
# Ultra-low cost ionic liquids for biorefining of waste wood

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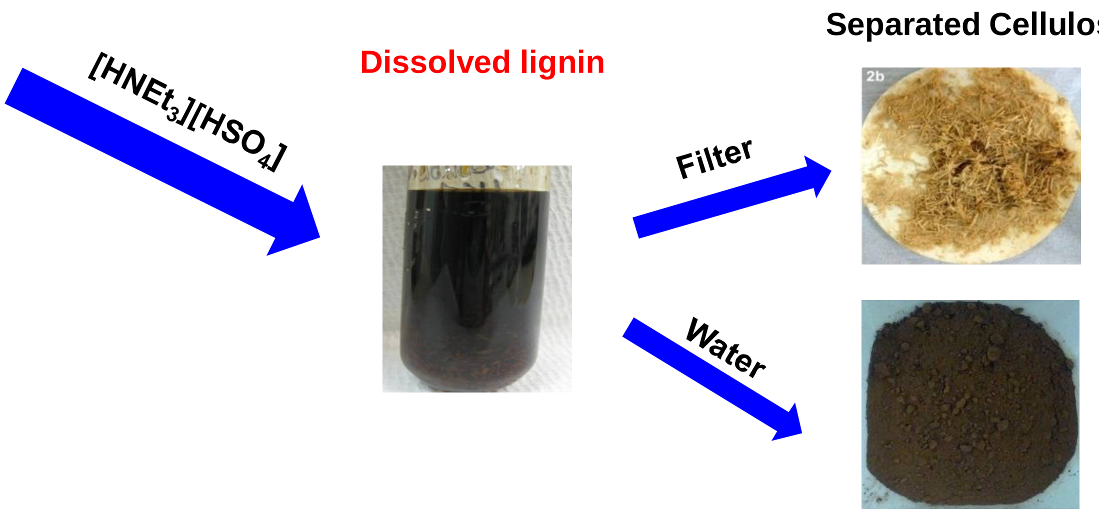
# Why use ionic liquids for lignocellulosic biofuels?

- Increase enzyme activity at minimal cost
  - Several options (kraft, ammonia, organosolv, etc.)
  - Ionic liquids provide highest activity
  - Ionic liquids are generally very expensive
- Ionic liquids are just organic salts
  - Have advantages over organic solvents
    - Can be designed for a specific function
  - Have disadvantages also
- The application must be logical
  - Rational choices must be made

# ionoSolv lignin extraction

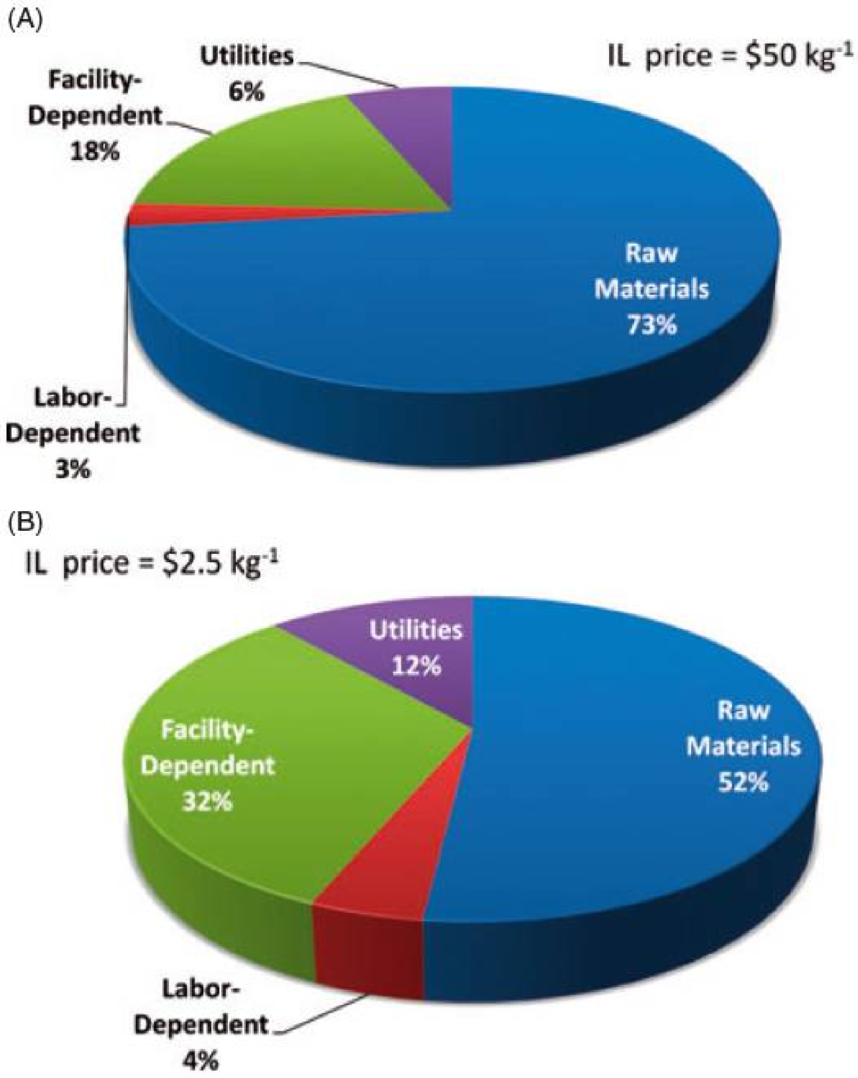
- Most ILs are not good solvents for cellulose
  - Biocatalytic conversion of cellulose to fuels
  - Want de-lignified cellulose
- ionoSolv: Dissolve lignin not cellulose
  - Highly pure cellulose easily recovered
  - Lignin solution for chemical conversion
  - Water helps the process
  - *Do salts have to be expensive?*




Ionosolv process

Brandt *et al*., *Green Chem.*, **15**, 550 (2013)

# Process economics – IL cost are critical

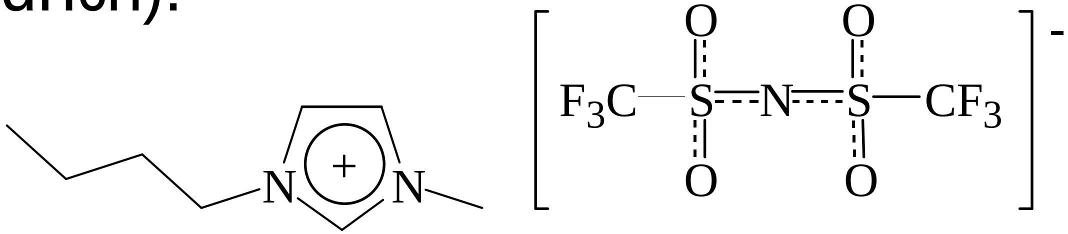


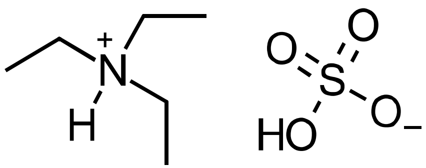

- Other important factors
  - Recycling rate
  - Biomass loading

Klein-Maruschamer *et al*., *Biofuels, Biproducts, Biorefining*, **5**, 562 (2011)

# Can Ionic Liquids be Cheap?

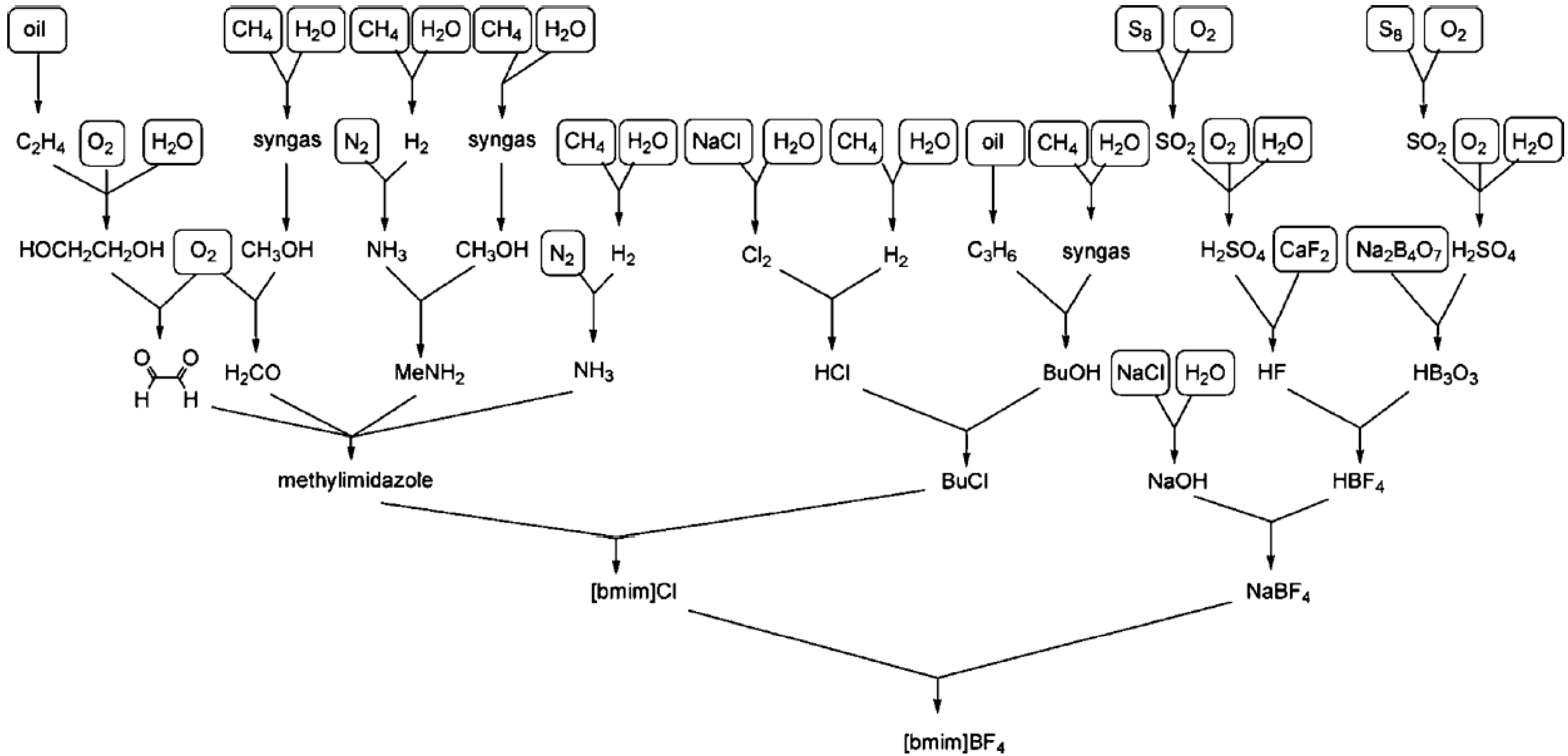
- $[C_4C_1im][NTf_2]$ (Sigma-Aldrich):
  - $2500/kg (250g)
- Ethaline (Scionix):
  - $60/kg (50kg)
- $[(C_8)_3C_1N][Br]$ (Solvent Innov.):
  - $40/kg (100t)
- $[C_2C_1im][acetate]$
  - $60/kg (bulk guesstimate)
- $[C_1Him][HSO_4]$
  - $2.60/kg (bulk estimate)
- $[(C_2)_3NH][HSO_4]$
  - **$0.84/kg (bulk estimate)**
- $[(C_4)(C_1)_2NH][HSO_4]$
  - **$0.44/kg (bulk estimate)**
- **Acetone: $1.30/kg**





Chen *et al.*, *Green Chem.*, **16**, 3098 (2014)

# How NOT to make a Green solvent

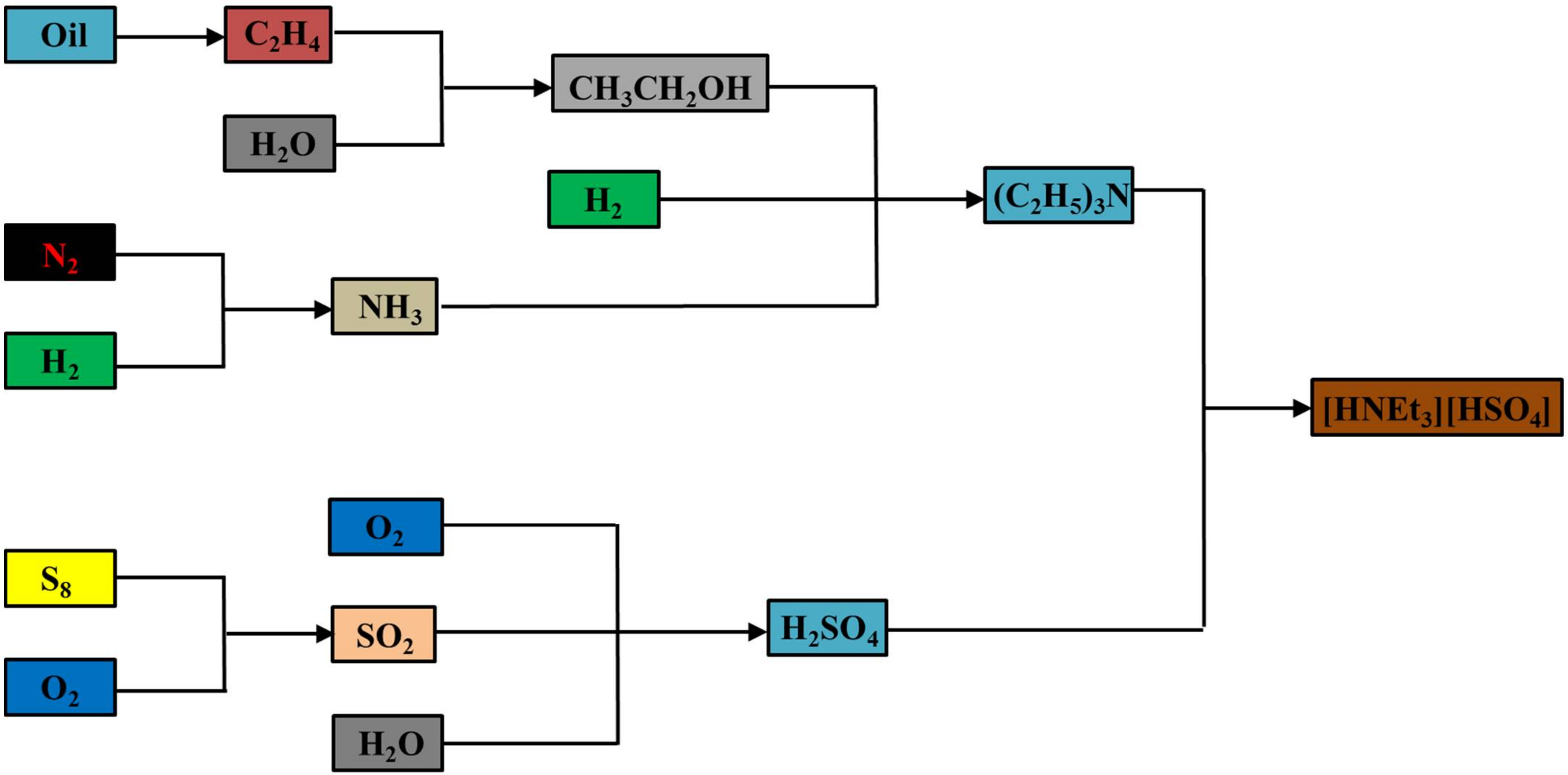



Waste in every step!

Cost = $2500/kg; E-factor > 100

Jessop, *Green Chem.*, **13**, 1391 (2011)

# How to make a Green solvent

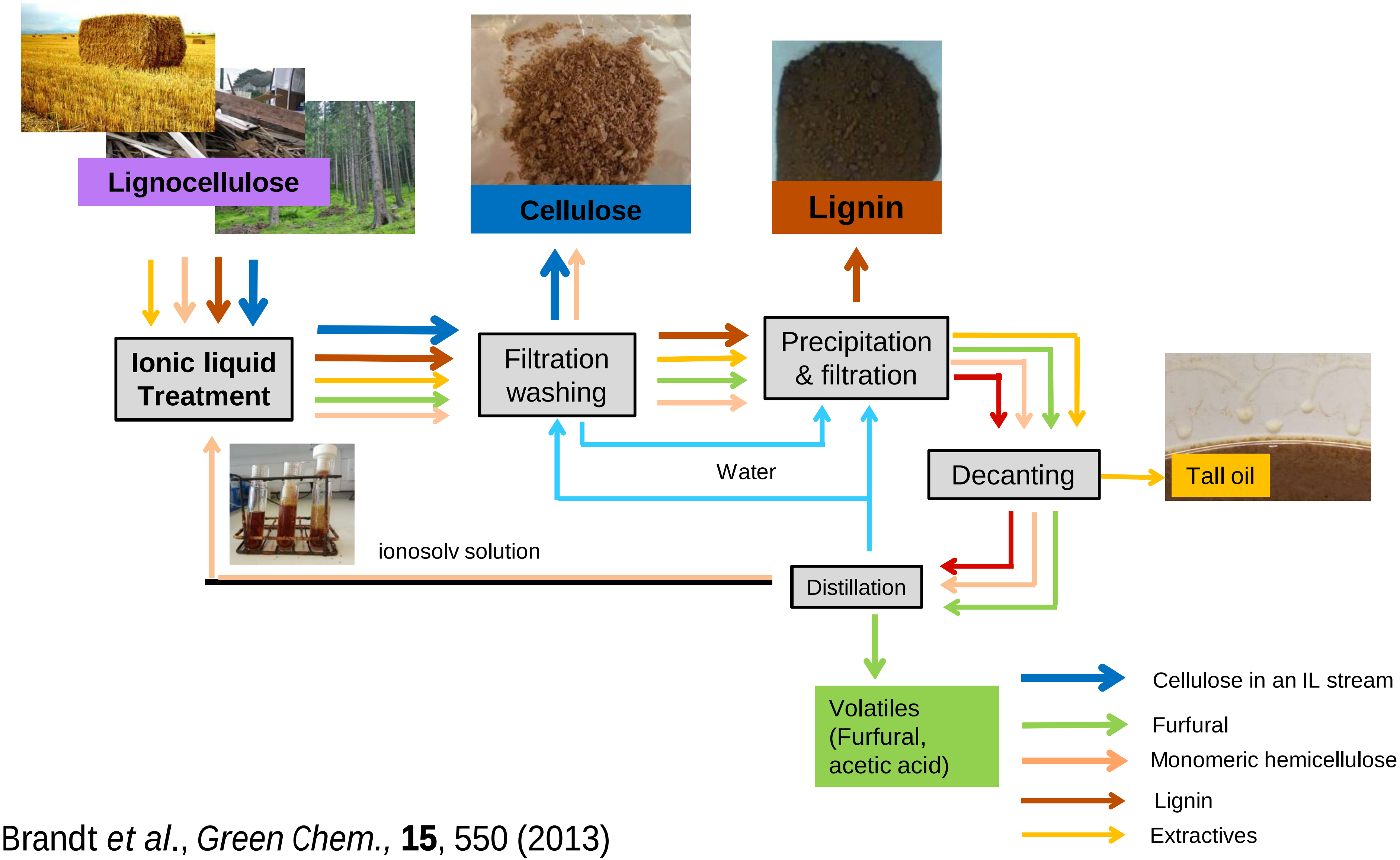



Cost = €1/kg; E-factor < 0.1

Fewer steps = lower cost = less waste

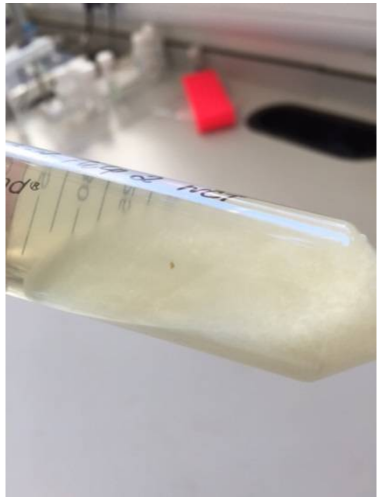
Chen *et al.*, *Green Chem.*, **16**, 3098 (2014)

# Material flow diagram




Brandt *et al*., *Green Chem*., **15**, 550 (2013)

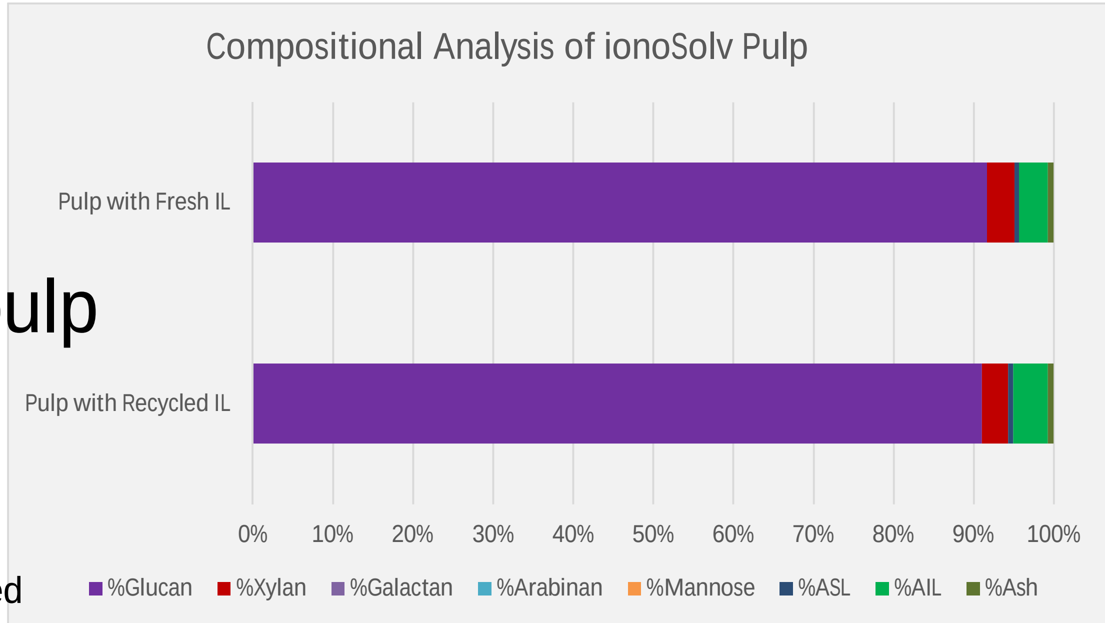
# Fun facts about the cellulose



Ionosolv cellulose

- We typically get ca. 96% glucan recovery (relative to native biomass)
  - 5% of the glucan is in the hemicellulose
- Max saccharification yields (rel. to native)
  - Miscanthus: 96%
  - Willow: 90%
  - Pine: 100%
- Most ‘pure’ cellulose pulp

*ca*. 94% glucan
  - 1 h, 150 C, 20% solids




Gschwend *et al*., *Green Chem.*, **20**, (2018), accepted

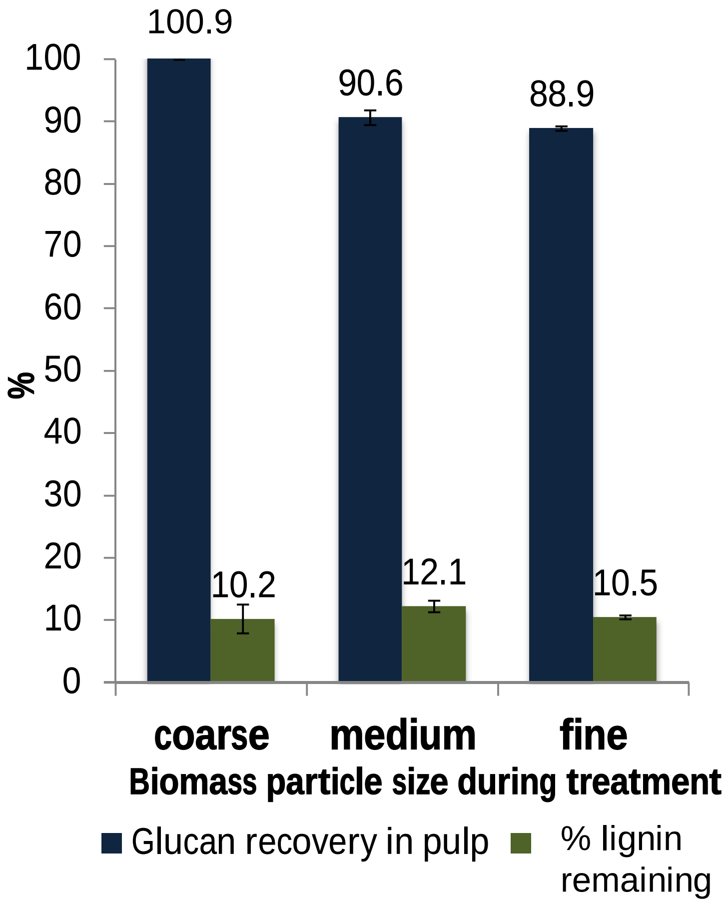
# Results – Particle size

*coarse* *medium* *fine*

Chambon *et al*., (2018), under review

# Results – Scale up

- Max sacch. yields at 20% (**50%**) solids
  - Miscanthus: 96% (**78%**)
  - Willow: 90% (**??**)
  - Pine: 100% (**82%**)

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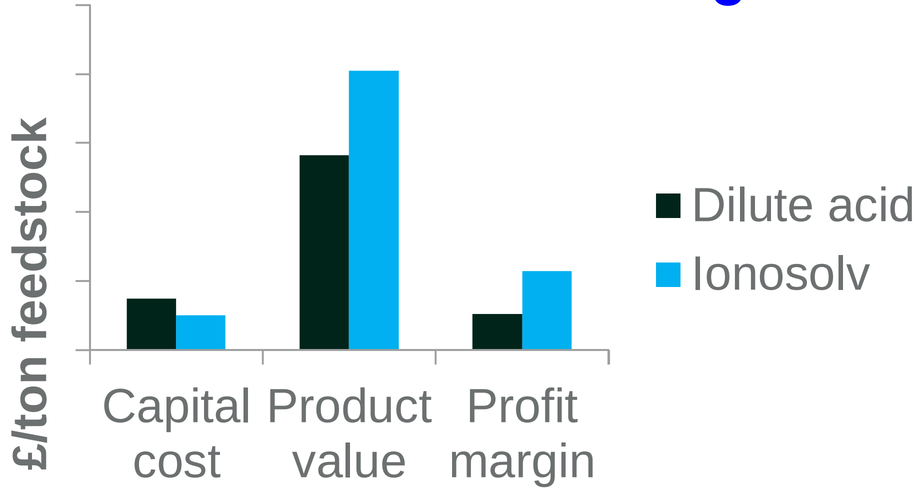
TECHNOLOGIES

# Comparison of economics with other technologies

| | Virgin wood/ton |
|---|---|
| Plant size | 100,000 tpa |
| Solvent | £11 |
| Biomass | £52 |
| Water | £ 4 |
| Capital | £25 |
| Energy | £51 |
| **COST** | **£142** |
| Cellulose | £ 84 |
| Lignin | £ 88 |
| Hemicellulose | £ 36 |
| **VALUE** | **£207** |
| **NET** | **£ 65** |
| **MARGIN** | **46%** |




•Compared to (dilute acid pretreatment

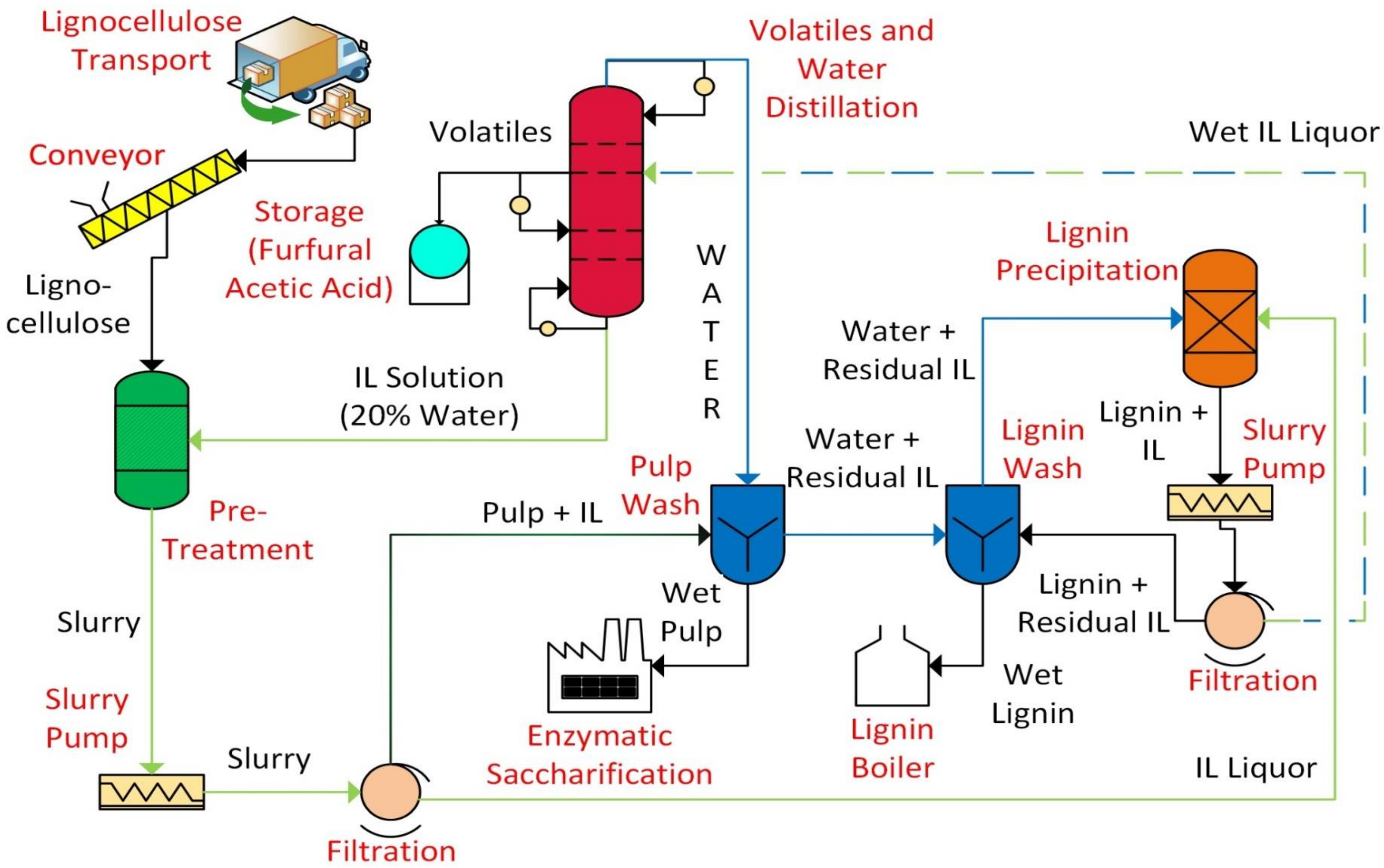
- **30%** lower capital costs
- **40%** higher product value
- **100%** larger profit margin

**Glucose can be sold at €0.16/kg**
**Also lower energy costs per ton of sugar than steam explosion**

- **Higher solids loading possible**
  - **(based here on 20%)**
  - **100% sugar release from grasses or softwoods at 10% solids loading**
  - **80% sugar release from softwoods at 50% solids loading**
- **Less phase change = less cost**

Brandt *et al.*, *Green Chem.* **2017**, *19*, 3078-3102.

# Process Flow Scheme

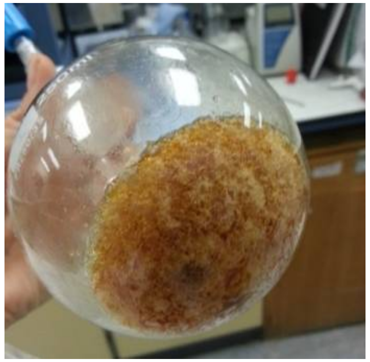



Brandt *et al.*, *Green Chem.* **2017**, *19*, 3078-3102

# IL recovery and recycling

- **Very high IL stability (>330 C)**
- **99.5 +/- 1% IL recovery**
- **ca. 100% lignin recovery**
- **No inorganic salt buildup**

Fresh IL

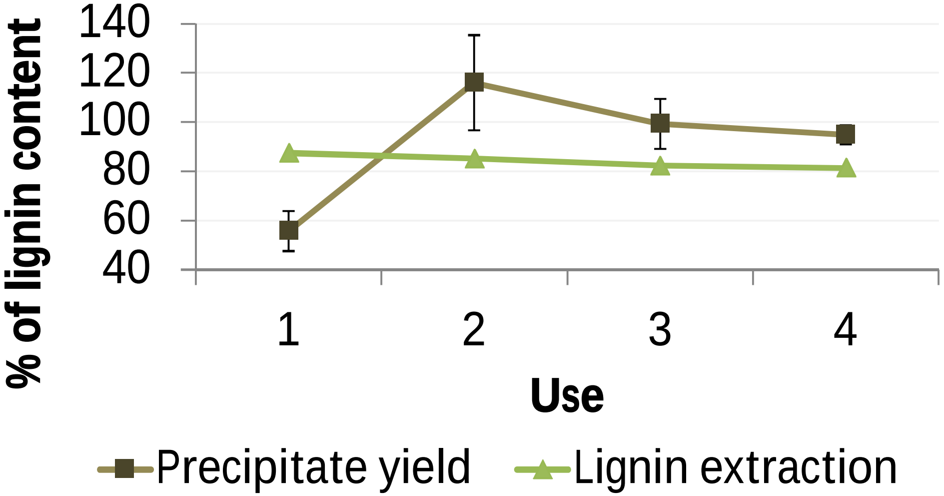


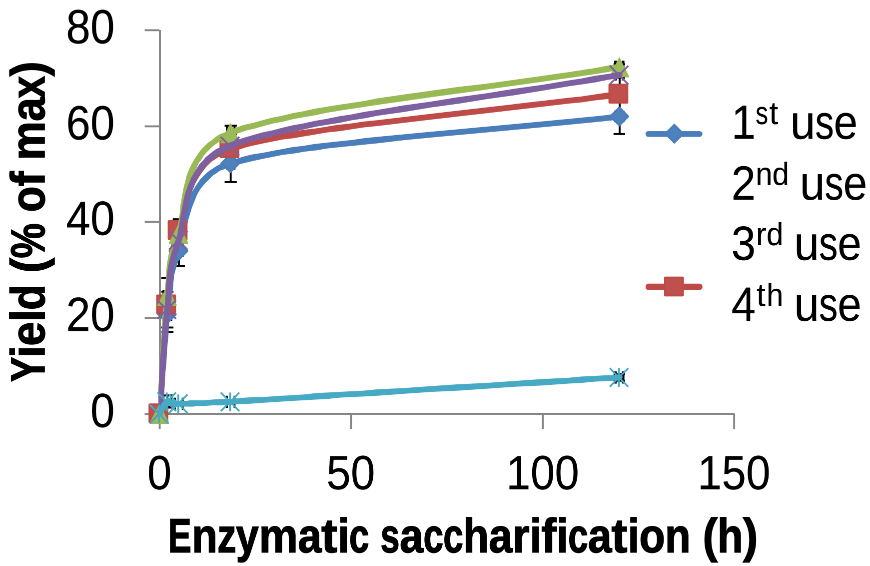
After $1^{st}$ use

After $4^{th}$ use

| | IL Recovery (%) | |
|---|---|---|
| $1^{st}$ use | **99.0** | ±3.7 |
| $2^{nd}$ use | **97.9** | ±1.7 |
| $3^{rd}$ use | **99.4** | ±8.4* |
| $4^{th}$ use | **99.3** | ±0.9 |

* error due to mixing two replicates during pulp washing

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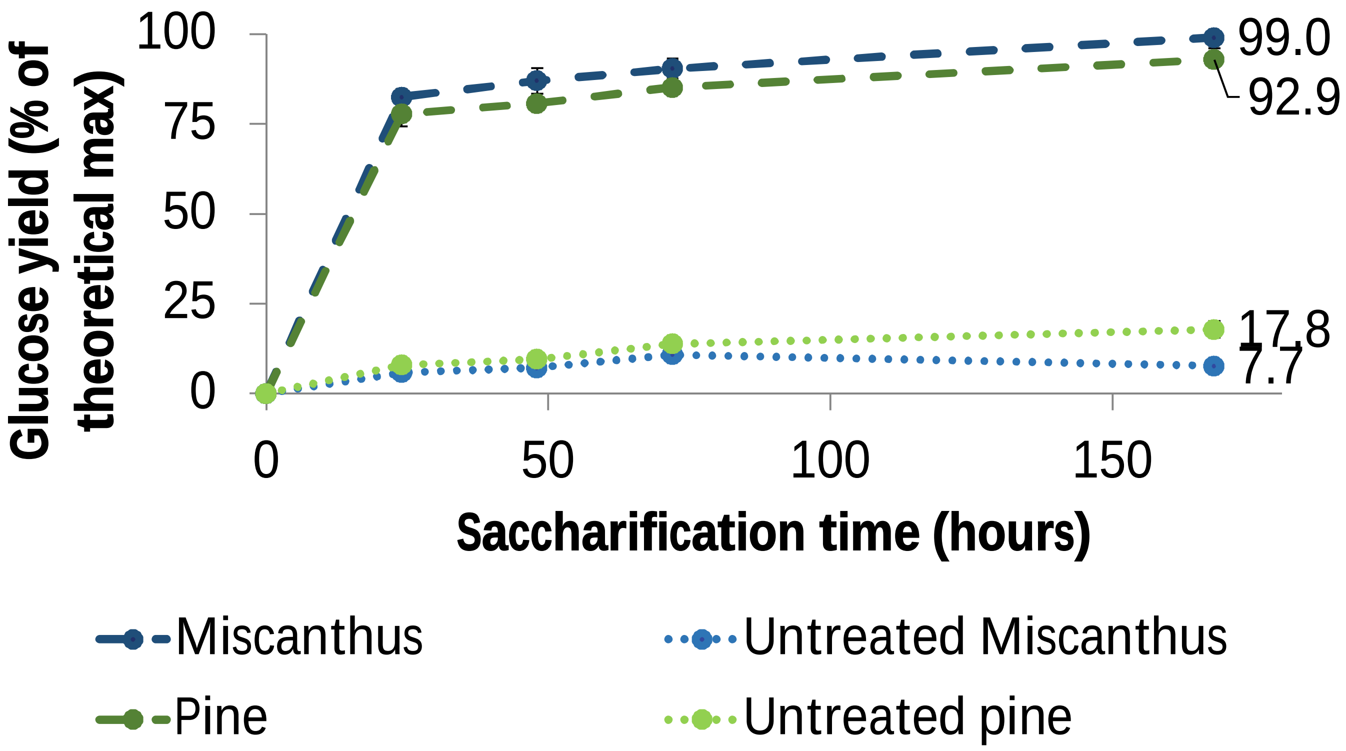
# Feedstock doesn't matter?



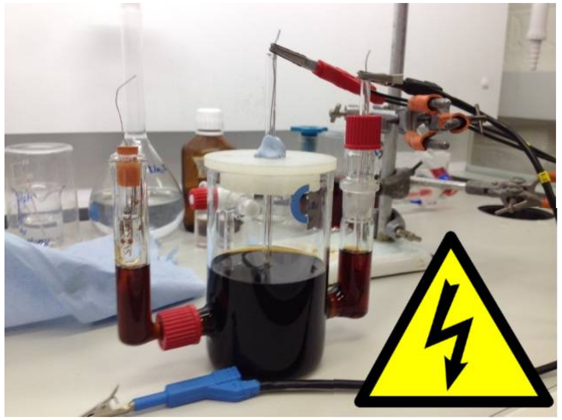

High Biomass loadings

| | **Saccharification yield** | |
|---|---|---|
| **Loading** | **with air drying** | **without air drying** |
| 10% | 64.8±3.5% | 99.2±1.9% |
| 50% | 34.4±3.2% | 74.9±2.9% |

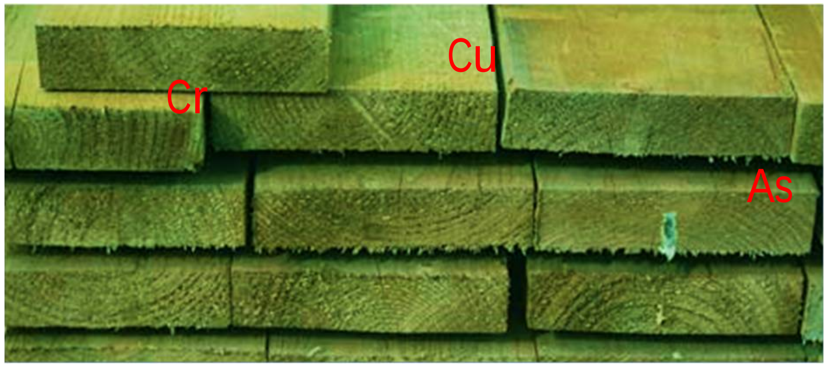
- ✓ Higher yields if pulp drying is avoided
- ✓ Larger impact at high loadings
- ✓ Multiple feedstocks combined

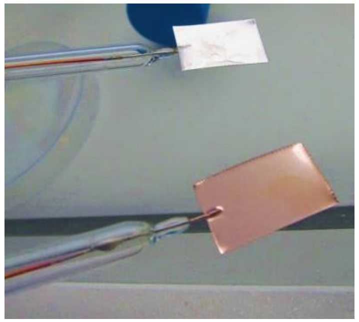
# Metal-containing waste wood

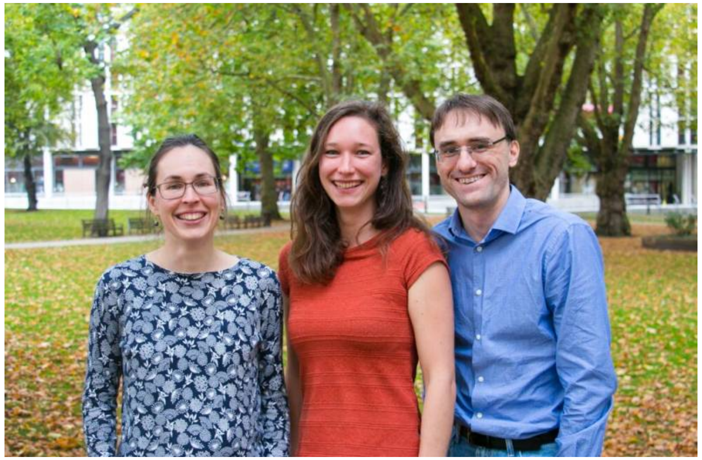
- ✓ Extraction of Cu, Cr and As
- ✓ Recovery of the metals through electro-plating
- ✓ High sugar yields



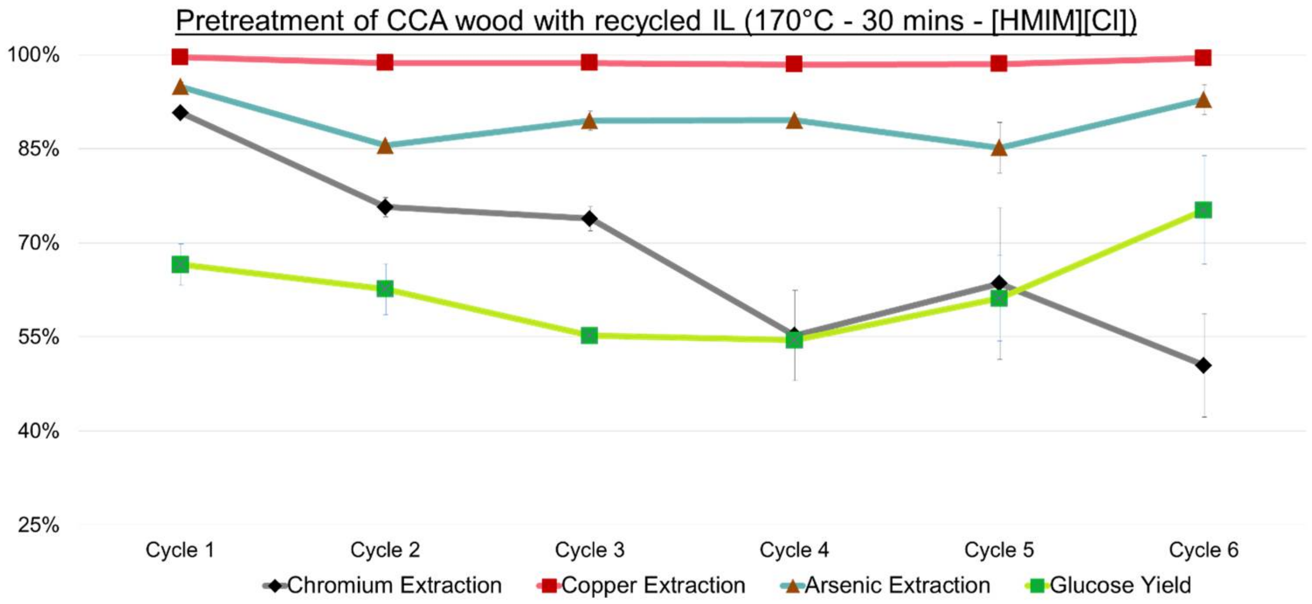
- ✓ 60 Mt/y US; 70 Mt/y EU
- ✓ Cannot be incinerated for biopower
- ✓ UK: £130/t for landfilling

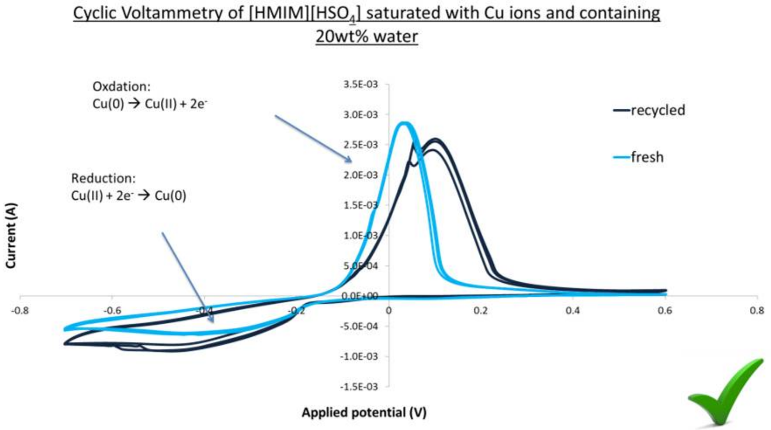


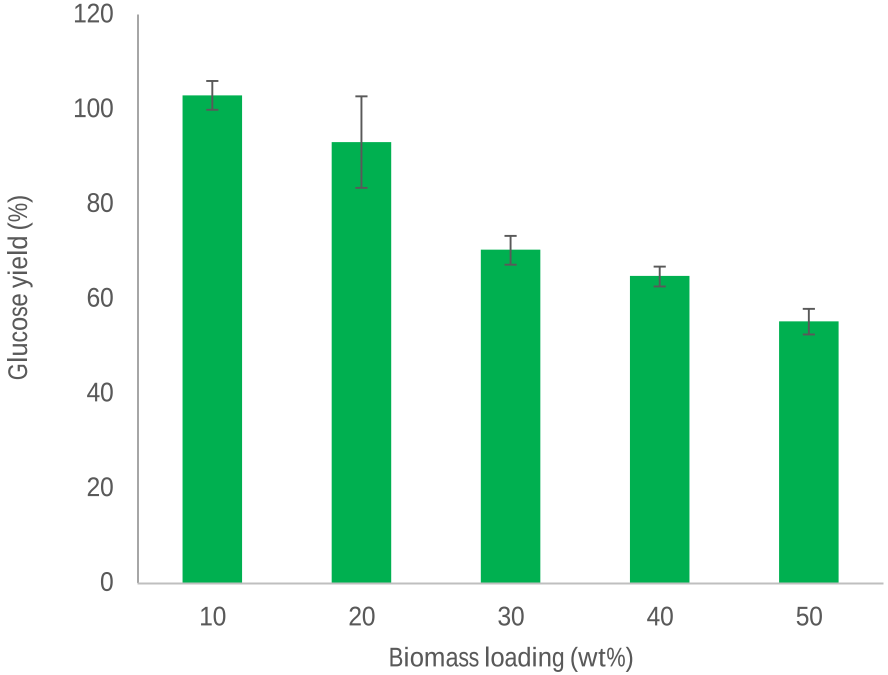


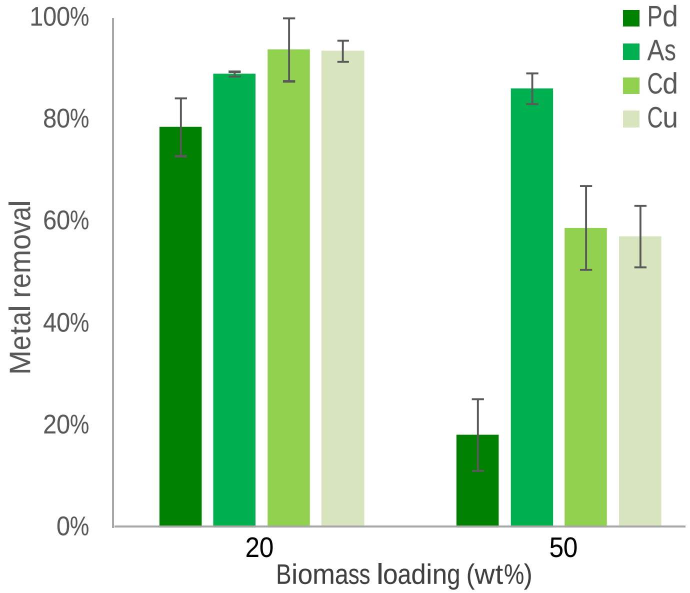
# OK, So It Works



# Any Waste Wood?



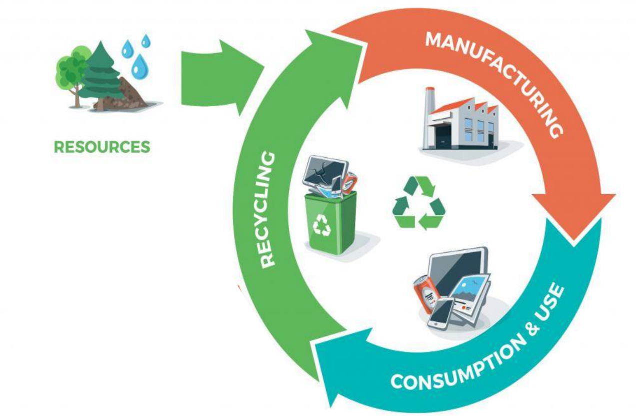


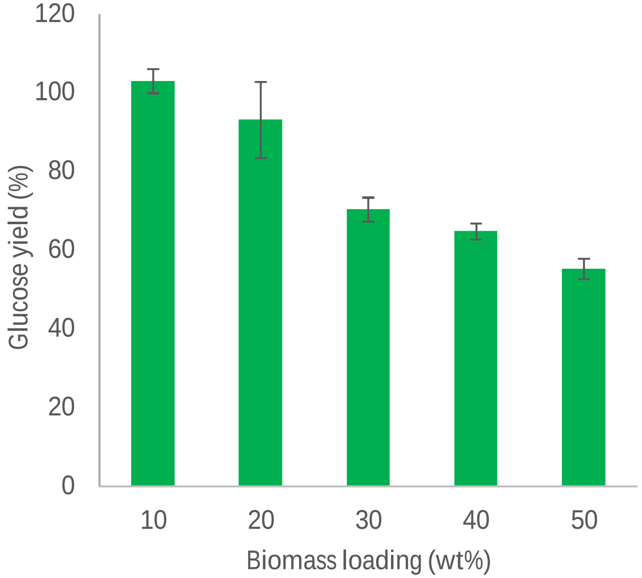
You don't get to choose what is in waste!

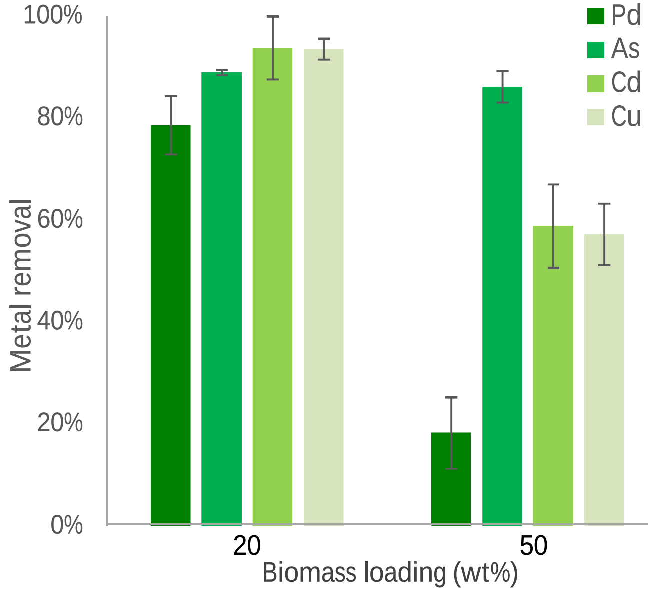
# Waste wood to fuels & materials


*Contributing to circular economy*

- Use post-consumer waste wood as very cheap (negative) feedstock for biorefinery
- Use low-cost ionic liquid process to:
  - *Save environment:* divert from landfill and remove heavy and toxic metals
  - *Make fuels & chemicals:* fractionate decontaminated waste wood to cellulose & lignin



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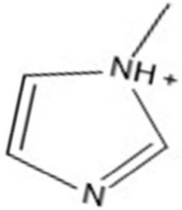
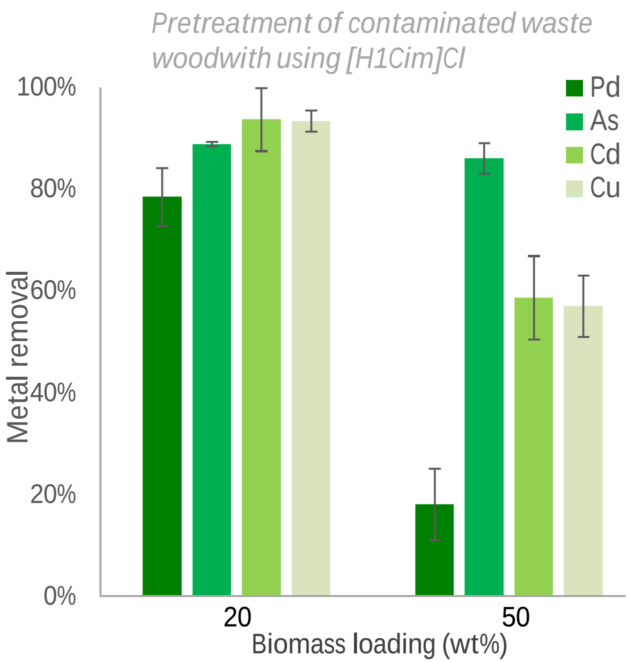


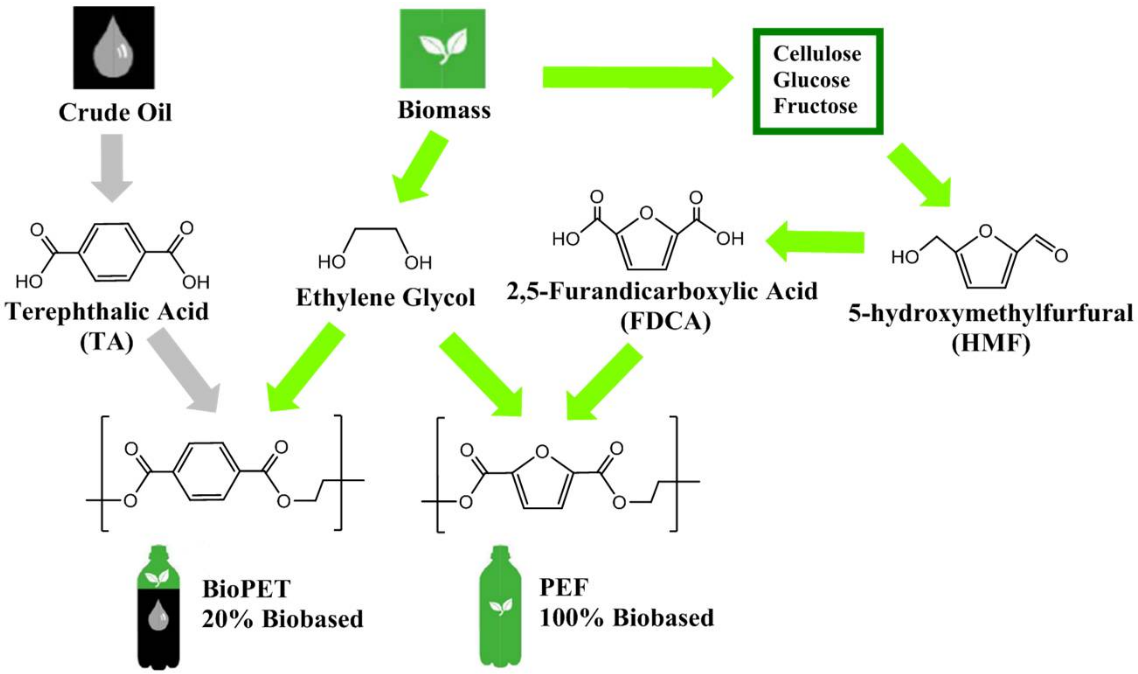

Ionic liquid processing

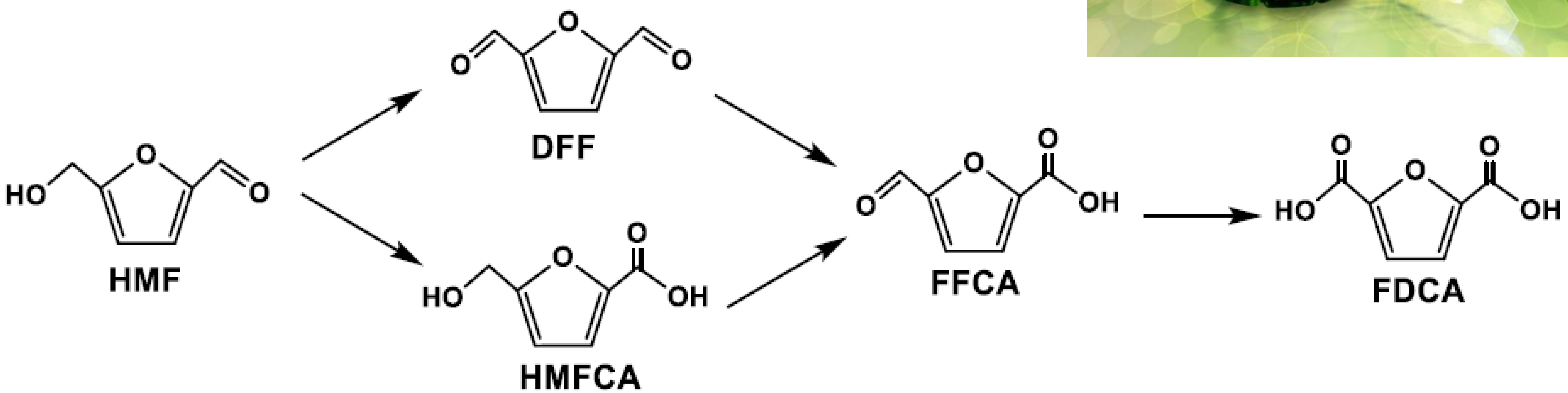



# Feedstock-controlled economics?

| | Waste wood/ton | Virgin wood/ton |
|---|---|---|
| Plant size | 20,000 tpa | 100,000 tpa |
| Cellulose | £ 90 | £ 90 |
| Lignin | £ 94 | £ 94 |
| Hemic/Furfural | £ 38 | £ 38 |
| Gate fee | £ 54 | - |
| **REVENUE** | **£ 276** | **£ 222** |
| | | |
| Solvent | £ 11 | £ 11 |
| Biomass | - | £ 56 |
| Water | £ 4 | £ 4 |
| Capital | £ 43 | £ 26 |
| Energy | £ 55 | £ 55 |
| **COST** | **£ 113** | **£ 152** |
| | | |
| PROFIT | **£ 163** | **£ 70** |
| **GROSS MARGIN** | **59%** | **32%** |

# Onward to bioderived plastics!



# Conclusions

- Ionic liquids do not have to be expensive
  - Targeted applications still possible
  - Use common sense when designing
- Delignification of biomass
  - Simple process
  - Stable, recoverable, recyclable solvents
  - High solids loadings possible
- Recycling improves performance
- Economics-driven approach to solvent design
  - Can be application specific

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