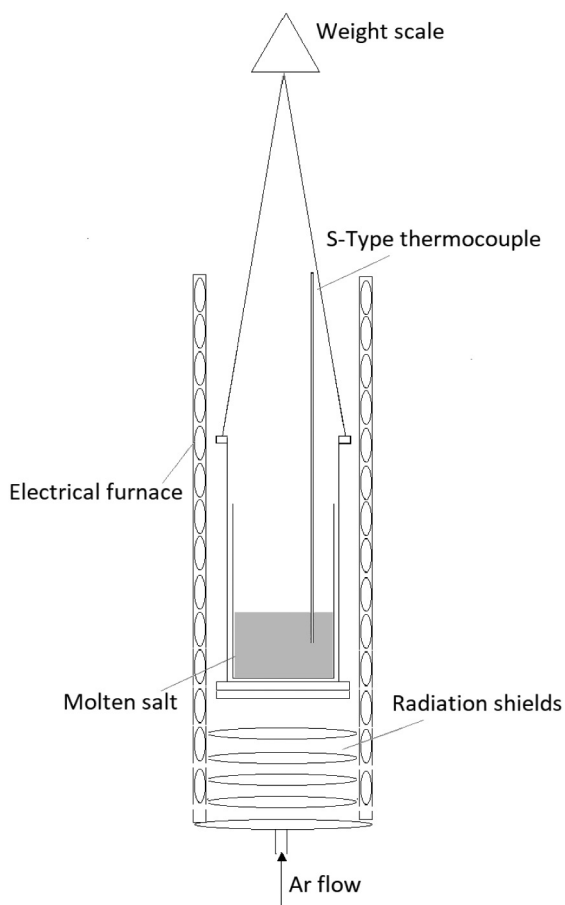
Fig. 3. Schematic representation of the experimental setup for TGA studies. The setup is hanged from the weight scale which records the weight. The temperature is measured by a type S thermocouple.

Fig. 4. Schematic representation of the experimental setup for hydrolysis studies. The inner crucible and the feed tube are made of nickel, and the outer container is made of stainless steel. The melt temperature is measured by a type S thermocouple.

particles entrained in the gas stream. High voltage was supplied from a power supply (Spellman SL300). Afterwards, the filtered gas was analysed by Fourier Transform Infrared spectroscopy (FTIR). The FTIR unit (Thermo Nicolet 6700) was equipped with a 2 m gas cell running the commercial Fire Science method (Thermo Fisher). The gas escaping from the system was continuously monitored by FTIR from the beginning. During the experiments, the salt temperature was increased in intervals of 50 °C up to 500 °C. The melt was kept at each temperature interval for at least 30 min to get an approximate stable level of HCl.

In order to investigate the effect of ZnO on hydrolysis, the salt with the highest hydrolysis rate was chosen as a suitable candidate. The same setup and procedure as the hydrolysis experiments were used. Two different amounts of dried ZnO powder, namely 5 wt% and 10 wt %, were added to the chosen salt (Salt #1) at the stage of preparing the salt mixture and the same procedure was carried out for both ZnO concentrations.

4. Results and discussion

4.1. Eutectic composition and melting point experiments

Fig. 5 shows the cooling curves of four selected compositions of $ZnCl_2$:KCl:NaCl. For Salt #1, 2 and 4 three parallels were conducted while for Salt #3 there were two parallels. In the cases of Salt #1, 3 and 4 the molten salt was seeded just before solidification to smooth undercooling while for Salt #2 this was not necessary because no large undercooling was observed even without seeding. The results from the cooling curves for Salt #3 show two occasions of undercooling and superheating, indicating that this composition is in fact not a true
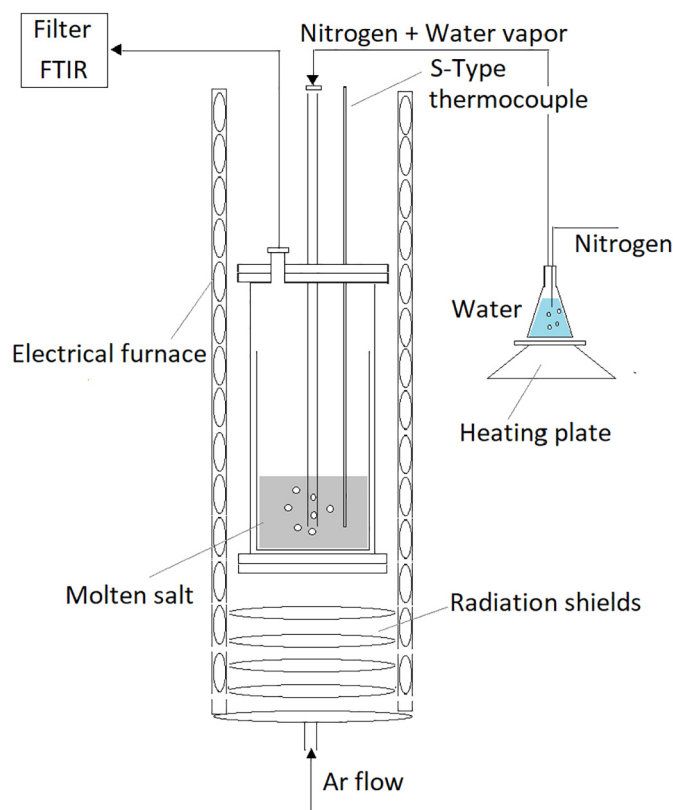
eutectic composition. However, this is not crucial for the biomass liquefaction, as long as the liquefaction temperature is above the highest melting point. In the cooling curves for Salt #4 small shoulders are observed which were recorded very quickly after the first undercooling.

Temperature calibration is necessary in order to minimize the systematic errors of the thermocouple. The thermocouple was calibrated using deionized ice and water, deionized boiling water, pure tin and pure zinc. The measured melting points based on cooling curves were calibrated according to Table 2 using linear regression.

Fig. 6 presents the average value of the measured melting points for all four compositions, before and after calibrating calculations. The data shows almost similar melting points for Salt #1, #2 and #4, in the range between 202 °C and 205 °C. However, the melting point for the non-eutectic composition #3 is relatively higher (the first transition temperature around 217 °C and the second one around 212 °C). These values are closer to the experimental melting points from literature [21] rather than the values based on the reported phase diagram [23] listed in Table 1. The difference of theoretical analysis with the measured value may be due to various reasons. Uncertainty of salt properties of individual salts in theoretical analysis and impurities in the salts in experimental values can be the most relevant explanation.

4.2. Thermal stability

Fig. 7 shows the mass loss as a function of temperature for the selected compositions of $ZnCl_2$:KCl:NaCl. According to the TGA results, the mass loss is relatively small when the temperature is below 500 °C. Salt #1 (60:20:20 mol%) started to lose mass earlier than the others, and totally lost 2% of mass when the temperature reached 500 °C. In Salt #2 (59.5:21.9:18.6 mol%) around 1% mass loss was observed at the same temperature, while Salt #3 (52.9:33.7:13.4 mol%) and #4 (44.3:41.9:13.8) presented the lowest mass loss at 500 °C,
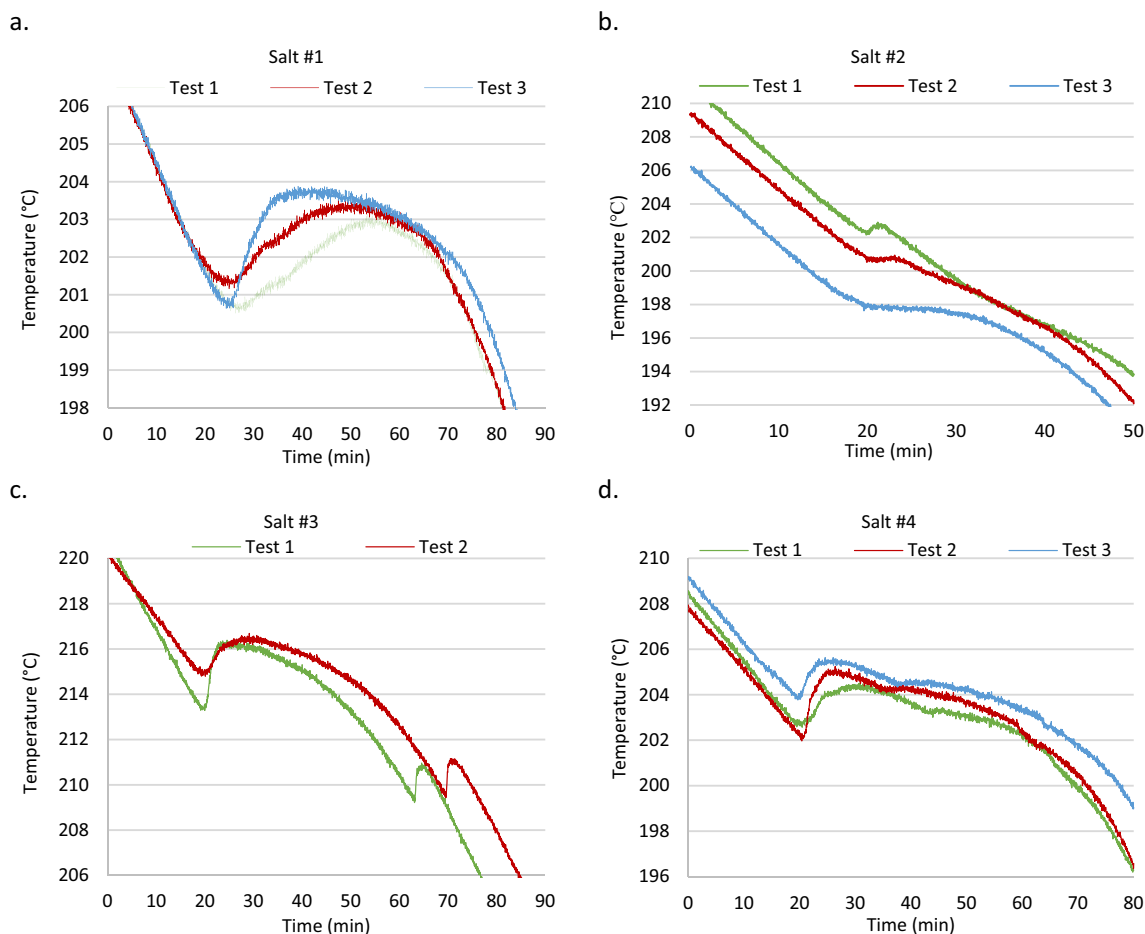
Fig. 5. Cooling curves for the molten salts including a. Salt #1 (60:20:20 mol%) b. Salt #2 (59.5:21.9:18.6 mol%) c. Salt #3 (52.9:33.7:13.4 mol%) d. Salt #4 (44.3:41.9:13.8 mol%). For a, c and d the cooling rate is 0.3 and 0.1–0.15 g of solid salt crystal was added right before the solidification to smooth the undercooling. For case b the cooling rate is 0.5 °C/min and no salt crystal was added.

with around 0.5% and 0.2%, respectively. The results show that by decreasing the concentration of $ZnCl_2$ and increasing the concentration of KCl in the salt mixture, the thermal stability is strengthened.

Nitta et al. have reported similar results. They carried out TG-DTA (Thermogravimetry/Differential Thermal Analysis) curves of three selected compositions, $ZnCl_2$:KCl:NaCl, 55:22.5:22.5, 60:20:20 and 65:17.5:17.5, in mole fraction [26]. For all the TG curves, no weight decrease was observed up to 350 °C. Xu et al. carried out TGA simultaneously on three eutectic compositions of the salt [21]. They have investigated the melting points and reported slight mass loss, less than 1%, with the increase of the temperature up to 400 °C. The current study goes a bit higher temperature up to 500 °C, because these temperatures are more relevant for hydropyrolysis of biomass.

4.3. Hydrolysis experiments

Fig. 8 shows the level of HCl formation for each temperature interval, from 250 °C to

Table 2
Standard and measured calibration points for S-type thermocouple.

Sample	Deionized ice+ water	Deionized boiling water	Pure tin	Pure zinc
Calibration point (°C)	0.0	100.0	231.9	419.5
Measured value (°C)	0.06	97.9	231.2	417.1
Relative error	–	2.1%	0.3%	0.57%

500 °C, for the four selected compositions of $ZnCl_2$:KCl:NaCl. As the figures show, increasing temperature usually leads to higher HCl levels. Salt #1 produces very low levels of HCl (~0 ppmv) at 250 °C, however, they increase dramatically by increasing temperature and reach more than 4500 ppmv at 500 °C. Salt #2 has lower levels of HCl in all temperature intervals and produces low amounts of HCl below 400 °C. Then it increases to more than 2300 ppmv at 450 °C and around 4000 ppmv at 500 °C. Salt #3 shows unstable HCl level production more or less in all intervals but still higher level of HCl at temperature above 400 °C and form around 2000, 3000 and 5000 ppmv at 400, 450 and 500 °C,
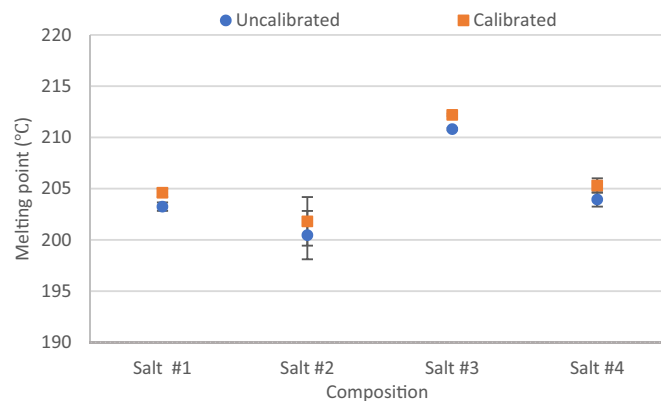

Fig. 6. Experimental melting points for four compositions of $ZnCl_2$:KCl:NaCl before and after calibration.

Fig. 7. Mass loss as a function of temperature for four different compositions of ZnCl$_2$:KCl:NaCl.

of HCl are detected at the highest temperatures. In Salt #1 with the highest amount of ZnCl$_2$ and lowest amount of KCl (60:20:20 mol% ZnCl$_2$:KCl:NaCl), HCl forms readily at and above 300 °C. Salt #4 (44.3:41.9:13.8 mol% ZnCl$_2$:KCl:NaCl), with the lowest amount of ZnCl$_2$ in the composition, shows the lowest levels of HCl at almost all temperatures, with almost no HCl below 400 °C.

Addition of ZnO to Salt #1 raises the temperature for onset of hydrolysis. HCl formation started above 400 °C and again the HCl formation increased with higher temperature. The results in Fig. 10 show that adding 5 and 10 wt% ZnO to Salt #1 can reduce the levels of HCl from 1700, 2600 and 3400 ppmv to less than 300 ppmv at temperatures below 400 °C while these were not very effective at higher temperatures. Adding 10% ZnO decreases the HCl formation at 450 °C more than 1000 ppmv, however no positive effects were observed in higher temperatures with adding 5% ZnO.

5. Conclusion

The properties of molten ZnCl$_2$:KCl:NaCl including melting points, thermal stability and hydrolysis have been studied experimentally. Four different compositions were chosen: Salt #1: 60:20:20 mol%, Salt #2: 59.5:21.9:18.6 mol%, Salt #3: 52.9:33.7:13.4 mol%, Salt #4: 44.3:41.9:13.8 mol% ZnCl$_2$:KCl:NaCl. These four compositions have been considered to be candidate molten salts for biomass liquefaction, with sufficiently low melting point around 200 °C.

respectively. The formation of HCl in Salt #4 is clearly less than the other salt compositions and almost no HCl formation was observed at 350 °C and lower. The first sign of HCl formation was at 400 °C around 1000 ppmv and increased to 1300 ppmv at 500 °C.

The average value of the HCl formation for each composition and each temperature interval was calculated and shown in Fig. 9. For all compositions, similar trends were observed, and the maximum amount
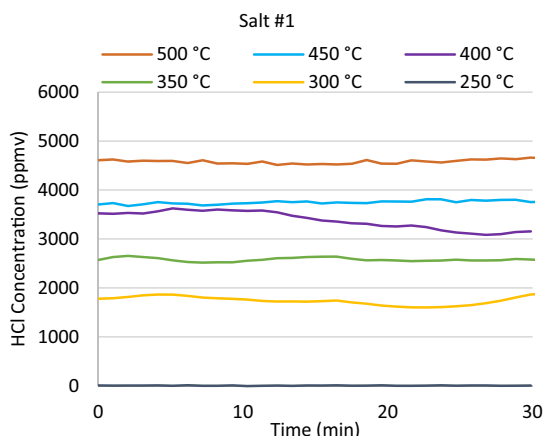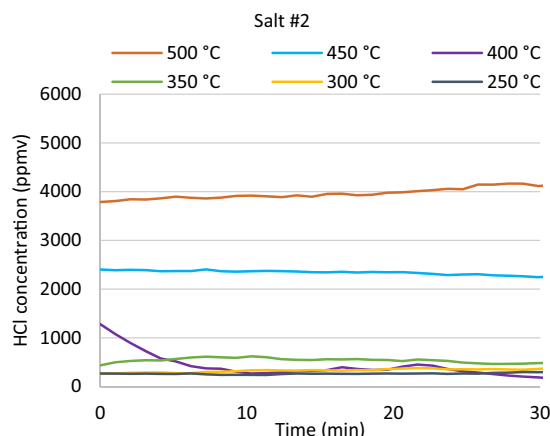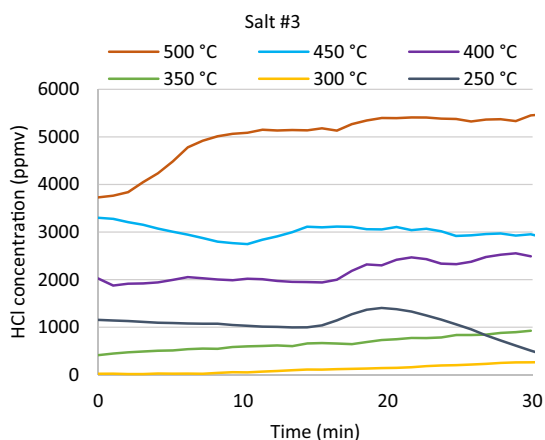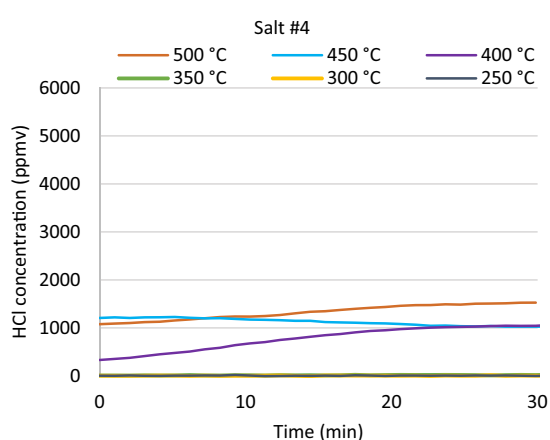
a.

b.

c.

d.

Fig. 8. The content of HCl in the exit gas as a function of temperature from 250 °C to 500 °C when 10 vol% water in N$_2$ is added to a: Salt #1 (60:20:20 mol%) b: Salt #2 (59.5:21.9:18.6 mol%) c: Salt #3 (52.9:33.7:13.4 mol%) and d: Salt #4 (44.3:41.9:13.8 mol%) ZnCl$_2$:KCl:NaCl.
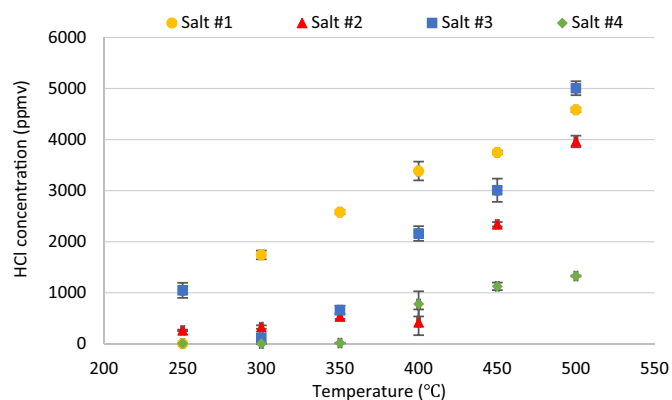
Fig. 9. The average content of HCl in the exit gas as a function of temperature from 250 °C to 500 °C when 10 vol% water in N_2 is added to Salt #1 - #4.

The melting point experiments for Salt #3 indicated that this composition is not a true eutectic composition. However, this is not considered as an issue in this study as long as the biomass liquefaction temperature is above its melting point. The other compositions had melting points in the range of 203–205 °C. TGA was employed to analyse the thermal stability of all compositions up to 500 °C. In the cyclic short-term thermal stability experiments, Salt #1 showed the highest mass loss around 2% at 500 °C. The mass loss for the other mixtures decreased with lower concentration of $ZnCl_2$ in the mixture and the weight loss for Salt #4 was negligible. Hydrolysis reactions are of special importance since these could form undesired and corrosive gases such as HCl. The results show that molten chlorides react with water vapor and form HCl. Furthermore, the reaction is quite temperature dependent. Lower amounts of $ZnCl_2$ in the mixture leads to lower rates of hydrolysis and Salt #4 shows the minimum amount of HCl compared to the other compositions. The experiments have been performed at ambient pressure due to limitations of the experimental setup. Hydro pyrolysis is, on the other hand, a high-pressure process which can supress vapor pressure and HCl formation. Therefore, the hydrolysis rate could be lower than reported values in this study. Moreover, addition of ZnO to Salt #1 shows a significant reduction effect on HCl production especially at the lower temperatures.

In total, Salt #4 seems to have the most promising properties relevant for thermochemical conversion of biomass. It has a relatively low melting point (~205 °C), the highest thermal stability (~0.2% mass loss at 500 °C) and exhibit the least tendency to form HCl during hydrolysis experiments. In order to avoid HCl formation completely, it is advised to keep the reaction temperatures below 400 °C and/or add ZnO as a hydrolysis inhibitor.
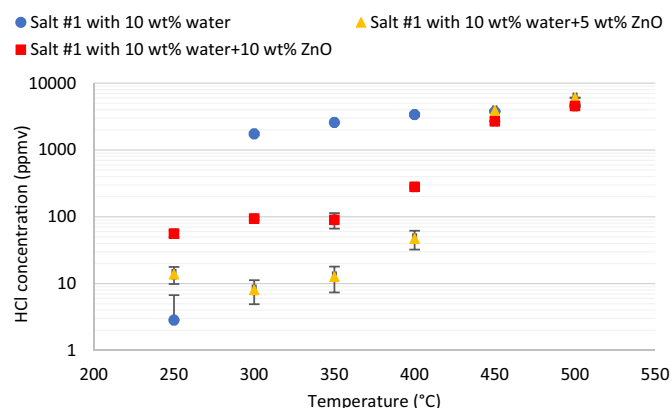

Fig. 10. The content of HCl in the exist gas for Salt #1 by using 0%, 5% and 10% ZnO.

CRediT authorship contribution statement

Sepideh Niazi: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing - original draft, Writing - review & editing. **Espen Olsen:** Conceptualization, Methodology, Supervision, Validation, Writing - review & editing. **Heidi S. Nygård:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Writing - review & editing.

Declaration of competing interest

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