CSIR NATURAL RESOURCES AND THE ENVIRONMENT

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Conference presentation: Dissolution of South African Eucalyptus Sawdust Wood in [Emim][OAc]/ Co-solvent Mixtures

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Dissolution of South African *Eucalyptus* Sawdust Wood in [Emim][OAc]/ Co-solvent Mixtures

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Dr Bruce Sithole (CSIR/UKZN)

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Introduction

- Biomass is one of the bio renewable resources- est. global production of around 1.0 x 10 ^{11} tons per year
- Efficient utilization of biomass is increasingly important-due to diminishing resources of fossil fuels
- Wood- mainly used for production of paper from cellulose & most of other components of wood are burnt to produce energy
- The major constituents of biomass -cellulose 45-50 %, hemicellulose 15-25 %, lignin 23-33 % and extractives

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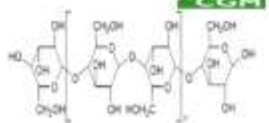
Introduction cont…



- Cellulose-abundant biopolymer
- Useful fibre applications- textile, food and motor industry
- Dissolution of biomass in common solvents is difficult- due to 3-D network structures of lignin which binds the plant cells together
- Traditional solvents have been used for dissolving biomass $CaS_2/NaOH/H_2SO_4$, N-methlmorpholine-N-oxide, DMAc/LiCl

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Introduction cont…

- Disadvantages: cause serious environmental problems-solvents used costly, toxic, corrosive, instable, cannot be recovered and reused.
- Better solvents are needed- interest in ILs stems primarily from awareness of Green chem & associated emphasis on clean manufacturing processes
- ILs - class of organic salts that are liquid at temps below 100 ˚C & forms liquid consists purely of cations and anions

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Introduction cont…

- ILs advantages- high thermal stability, low volatility, operate at severe conditions, non-flammable, recyclable and excellent solubility with organic cmpds
- ILs-high potential towards biomass dissolution, with aim to reduce lignin to enable easy accessing of cellulose
- Initial use of ILs for cellulose dissolution was discovered by Rogers and his group who carried out comprehensive studies on cellulose dissolution and regeneration

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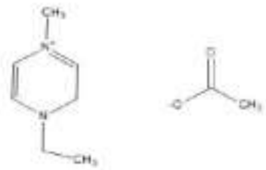
Literature review

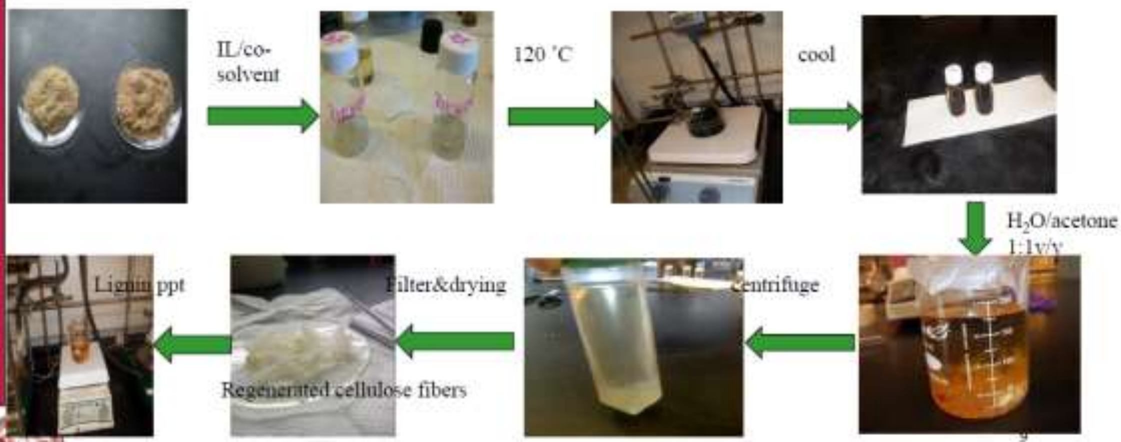
- Acetate based ILs -interesting due to low melting pt, lower viscosity & have less toxic and corrosive character compared with other ILs
- So based on literature review IL: 1-Ethyl-3-methylimidazolium acetate [Emim] [OAc]



Why Co-solvents?

- To decrease the viscosity of IL-facilitate the penetration of solvent into the cellulose which leads to additional swelling and destruction of the hydrogen bonds in the cellulose structure, decrease dissolution time.
- Co- solvents used: DMF and DMSO
- Both polar, aprotic solvents with high boiling point
- Miscible in a wide range of organic solvents as well as water

Methodology



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Results & Discussions

Percentage yield of regenerated cellulose after dissolution of Sawdust wood in [Emim][OAc]/ DMSO and DMF mixtures

IL + co-solvent mixtures	Sawdust Wood
[Emim][OAc]/ DMSO	17.83 %
[Emim][OAc]/ DMF	32.50 %
Pure IL	7.21 %

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Results and Discussions

- IL/DMF higher % yield than IL/DMSO, attributed to the fact that DMSO has high dielectric constant of 46.7, than DMF 36.7, which makes DMSO more polar- has strong ion-dipole attraction interaction which results in force of attraction becoming stronger bet. ions in soln and H-bonding bet. solvent molecules
- reduce cellulose solubility DMSO forms competing H-bond to chains of cellulose
- Results are consistent with literature

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FTIR

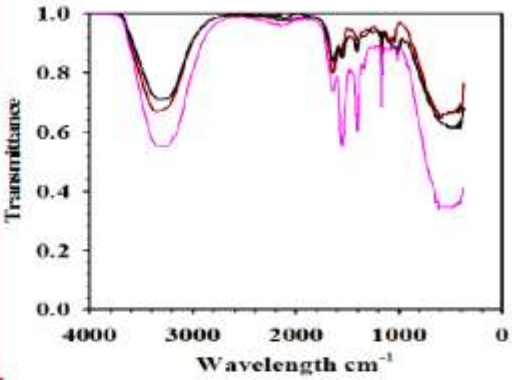

Fig.1 FTIR spectra of cellulose regenerated from the sawdust wood previously dissolved in [Emim][OAc]/ DMSO (black) and [Emim][OAc]/ DMF (red) mixtures compared to the MCC standard of cellulose (pink).

- it can be seen that structure of MCC standard & reg. cellulose material from [Emim][OAc]/ DMF and DMSO mixtures, showed same basic structure as shown in Fig.1, this was similar to the results reported in literature
- broad O-H stretching absorption around ~3400 cm^{-1} & a prominent C-H stretching absorption around ~2900 cm^{-1} in all spectras
- absorbance at ~1600 cm^{-1} is because of bending mode of absorbed water
- C-O stretching absorption around ~1500 cm^{-1} (in hemicellulose) which had a greater intensity in the MCC std spectra than reg. cellulose which was lower due to loss of hemicellulose during dissolution & reg.
- absorbance at ~1420 cm^{-1} viewed as typical of crystalline regions of cellulose & band at ~893 cm^{-1} typical of amorphous regions
- spectrums of regenerated fiber, both shows presence of lignin small bands at the region of ~1550-1640
- peaks around ~1300 cm^{-1} cm-1, ~1100 cm-1,~1000 cm-1 and ~900 cm^{-1} were mainly related to carbohydrates in all spectra

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P'XRD

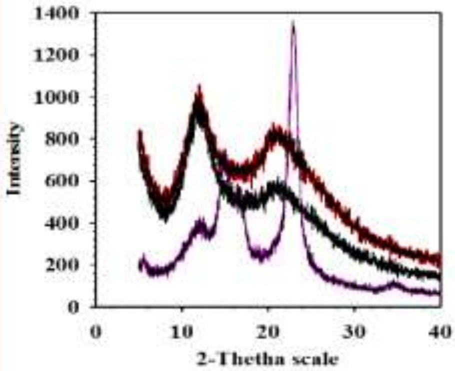

Fig.2 pXRD diffractograms of cellulose regenerated from sawdust wood previously dissolved in [Emim][OAc]/DMF and DMSO mixtures compared to MCC standard of cellulose.

- MCC shows a diffraction curve of native cellulose, strong crystalline peaks at 15° , 17° and 23° & weak crystalline peak at 35° .
- After dissolution and regeneration, diffraction curves of reg. cellulose are of typical diffraction patterns of cellulose II by presence of broad crystalline peaks at around 21° .
- Decrease in intensity of diffraction peaks implies transformation of cellulose I to II, intermolecular bonds were destroyed by IL to amorphous

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SEM

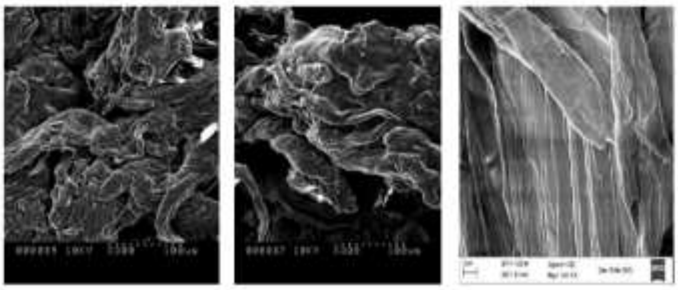

Fig.3 SEM photographs of the cellulose regenerated from sawdust wood in A) [Emim][OAc]/DMSO mixture, B) [Emim][OAc]/DMF mixture compared to pure cellulose sample C.

- fibers disordered and curly ,this was probably due to removal of lignin & decrease of cellulose crystallinity, which have already been confirmed by FTIR and P'RXD .
- This resulted in regenerated cellulose structure to be loose because of breakage of bonds which will create a favourable environment for IL penetration.
- In both the cases, results clearly indicates that morphology of fiber material was significantly changed after dissolution which confirms highly crystalline cellulose structure in Sawdust was transformed to amorphous form after treating with IL/ co-solvents

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TGA

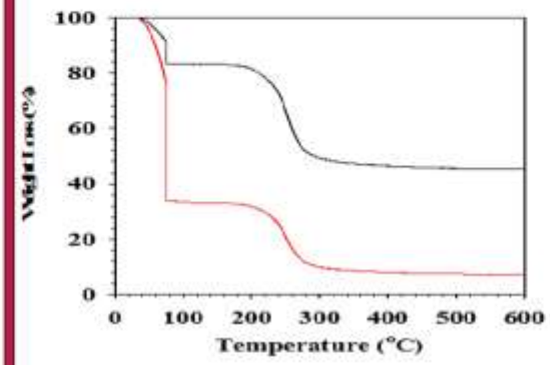

Fig.4 TGA curves of regenerated cellulose from sawdust wood in [Emim][OAc]/ DMSO mixture (black curve) and [Emim][OAc]/DMF mixture (red curve).

- TGA curves shows initial drops near 100 °C in both cases- due to evaporation of retained moisture
- TGA showed original cellulose sample as shown in literature (Sun, 2010; Kilulya et al., 2011) started decomposing at about 228 °C whereas the reg. cellulose begin to decompose at around 200 °C, that clearly indicates that native cellulose has a higher thermal stability compared to reg
- In lit the original cellulose retained 8 wt% (Kilulya et al., 2011), while the reg. cellulose from sawdust and [Emim][OAc]/DMF retained 10 wt% and [Emim][OAc]/DMSO retained 48 wt%- attributed to the fact that DMSO reported to increase speed of dissolution and remained in soln, decreasing viscosity which makes it less efficient for dissolving biomass
- Thus reg. samples gave a higher char yield (non-volatile carbonaceous materials) on pyrolysis (Swatloski et al., 2002), which was exhibited by the higher mass residual after decomposition compared to the original cellulose

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Conclusions

- This work has reported successful use of ILs/ co-solvent mixtures as solvents in dissolution of biomass. It was observed that ILs possess ability to dissolve biomass & reconstitute cellulose upon addition of any precipitating solvents, as has been previously reported
- The use of ILs in such analytical procedures as solvent promotes reduction of environmental pollution and avoids use large amounts of volatile organic solvents in such analyses
- For large-scale application of ILs the development of energy-efficient recycling methods for ILs is a prerequisite and should be investigated in detail in further studies.

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THANK YOU!

- "My name is chemistry but no 'gases' are around me!"

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