Ionic liquid mediated biomass deconstruction: from analysis challenges to fermentable sugars


POKE Summer School in Saaremaa, Estonia, August 2014
The **focus/aim** of the research

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Saccharides & their derivatives – why?

- Furfural
- 5-HMF
- Cellobiose
- Gal
- Glc
- Man
- Fru
- Ara
- Xyl

Valuable platform chemicals

monosaccharides
Background & reasons for this research work

- Climate change
  - EU legislation to promote the biofuels & renewable energy sources

- Increased demand for oil, especially in Asia
  - We should not be too dependent on oil
...Background

How about possibilities to compensate or substitute petrochemical based industry?

- Replacing of some oil based industrial products with the ethanol based ones:
  - E.g. Örnsköldsvik, Sweden in wartime
    Paper mill cellulose → Glc → fermentation to EtOH → used as fuel etc.
  - USA and Brazil are interested in ethanol as a chemical feedstock →
    (e.g. ethylene from ethanol instead of olefins from petrochemical steam cracking)
SAMPLES
The studied LIGNOCELLULOSICS

Softwood from Central Finland:

- Scots pine (*Pinus sylvestris*)
- Norway spruce (*Picea abies*)
- Silver Birch (*Betula pendula*)

Forest residues:
- Eucalyptus
- Lenga (*Nothofagus pumilio*)

Crops residues:
- Corn
- Wheat straw

...and in Chile
Sample collecting and sampling

To be considered before collecting sample
- Things that might affect the results

- heart wood vs. sapwood
- growing place (e.g. heavy metals in soil?)
- age of wood
- condition/healthy of wood (fungi etc.)
- height where sample is taken from (1.2 - 1.50 m)
- Usually samples should be free from reaction wood & compression wood, branches and knots
EXPERIMENTAL PROCEDURES
Experimental conditions & procedures:

- Wood
  * milling
  * freeze-drying
- IL & HEAT TREATMENT
  - 80-120°C
  - 2-100 h
  - mixed sawdust or woodchips + IL
- ANALYSIS OF MONO-, DI-SACCHARIDES:
  - GC (or GC-MS)
  - HPLC
  - CE

**Heat, microwaves and ultra sound contribute to the degradation of the polysaccharides!**
IONIC LIQUIDS (ILs)
# 1-Ethyl-3-methylimidazolium chloride

**EmimCl or [emim]$^+$ [Cl]$^-$**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass</td>
<td>146.62 g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>1,1120 g/cm$^3$ (at 80 °C)</td>
</tr>
<tr>
<td>Melting point</td>
<td>77-80 °C ← impurities effect</td>
</tr>
<tr>
<td>Flash point:</td>
<td>186 °C</td>
</tr>
<tr>
<td>Viscosity</td>
<td>47.4 mPas (at 80 °C)</td>
</tr>
<tr>
<td>Flame point</td>
<td>515 °C</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>$\infty$</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Information</td>
<td></td>
</tr>
<tr>
<td>Solubility in water</td>
<td></td>
</tr>
<tr>
<td>Very hygroscopic</td>
<td></td>
</tr>
</tbody>
</table>

Information concerning melting point varies in literature
1-Ethyl-3-methylimidazolium acetate
EmimOAc or [emim]$^+$ [CH$_3$COO]$^-$

- Molar mass: 170.21 g/mol
- Density 1.027 g/cm$^3$ at 25 °C
- Melting point > 30 °C
- Flash point: 164 °C
- Viscosity 10 mPas (at 80 °C)
- Solubility in water ∞
THE ANALYSIS METHODS
(CE, GC & HPLC)
AND COMPARISON OF THEM IN
THIS PARTICULAR CASE

(FOR ANALYSIS OF CARBOHYDRATES & THEIR
DEGRADATION PRODUCTS IN LIGNOCELLULOSIC
SAMPLES IN THE PRESENCE OF IONIC LIQUIDS)
GC, HPLC & CE

**GC analysis**

Analysis of carbohydrates on extract

Without acid methanolysis

- calibration samples: STD sugars with xylitol in MeOH
- ISTD: xylitol instead of sorbitol
  - Evaporation (N₂) + vacuum oven
- silylation:
  - pyridine, HMDS and TMCS
  - shaking (and ultrasonic bath)

**HPLC analysis**

- calibration samples in eluent solution
- no derivatization/silylation needed

**CE analysis**

- calibration: STD sugars + ISTD (e.g. sucrose)
- no derivatization/silylation needed
- liquid phase can be analyzed after centrifuging and filtering

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Differences in analysis methods

Sample results: GC analysis

Reliability problem with GC monosaccharide calibration
HPLC analysis

Chromatography involves a mass transfer process involving adsorption.
CE (Capillary electrophoresis)

- Separates ions based on their electrophoretic mobility
- Electrophoretic mobility depends on the charge of the molecule, the viscosity, and the atom's radius.
CE (Capillary electrophoresis)

- Detector: diode array UV/Vis
- Background electrolyte/buffer solution:
  
  130 mM NaOH containing 36 mM Na$_2$HPO$_4$

  - must always be fresh

- Sample derivatization is not needed

  → instead: dilution, centrifugation & filtration
CE calibration standards

STD mixture 0.10 mM

STD mixture 2.00 mM
A typical example of CE results

Norway spruce (sawdust 5 mm) @ 100°C with EmimCl in 6.2h diluted 1:9 & filtered in prior to analysis

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HMF

in pine, spruce and birch samples
5-HMF in pine, spruce & birch: amount per sample’s total mass vs. wood in the sample (samples consist of wood & IL)

- pine, HMF/wood
- spruce, HMF/wood
- birch, HMF/wood
- birch, HMF/sample
- spruce, HMF/sample
- pine, HMF/sample

IL and heating treatment time in hours
Comparison summary (CE, HPLC, GC)

• CE analysis is the method of choice
• GC (+ STD sugar column) is unreliable when ILs are present: concentration of IL is critical
• HPLC suffers from peak overlapping
Conclusions

IL pretreatment leads to significant formation of HMF and in some cases furfural

(like all depolymerization/ degradation processes) – good indicator to follow up (e.g. fermentation inhibitors, degree of depolymerization, colorization ...)

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