

Molten Salt Discussion Group

Christmas 2012 Research Meeting

Programme & Abstracts

17th December 2012
Chemistry Centre, RSC, Burlington House, London

Authors' Abstracts

Abstracts presented on the following pages are compiled by the MSDG for distribution amongst attendees of the 2012 MSDG Christmas Research Meeting and are made available on-line at the MSDG's website. The abstracts are "as submitted" by the authors who are responsible for issues related to scientific correctness and copyright.

Programme

Monday 17th December

09:00 - 09:55 Registration with Tea/coffee & Danish pastry

09:55 – 10:00 Welcome Professor Andy Abbott (Chairperson of the MSDG)

10:00 – 10:40 Invited Lecture
(Chairperson: Professor Andy Abbott)

Professor Andy Mount

School of Chemistry, University of Edinburgh

10:40 – 12:40 Technical Session 1
(Chairperson : Professor George Chen)

10:40 – 11:10 **Rob P. Campbell-Kelly**
AWE, Aldermaston, Reading, RG4 4PR, UK.

Development of a Solid Anode Electrorefining Process using Cerium as an Analogue for Actinides

11:10 – 11:40 **Viktorija Tomkute¹, A. Solheim², E. Olsen¹**
¹ *Dep. of Mathematical Sciences and Technology, Norwegian University of Life Sciences (UMB), P.O.Box 5003, Drøbakveien 31, NO-1432 Ås, Norway*
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Investigation of high temperature CO₂ capture by CaO in CaCl₂ molten salt

11:40 – 12:10 **Magaly Oudot¹, L. Cassayre¹, P. Chamelot¹, M. Gibilaro¹, L. Massot¹, M. Pijolat²**
¹ *Laboratoire de Génie Chimique, Université Paul Sabatier, INP-CNRS, 31062, Toulouse Cedex 9, France*
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Oxide layers formation on a Fe electrode under anodic polarisation in cryolite melts

12:10 – 12:40 **Geir Martin Haarberg¹, Eirin Kvalheim¹, Ana Maria Martinez², Sverre Rolseth², and Henrik Gudbrandsen²**
¹ *Department of Materials Science and Engineering Norwegian University of Science and Technology, NO-7491 Trondheim, Norway*
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High Temperature Electrolysis for Liquid Iron Production

12:40 – 14:00 Lunch

13:30 – 14:00 MSDG AGM

14:00 – 15:00 Technical Session 2
(Chairperson : Dr Carsten Schwandt)

14:00 – 14:30 **Peter Thomassen, Andreas J. Kunov-Kruse, Susanne L. Mossin, Helene Kolding, Søren Kegnæs, Anders Riisager, Rolf W. Berg and Rasmus Fehrmann**

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Flue Gas Cleaning by Ionic Liquids - Fundamental Chemistry and Industrial Application

14:30 – 15:00 **Happiness V. Ijije, Richard C. Lawrence, Chenggong Sun and George Z. Chen***

*Department of Chemical and Environmental Engineering, and Energy and Sustainability Research Division, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK. *Corresponding author: george.chen@nottingham.ac.uk*

Molten Salt Assisted Electro-reduction of Carbon Dioxide to Carbon

15:00 – 16:00 POSTER SESSION with tea, coffee & biscuits

16:00 – 17:00 Technical Session 3
(Chairperson: Professor Tom Welton)

16:00 – 16:30 **Trevor R Griffiths, Vladimir A Volkovich and Derek J Fray**
Redston Trevor Consulting Ltd., Leeds, LS17 8RF, UK.

The preparation and solubility of alkali metal uranates in molten carbonate and the effect of temperature on their chromaticity over a 700 °C range.

16:30 – 17:00 **Gero Frisch, Jennifer Hartley, Loretta Jones and Andrew Abbott**
Chemistry Department, University of Leicester, Leicester, LE1 7RH

Ionic Dissociation in Ionic Liquids – Activity Coefficients and pH Measurements

17:00 – 18:30 Cheese/biscuits plus Tortilla chips/dips & wine

18:30 Close of meeting

Abstracts

Development of a Solid Anode Electrorefining Process using Cerium as an Analogue for Actinides

R.P. Campbell-Kelly¹

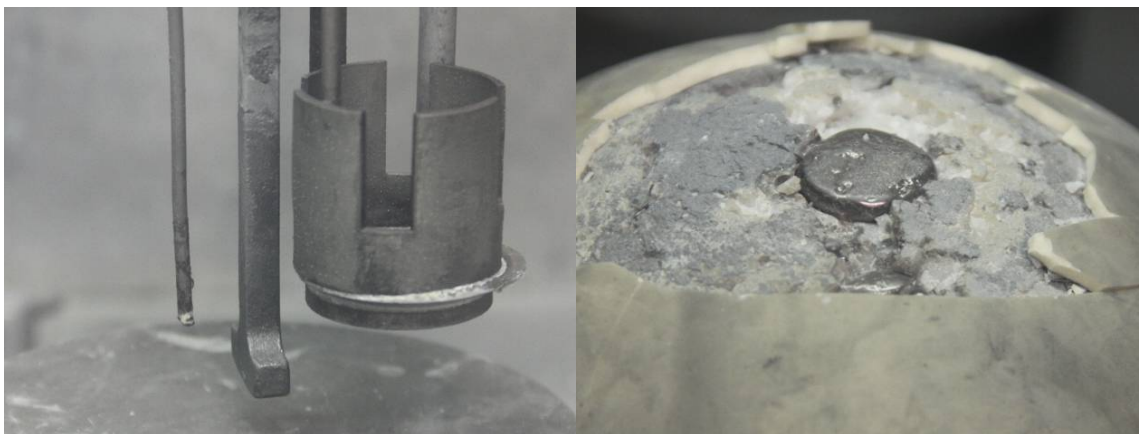
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Plutonium is purified at AWE using molten salt electrorefining, with the Pu kept molten throughout the process. Typically at the end of the run a small fraction of the feed is left as a highly impure “spent anode” which cannot be processed further using the standard electrorefining process. A Solid Anode process has been proposed to recover Pu from these residues.

Previously reported work [1] using Ce as an inert analogue demonstrated the feasibility of a Solid Anode Electrorefining process using LiCl-KCl salt at 450°C; however the equipment design allowed only small amounts to be processed in a single run, typically less than 20g. The product formed bulky deposits which required consolidation under CaCl₂ in a separate process.

In the current work a new medium-scale equipment design is demonstrated with the capacity to process over 200g per run. Initial experiments highlighted some flaws in the equipment design, but also showed the potential to improve yields over the small-scale work. Over five successful experiments, an average of 88% of the feed was oxidised, and the process efficiency was 60%.

The electrochemistry takes place at a constant potential without a reference electrode. The electrode design allows the cathode product to be consolidated at the end of the experiment by increasing the temperature above 800°C; the use of CaCl₂-LiCl-KCl reduces the volatility associated with the alkali chlorides at this high temperature.



Electrodes and stirrer used for current medium-scale work (left) and consolidated Ce product on experiment break-out (right).

References

[1] R.P. Campbell-Kelly, T.J. Paget, *Proceedings of the 1st ACSEPT International Workshop* (2010)

Investigation of high temperature CO₂ capture by CaO in CaCl₂ molten salt

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It has been demonstrated that calcium oxide based materials are promising and cost-effective sorbents for reducing carbon dioxide emissions from fossil power plants at high temperature [1, 2]. Nevertheless, many studies have shown that the CO₂ capture capacity of such sorbents decreases with increasing number of absorption-desorption cycles [1-5]. Therefore, it is a fundamental challenge in CaO-based sorbent applications to increase the reversibility for extended operation [3-6]. The present paper focuses on the development of a novel CaO sorbent in molten CaCl₂ [7]. CO₂ capture achieved by carbonation/de-carbonation of synthetic CaO with different concentrations in a matrix of molten CaCl₂ melt was studied experimentally. The CaO carbonation process was performed at moderate temperatures (790-810 °C) by bubbling a gas mixture consisting of ~27 % CO₂ and ~73 % N₂ (controlled by mass flow controllers) into the CaO-CaCl₂ mixture. Subsequently, decomposition of the formed CaCO₃ back to CaO and CO₂ was carried out by increasing the temperature to 930-950 °C. Several absorption/desorption cycles in CaCl₂ with varying amounts of CaO were tested, using FT-IR gas analysis as well as thermogravimetric analysis. The results indicate that increasing concentration of CaO enhances the carbonation reaction. The sorbent prepared with 80 weight percent of calcium dichloride salt showed the best carbonation conversion; about ~60 % conversion of CaO was obtained in the first CO₂ capture cycle. CaO reversibility into CaCO₃ in 95 weight percent of CaCl₂ salt after 4 cycles has increased from 50% to 60% (Figure 1). All samples decarbonation process shows extremely rapid desorption of CO₂ reaching 100 % efficiency.

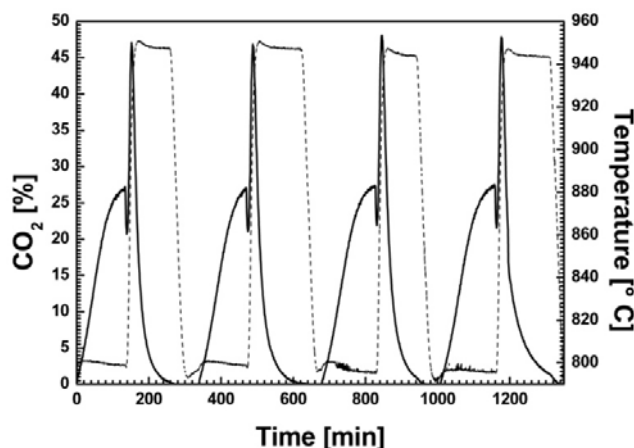


Figure 1. Repeated carbonation/decarbonation cycles of CaO in molten CaCl₂. Full line – recorded outlet CO₂ concentration recorded by FT-IR (during absorption, the inlet contains 27% CO₂ in N₂, and during desorption the inlet contains pure N₂), dashed line – melt temperature.

References

- [1] J. Blamey, E.J. Anthony, J. Wang, P.S. Fennell, *Prog Energy Combust*, 36 (2010) 19.
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- [5] V. Manovic, E.J. Anthony, G. Grasa, J.C. Abanades, *Energy Fuel*, 22 (2008) 3258-3264.
- [6] D. Karami, N. Mahinpey, *Ind Eng Chem Res*, 51 (2012) 4567-4572.
- [7] Norwegian patent No. 20092083.

Oxide layers formation on a Fe electrode under anodic polarisation in cryolite melts

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The anodic behaviour of iron has been investigated in a laboratory electrolysis cell, in a NaF-AlF₃-CaF₂-Al₂O₃ electrolyte, at 960 °C, by the mean of electrochemical techniques, *ex situ* microstructural characterizations and thermodynamic calculations. The oxidation of iron was studied over the potential range between the rest potential and the oxygen evolution potential (E(O_{2g})). At low potential (~ -1 V / E(O_{2g})), anodic dissolution of Fe occurs. At some point, the Fe^{2+/3+} concentration at the interface metal/electrolyte reaches a saturation limit, leading to the precipitation of a Fe_xAl_{3-x}O₄ aluminate phase at the metal/electrolyte interface. When increasing the polarization duration, a FeO layer grows at the metal/aluminate interface.

After polarizations at medium potentials (~ -0.8 V / E(O_{2g})), the same layers of aluminate and FeO are formed, but the latter contains porosities, especially at the metal/FeO interface, eventually leading to the loss of adherence of the layer.

Polarizations at high potentials (~ -0.3 V / E(O_{2g}) and higher) or high anode current density (i=0.8 A.cm⁻²) lead to the formation of dense, thick, but non adherent layers of iron oxides at the metal surface.

High Temperature Electrolysis for Liquid Iron Production

Geir Martin Haarberg¹, Eirin Kvalheim¹, Ana Maria Martinez², Sverre Rolseth², and Henrik Gudbrandsen²

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The production of iron and steel is a major industry, and it contributes to almost 10 % of the global emissions of CO₂. A possible alternative to reduce or eliminate the CO₂ emissions is to develop an electrolysis process with inert oxygen evolving anodes. Attempts to develop a high temperature electrowinning process to produce liquid iron at temperatures above 1535 °C have been reported [1-3]. The main feature of this technique is to dissolve iron oxide in a mixture of other molten oxides and use this as an electrolyte during electrolysis at high temperatures. At such a temperature and in such an environment, the choice of materials is important and very difficult. In particular the selection of an oxygen evolving anode is challenging.

An oxide electrolyte was prepared by premelting the desired mixture of SiO₂, MgO, Al₂O₃ and CaO. A liquid CaF₂ electrolyte was also used in separate experiments. Fe₂O₃ was then added, from 0.1 – 10 wt %. After a range of tests, Mo was chosen as the crucible material. The anode was a Pt wire, while the cathode and the reference electrode were Mo wires. Two types of experiments were performed; electrolysis to produce solid Fe at 1400 °C or liquid Fe at 1550 °C, and electrochemical measurements to determine the cathode kinetics.

Due to the presence of electronic conductivity of the molten oxide electrolyte, the cyclic voltammograms were difficult to interpret. In molten CaF₂-Fe₂O₃ corresponding cathodic and anodic reactions due to iron were observed (Figure 1), and the rate of the iron deposition reaction was found to be controlled by diffusion of Fe (II) species. Iron was found to alloy with the molybdenum cathode.

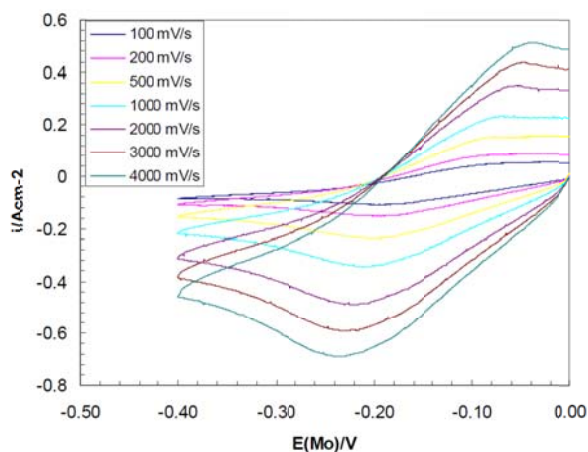


Figure 1. Cyclic voltammetry on Mo in molten CaF₂ after addition of 0.32 mol% Fe₂O₃ at 1400 °C.

References

- [1] D. R. Sadoway, JOM 10 (1995) 487-492
- [2] <http://web.mit.edu/newsoffice/1996/steelmaking.html> date 27.02.2009
- [3] <http://web.mit.edu/newsoffice/2006/iron.html> date 27.02.2009

Flue Gas Cleaning by Ionic Liquids - Fundamental Chemistry and Industrial Application

Peter Thomassen, Andreas J. Kunov-Kruse, Susanne L. Mossin, Helene Kolding, Søren Kegnæs, Anders Riisager, Rolf W. Berg and Rasmus Fehrmann

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Emission of acidic gases such as NO_x , SO_x and CO_x from, e.g. energy production by fossil fuels in power plants, ships and other industrial sources is a major concern in relation to atmospheric pollution and climate changes. Therefore, these gases have to be effectively removed from flue gases. Presently this is mainly achieved by relatively energy intensive and resource demanding technologies via selective catalytic reduction (SCR) of NO_x with ammonia, by gypsum formation after SO_2 wet-scrubbing while organic amines are being used as absorbents in CO_2 scrubbers. This leads to concern about, e.g. intensive energy requirements for desorption, corrosion of steel pipes and pumps, CO_2 absorption capacity and thermal decomposition of the amine. In this work, we demonstrate how ionic liquids (ILs) can be tuned by design to perform as selective, high-capacity absorbents of environmentally problematic flue gases like, e.g. SO_2 , NO , NO_2 and CO_2 .

Reversible absorption has been obtained for several different ILs at different temperatures and flue gas compositions. Furthermore, different porous, high surface area carriers like meso porous silica and titania have been applied as supports for the ionic liquids to obtain Supported Ionic Liquid-Phase (SILP) absorber materials (Figure 1).

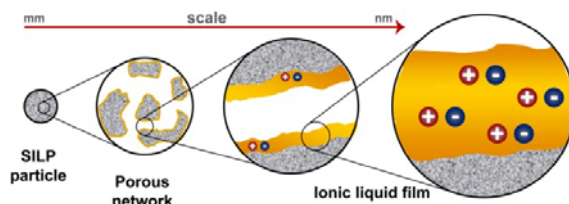


Figure 1. Principle of SILP materials.

These materials benefit from low mass transport resistance of the often highly viscous ionic liquids by the distribution of the liquid as a thin film (or small droplets) on the high surface highly porous carrier material which enable fast absorption/desorption rates of the particular gas exposed to the SILP absorber.

The results show that CO_2 , NO , NO_2 and SO_2 can be reversibly and selectively absorbed using different ILs, and that SILP absorbers are promising materials for industrial flue gas cleaning.

Absorption/desorption dynamics can be tuned by temperature, pressure, gas concentrations and the properties of the porous carrier.

The mechanism of absorption seems to be remarkably different depending on the gas and the type of ionic liquid chosen for the absorption process. Thus CO_2 seems to be absorbed by our applied amino acid based ionic liquids in the form of covalent bonded carbamate species stabilized by internal hydrogen bonding. SO_2 is absorbed by strong coordination to Lewis basic anions like chloride in our selected ionic liquid, while NO is transformed by a catalytic process assisted by strong Lewis bases, present in the ionic liquid, to nitric acid eventually changing the ionic liquid anion to nitrate by evaporation of the protonated original anion of the selected ionic liquid. The recent results of our ongoing research effort in this area will be highlighted.

Reference

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Molten Salt Assisted Electro-reduction of Carbon Dioxide to Carbon

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Carbon footprint as a result of many on-going campaigns against anthropogenic carbon dioxide emission has become a popular public enemy. The uses of carbon (e.g. power generation) had not been considered an issue until recent justification of the effect of increasing carbon dioxide emission on the atmospheric temperature. Technologies that can take away carbon dioxide from the emissions and, more importantly, reuse,¹ instead of simply storing the gas underground, are needed.

Using electrochemical reduction method, carbonate ions can be reduced to carbon and oxide ions in molten carbonate salts containing Li_2CO_3 .² The oxide ions formed in turn react with carbon dioxide from the reactor environment to regenerate more carbonate ions.³

In the present study, under a carbon dioxide atmosphere, carbon electro-deposition was carried out in a reactor system which contains molten Li_2CO_3 - K_2CO_3 . Current efficiencies of 70 – 100 % were obtained when carbon was deposited under different applied potential difference and temperatures.

Characterization of the deposited carbon samples using Thermogravimetric analysis (TGA) showed that the samples contain more than 80 wt. % carbon and elemental analysis using EDX further confirmed the high carbon content. The onset combustion temperature of the deposited carbon samples ranged from 315 – 367 °C and it varies with the amount of impurity in the carbon sample. Aggregated quasi spherical particles and ring like masses were the two main structures observed in the deposited carbon samples.

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Acknowledgement

This work has been funded by the Brian Mercer Feasibility Award of the Royal Society, the Doctor Training Accounts of the EPSRC (RCL), and the University of Nottingham Dean of Engineering Scholarship (HVI).

The preparation and solubility of alkali metal uranates in molten carbonate and the effect of temperature on their chromaticity over a 700°C range.

Trevor R Griffiths, Vladimir A Volkovich and Derek J Fray

Redston Trevor Consulting Ltd., Leeds, LS17 8RF, UK.

Alkali metal uranates and diuranates, the latter formed when UO_2 is oxidised in molten carbonates, have solubilities in carbonate melts in the ppm range and change colour reversibly upon heating. The diffuse reflectance spectra of the thermochromic alkali metal (Li, Na, K) mono- and diuranates have been recorded from room temperature down to nearly -200°C , and additionally for the potassium uranates up to 500°C . The colours, ranging from yellow to red, were characterised using the CIELAB and CIELUV system. An essentially linear relationship was found between chromaticity co-ordinates and temperature, provided no physical or chemical reaction occurred. The thermochromaticity has previously only been examined between ambient and 130°C , but it is here established that the colours of thermochromic materials can be predicted outside the experimentally measured range. The solid state reaction $x\text{M}_2\text{UO}_4 + (x - 1)\text{H}_2\text{O} \rightleftharpoons \text{M}_2\text{O}(\text{UO}_3 + (2x - 2)\text{MOH}$, where $x > 1$ and $\text{M} \neq \text{Li}$, was also followed by recording their diffuse reflectance spectra, at controlled humidity levels at room temperature. The reaction proceeds more readily as the radius of M increases, and the β form of Na_2U_4 was found to be more hygroscopic than the α form. Such studies readily provide information on crystal symmetry as a function of temperature.

Ionic Dissociation in Ionic Liquids – Activity Coefficients and pH Measurements

Gero Frisch, Jennifer Hartley, Loretta Jones and Andrew Abbott
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An understanding of the activity of the solute in solution is vital for utilising the full potential of a reactive species. The dissociation of ionic species in an ionic medium is extremely complex and affects two important application areas; proton dissociation in synthetic reactions and metal salt dissociation affecting speciation in metal deposition. In this work we determine the activity of metal salts in a variety of ionic liquids. The activity coefficient was found to decrease with increasing solute molality, whereas in a chloride based Deep Eutectic Solvent practically ideal solutions are observed up to a solute concentration of 1 mol kg^{-1} . This is important at both a fundamental level as it allows standard thermodynamic data to be measured and data from an ionic liquid standard hydrogen electrode is presented[1]

Conventionally the concept of acidity is identified with the quantification of hydrogen ion activity; for aqueous environments this problem was solved many years ago with the *pH* scale. The operative acidic and basic species are H_3O^+ and HO^- respectively and these species are formed in the presence of a solute that is either a stronger acid than H_2O , or a stronger base than HO^- . In ionic liquids, however, the situation is less clear partly because of high ionic strength and because of the number of different ionic species present. The latter complication comes not only from the possible number of ionic components but also from the existence of speciation equilibria for each component. Measurement of the position of acid base equilibria can, in principle, be attempted by potentiometric methods, but this has not been attempted. In a review of Brønsted acidity [2] of ionic liquids in synthesis it was concluded that the position of acid base equilibria in a wide range of liquids correlates more closely with gas phase proton affinities (of the conjugate base) than with *pKa* values determined from aqueous solution. This is presumably because of the high solvation energies in aqueous environment and the lack of solvent in most ionic liquids.

Here we present recent data on measuring standard electrode potentials for the H^+/H_2 couple for a variety of acids in a Deep Eutectic Solvent and show the first indicative behaviour of organic acids in high chloride strength media.

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Thermal history of wood particles in FLiNaK pyrolysis

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Fast pyrolysis is a thermochemical conversion process in which biomass is heated in the absence of any oxidizing agent, and converted to a mixture of liquids (pyrolysis oil), non-condensable gases and solid chars. In order to achieve high yields of liquids the biomass should be heated so rapidly that it reaches the pyrolysis temperature before it starts to decompose, and thus minimizing exposure to the lower temperatures that favor formation of char. In molten salt pyrolysis, biomass is fed into and heated up by a molten salt bath. Molten salts have very high thermal stability, good heat transfer characteristics and a catalytic effect in cracking and liquefaction of large molecules found in biomass.

In this study, the heat transfer characteristics of FLiNaK are studied by recording the thermal history undergone by wood particles in molten salt pyrolysis. Experiments have been carried out with cylindrical beech and pine wood particles with constant length ($L = 30$ mm) and varying diameter ($d = 1$ – 8 mm) in a FLiNaK melt with temperature of 500 °C. The thermal history at the particle center has been used to evaluate the reaction temperatures, the heating rates, and the devolatilization times [1]. Results have been compared with a similar study in fluidized sand bed [2].

It is found that the maximum heating rates observed are significantly higher in FLiNaK for wood cylinders with $d \leq 4$ mm (see Figure 1). For larger cylinders, the process is dominated by heat transfer within the wood particle, and the heat transfer medium is of less importance.

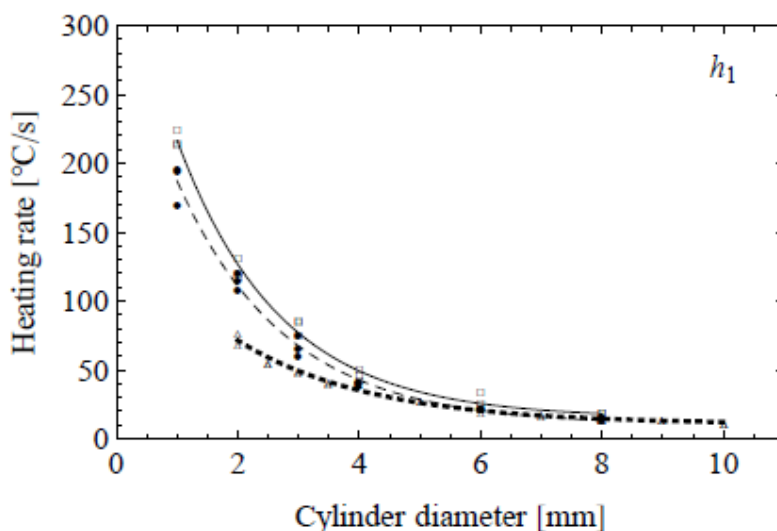


Figure 1. Maximum heating rate (h_1) at the particle center for beech (solid line) and pine (dashed line) wood cylinders in FLiNaK at 500 °C [1]. Reference values (dotted line) are estimated for beech wood cylinders in fluidized sand bed at 534 °C [2].

References

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Investigating Ionic Liquids For The Pre-Treatment of Lignocellulosic Materials

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Research into the use of ionic liquids as ‘green solvents’ is becoming ever more important. Current literature has shown the application of certain ionic liquids, based on the imidazolium cation in particular, to be suitable for solubilising lignocellulosic material.^[1,2] These natural polymers are very useful as green feedstocks and using ionic liquids as solvents to pre-treat lignocellulosic material could prove very valuable for the biofuel industry and could also provide added value chemicals from a renewable source.^[3,4] We are interested in developing a better understanding of the dissolution and processing of plant biomass in ionic liquids. Our work so far has been focussed on the use of both aprotic and protic ionic liquids for the dissolution and processing of a variety of different plant biomass. Experimental investigations into the nature of ionic liquid effects on the lignocellulosic material is underway, using techniques including powder XRD and electron microscopy. Detailed work using enzyme hydrolysis to explore the amount of sugars released after ionic liquid pre-processing shows some very promising initial results.

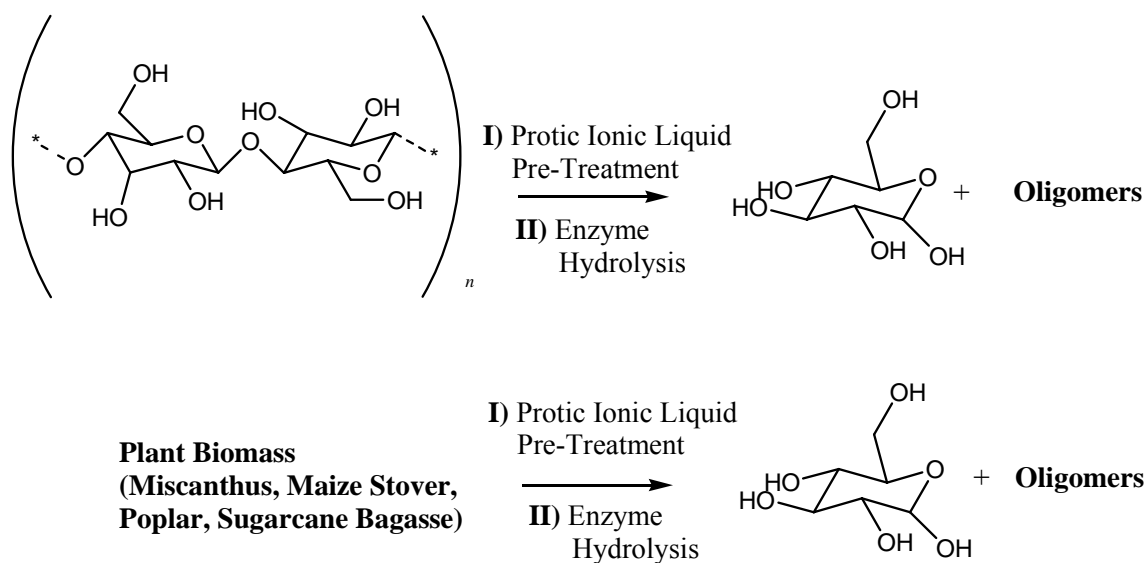


Figure 1: Scheme of cellulose/biomass to potential products

References

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Volumetric behavior and structure in ionic-liquid aqueous solutions

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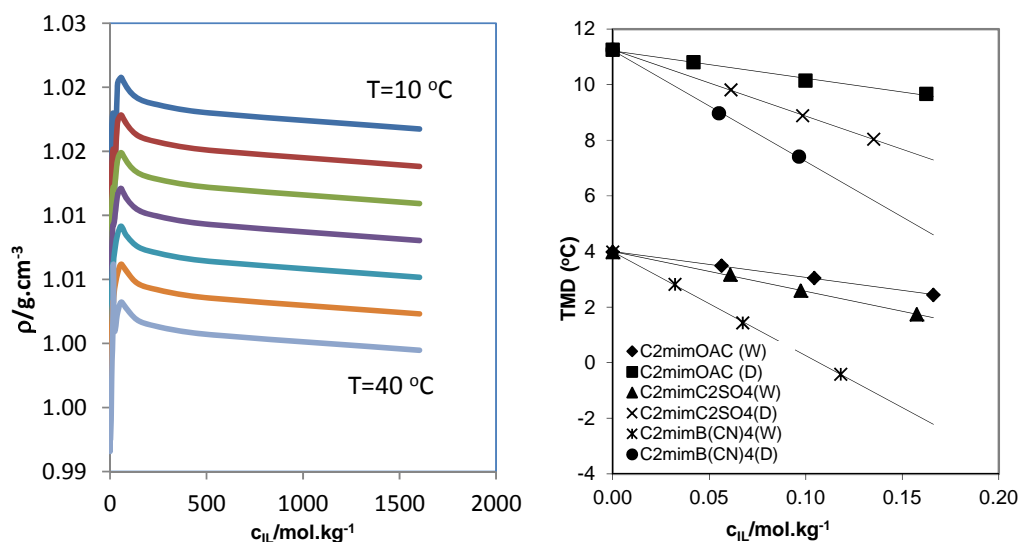
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In this presentation, we present different sets of high-precision volumetric data of ionic-liquid aqueous solutions. A careful analysis of the results is used to reveal some of the unique properties of ionic liquid solutes in terms of self-aggregation phenomena and structure-forming abilities.

The first part deals with the calculation of the apparent and partial molar volumes in aqueous solutions of long-chained imidazolium chloride ionic liquids, both in the diluted and concentrated concentration regimes. The trend shifts in these properties can be related to the formation of micelles in the diluted range and other more complex gel-like structures at higher concentrations. The density measurements were complemented by other tests, namely viscosity determinations and light-scattering experiments.

The second part deals with the measurement of the temperatures of maximum density (TMD) of water and deuterated water in the presence of different ionic liquid solutes. These isotope-effect studies can provide new insights concerning the effect of different ionic solutes in the structure of water near its melting point.



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Molten salt processing of carbide fuels

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An understanding of the behavior of silicon carbide fuels during the reprocessing of spent nuclear fuel in molten salts is vital in the development of the next generation of nuclear reactors. Silicon carbide-based fuels will play a crucial role in reducing the projected excess stockpiles of plutonium and other radiotoxic transuranium elements as well as diluting the fissile phase in nuclear fuel to the volumetric concentrations required for nuclear reactor control [1]. Also, the feasibility of the dissolution of either the fissile material or silicon carbide fuel must be assessed by pyrometallurgical methods [2]. In this poster, results on both chemical and electrochemical methods for the dissolution of silicon carbide in molten chloride salts will be presented. These results will be compared with those for the dissolution of chromium carbide in molten chloride salts. A diffusion-controlled and precipitation mechanism for the formation of insoluble products from dissolution studies will be proposed with subsequent implications towards the application of a pioneering solid state phase transformation model [3] discussed. Observations of the tendency of silicon carbide and chromium carbide to deform permanently in molten chloride salts under the influence of stresses will also be presented.

References

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