Acid catalysed alcoholysis of lignocellulose

Towards second generation furan-derivatives

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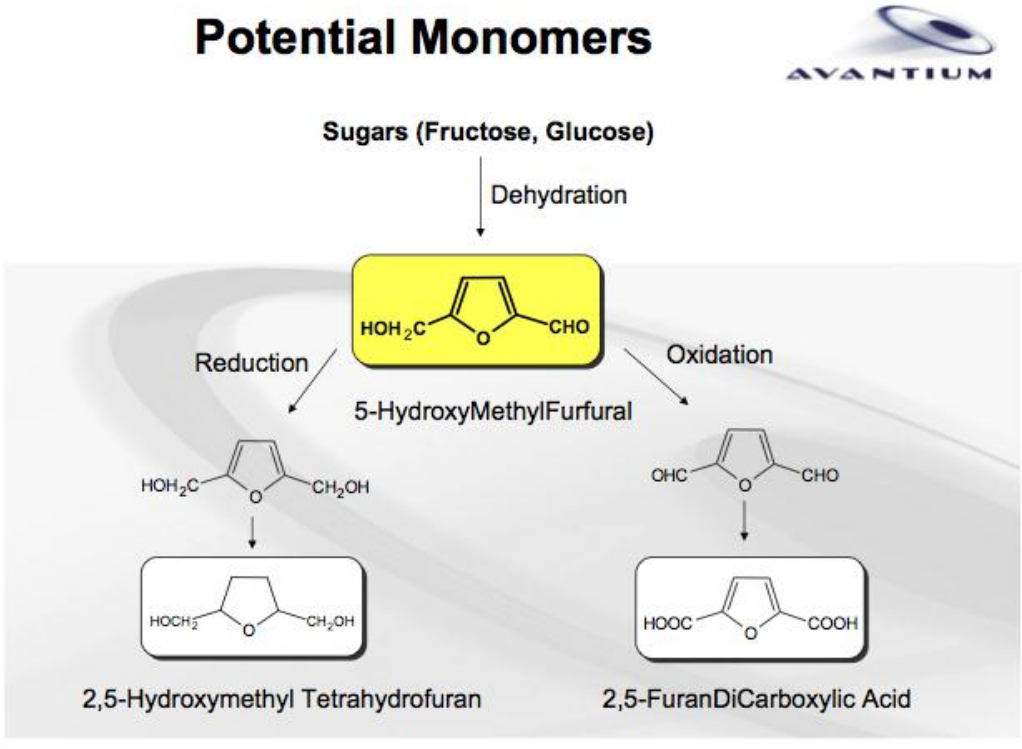
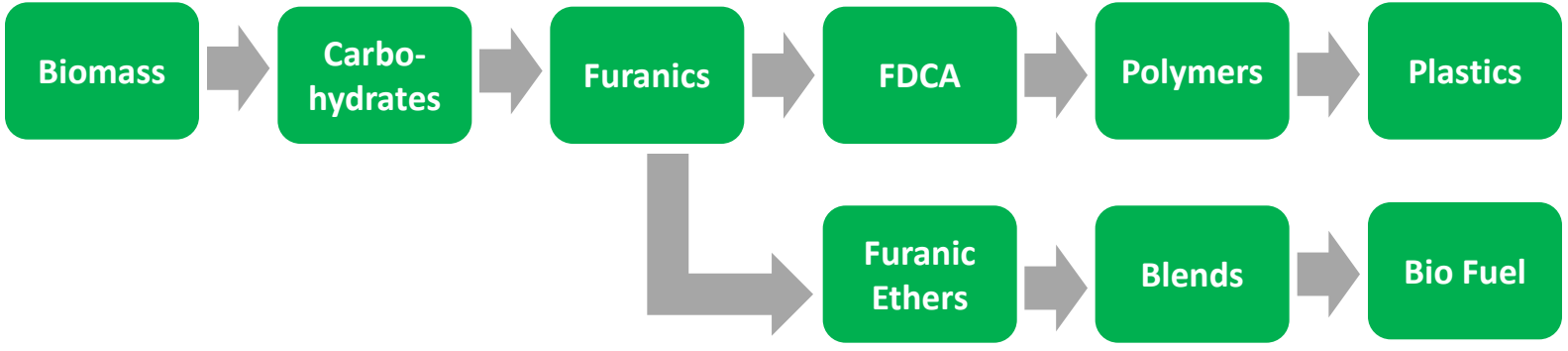
COST Action CM0903 (UBIOCHEM)
3rd Workshop, Thessaloniki (Greece), 1-3 November, 2012

Furanics

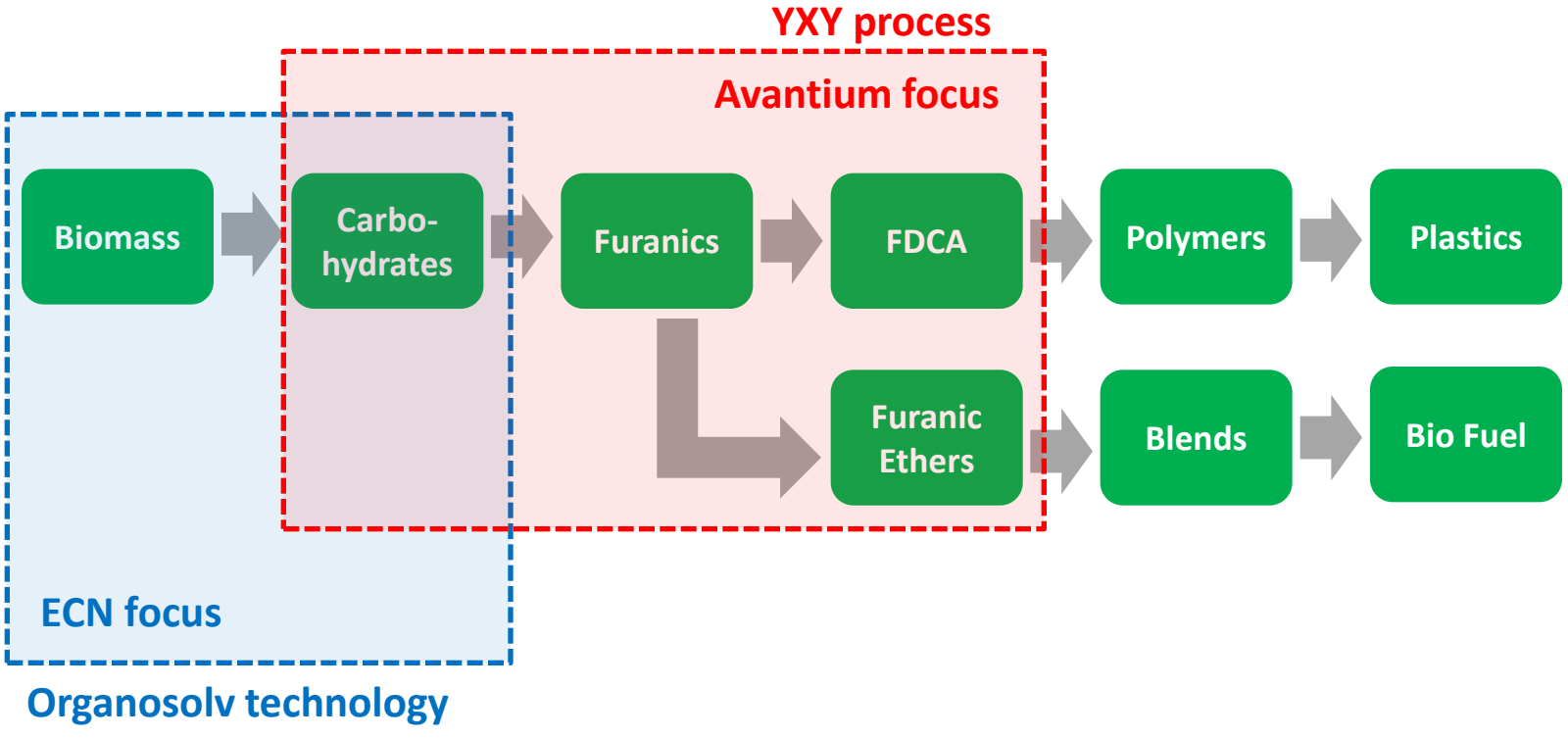


PEF plant bottle

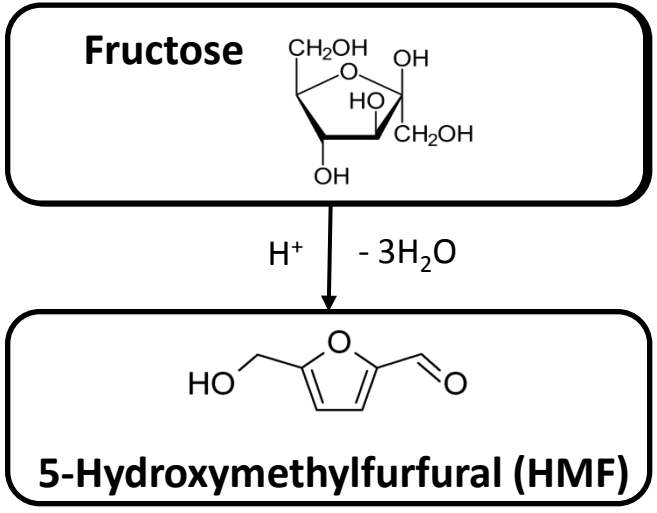
2nd Generation Furanics



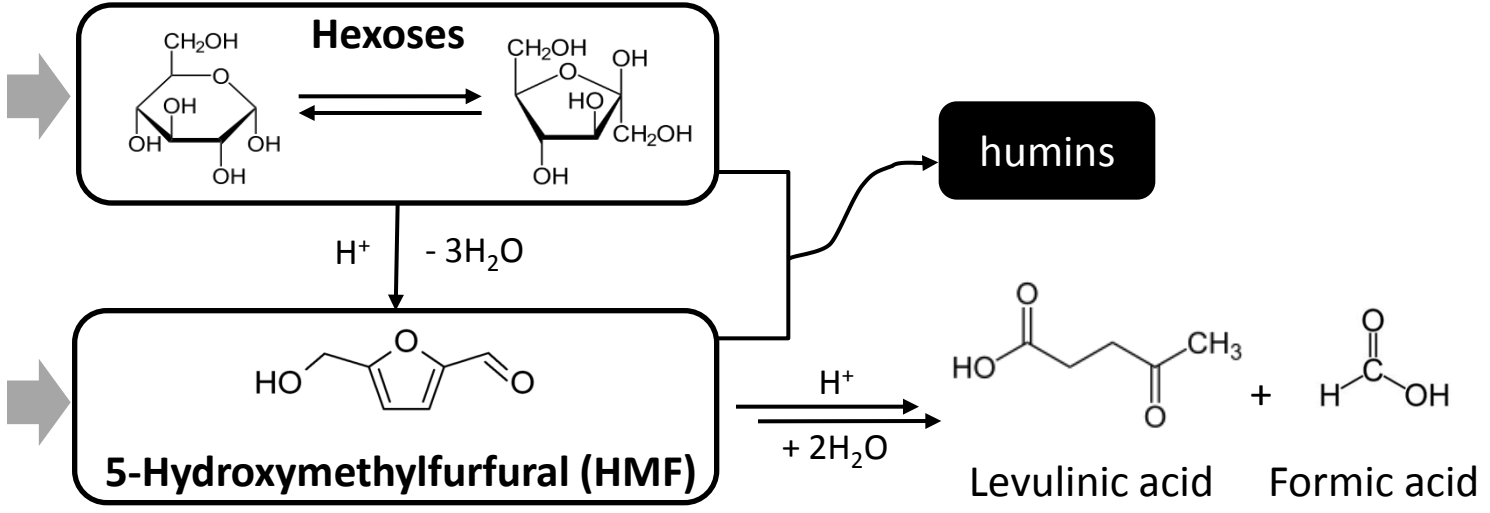
2nd Generation Furanics



Chemistry

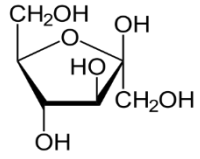

Fructose
CH2OH
OH
O
HO
CH2OH
OH
H+
- 3H2O
HO
O
O
5-Hydroxymethylfurfural (HMF)

Chemistry

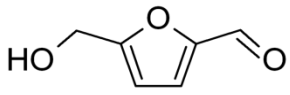

Hexoses
humins
H+
- 3H2O
5-Hydroxymethylfurfural (HMF)
H+
+ 2H2O
Levulinic acid
+
Formic acid

Chemistry

Fructose

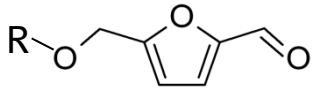


H^+ $- 3H_2O$



5-Hydroxymethylfurfural (HMF)

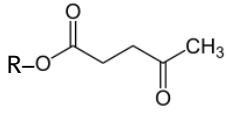
R-OH, cat $- H_2O$



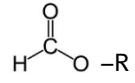
Alkoxy-methylfurfural (RMF)

H^+

$+ 2H_2O$



Alkyl levulinate

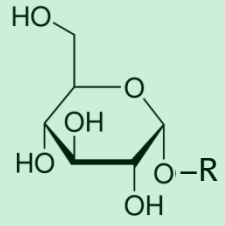


Alkyl formate

95% MeOH (w/w)
94% EtOH (w/w)

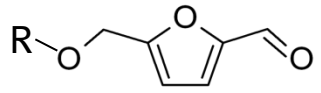
Alkyl-glucopyranoside intermediate

Fractionation / liquefaction



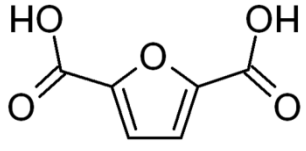
Alkyl-glucopyranoside

dehydration

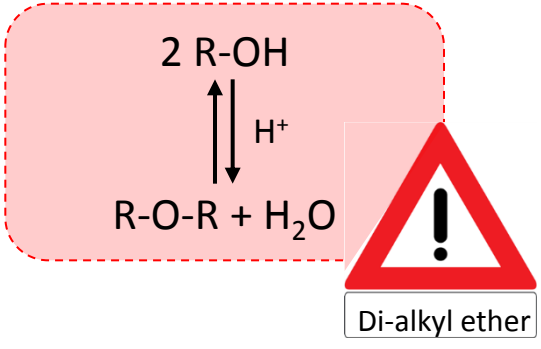


Alkoxy-methylfurfural (RMF)

oxidation



Furandicarboxylic acid (FDCA)



Di-alkyl ether

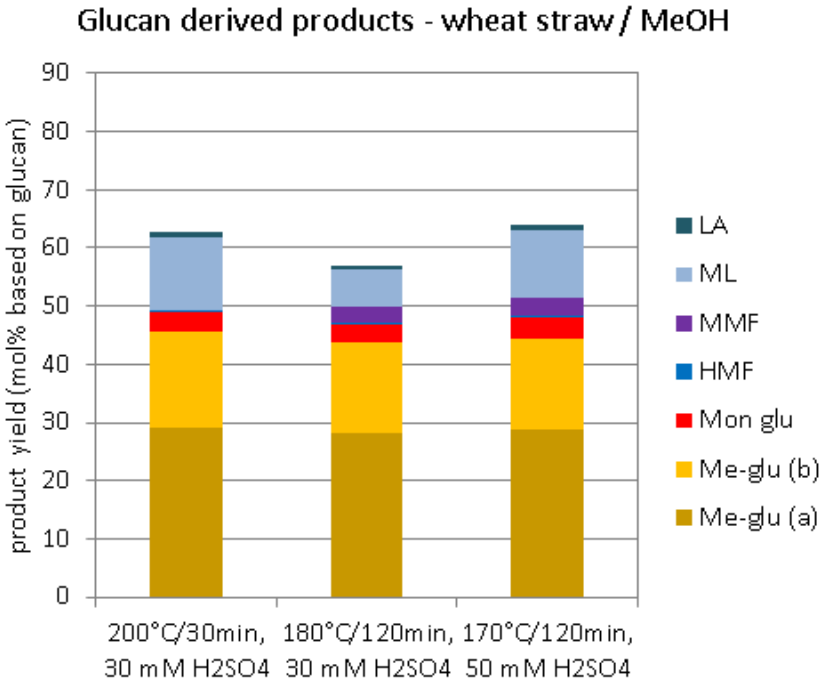
Experimental

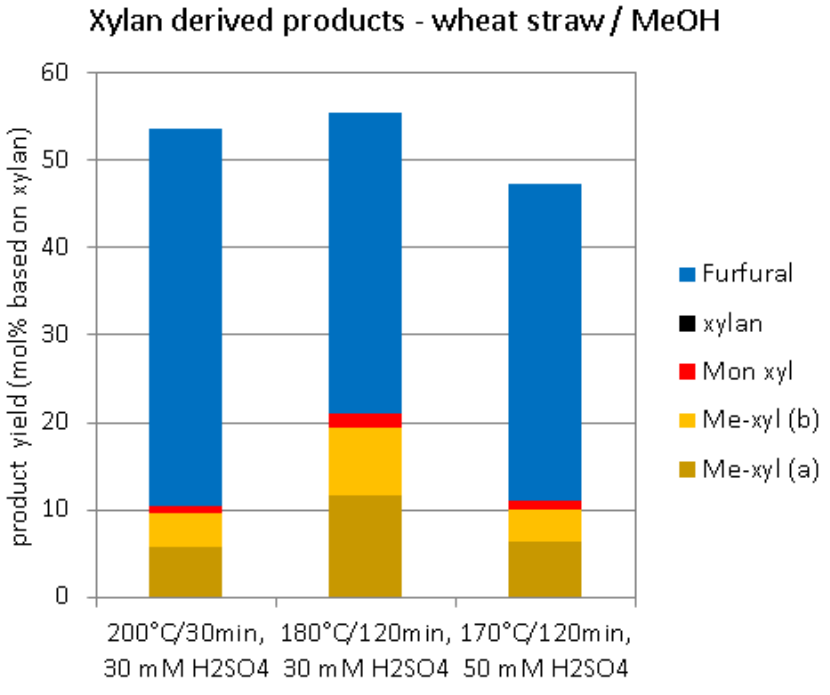
- Alcoholysis
  - Wheat straw optimisation of methyl-glucosides yield
  - Solvent: methanol, ethanol
  - Substrate: wheat straw, organosolv pulp, cellulose
  - Chloride: H_2SO_4 versus HCl, $MgCl_2$

  - 25 g biomass
  - 0 – 50 mM H_2SO_4
  - L/S = 11 L/kg dry mass
  - T = 160–200 C
  - t = 30–150 min

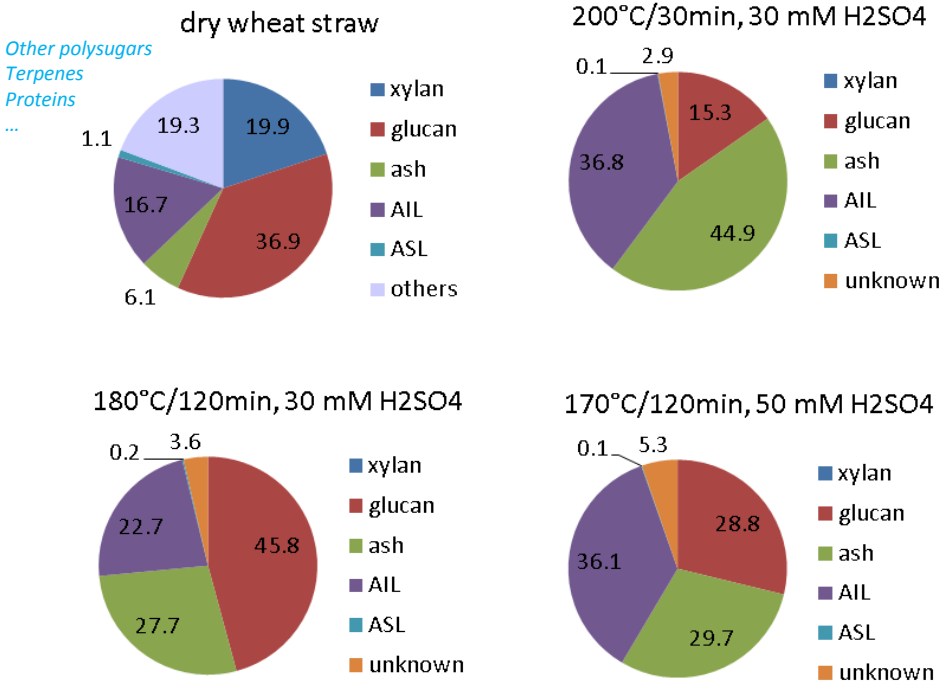

Autoclave reactor (0.5 L Hastelloy Kiloclave, Büchi Glas Uster AG, CH)

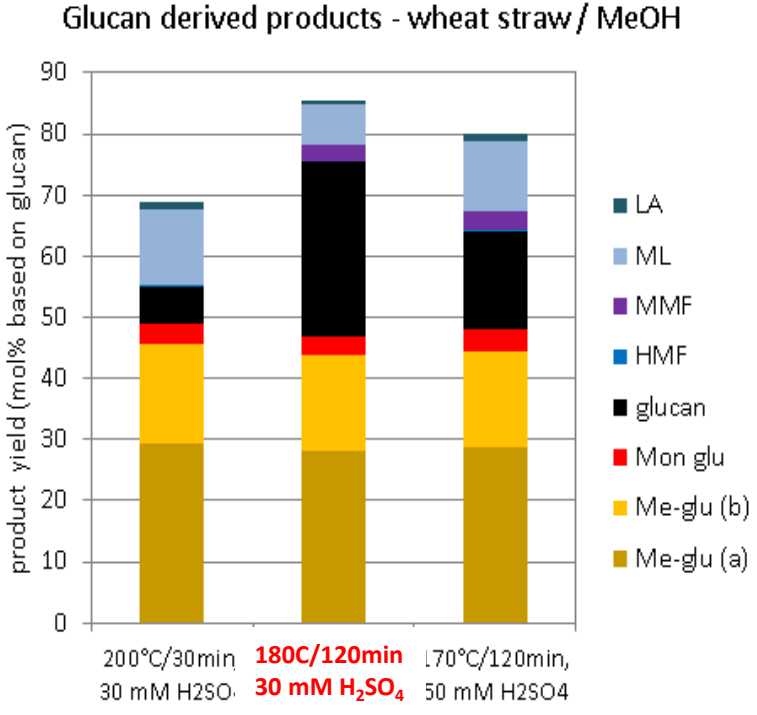
Screening


Glucan derived products - wheat straw / MeOH
product yield (mol% based on glucan)
90
80
70
60
50
40
30
20
10
0
200°C/30min, 30 mM H2SO4
180°C/120min, 30 mM H2SO4
170°C/120min, 50 mM H2SO4
LA
ML
MMF
HMF
Mon glu
Me-glu (b)
Me-glu (a)

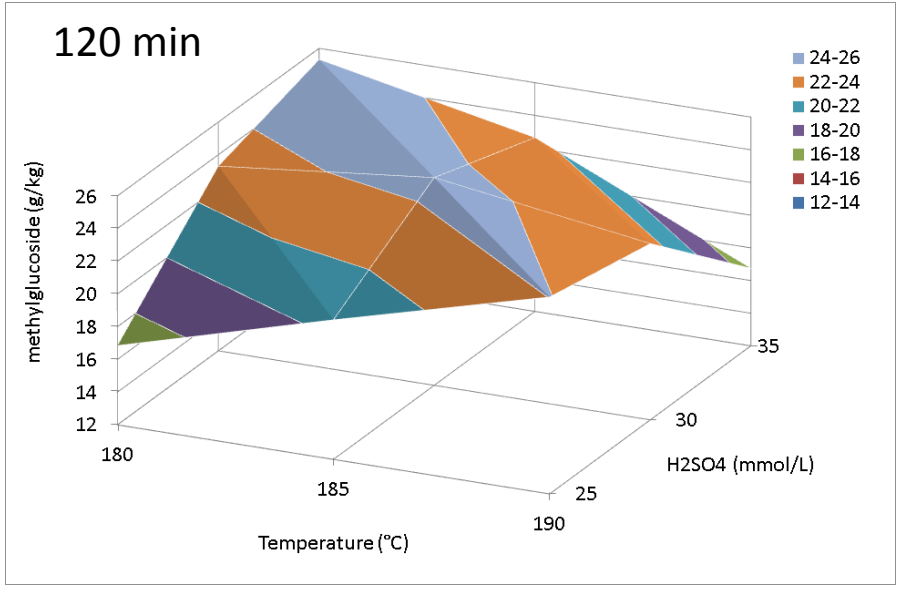

Xylan derived products - wheat straw / MeOH
product yield (mol% based on xylan)
60
50
40
30
20
10
0
200°C/30min, 30 mM H2SO4
180°C/120min, 30 mM H2SO4
170°C/120min, 50 mM H2SO4
Furfural
xylan
Mon xyl
Me-xyl (b)
Me-xyl (a)

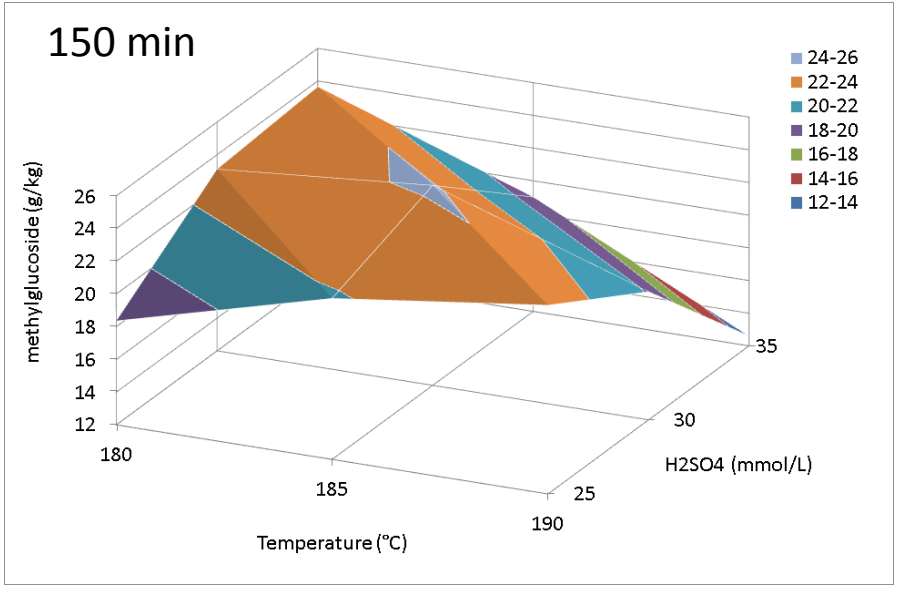
Screening: pulp potential included





Methyl glucosides optimisation

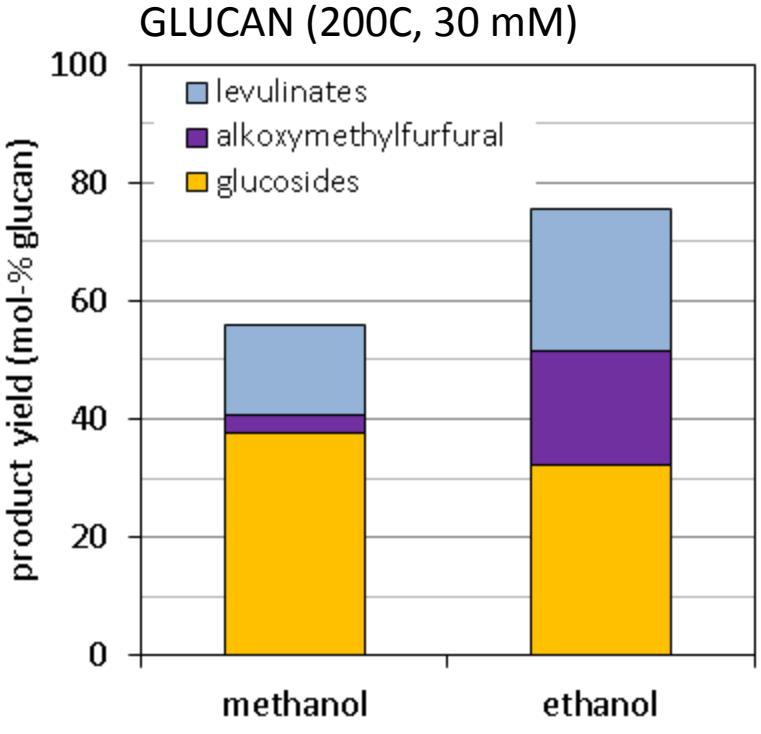


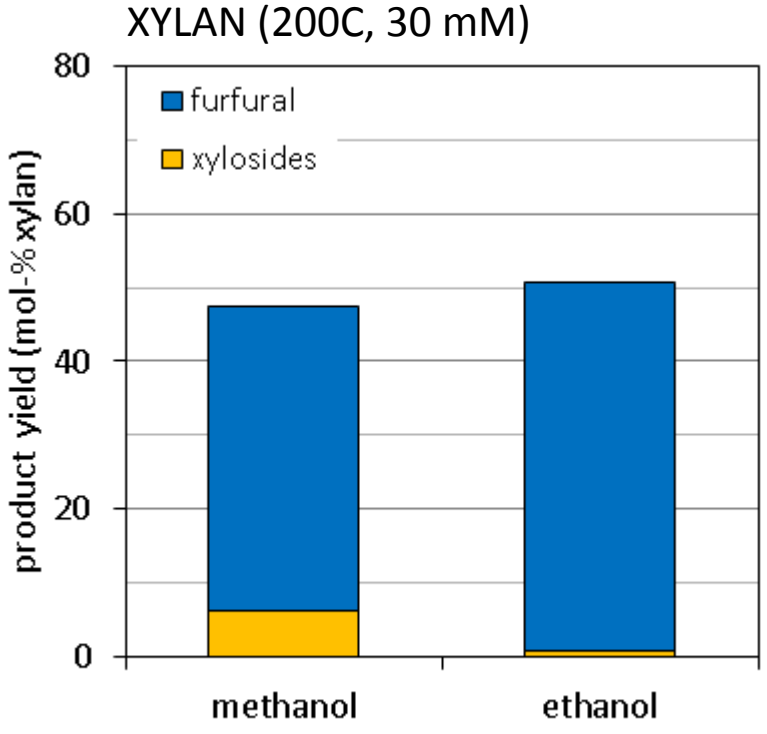


Extended optimisation
175 … 180C, 35 … 40 mM

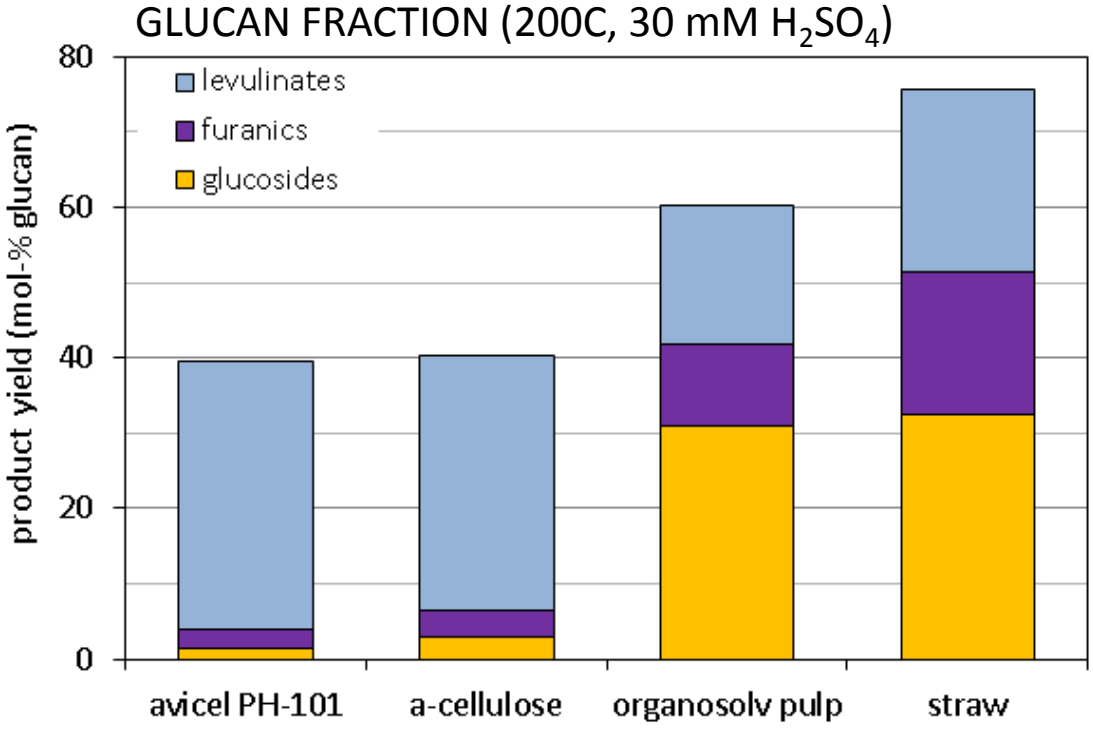
At 175C, 40 mM (120 min): yield 27.0 g/kg or
56 mol-% (based on initial glucan in straw)

Ethanol versus methanol





Substrate effect in ethanol

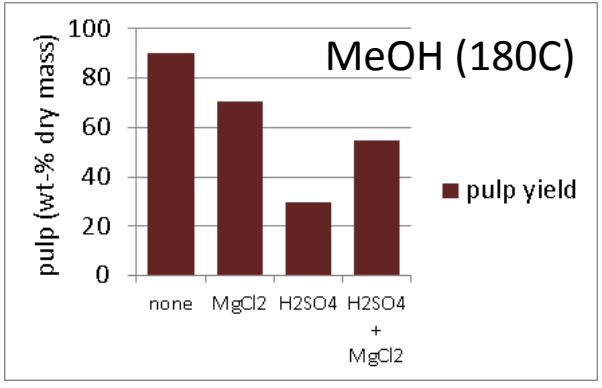


ANC straw 0.26 mol H^+/kg
(equivalent: 12 mM H_2SO_4)

ANC cellulose nil

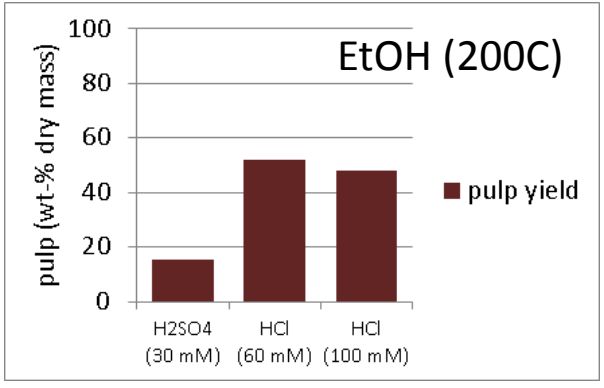
Ash content
- Straw 6.1% w/w
- Pulp 3.4% w/w

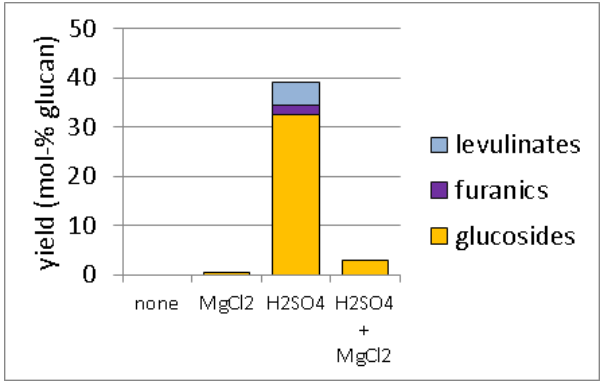
Effect of chloride



$$HCl + C_2H_5OH \rightleftharpoons C_2H_5Cl + H_2O + Cl^-$$

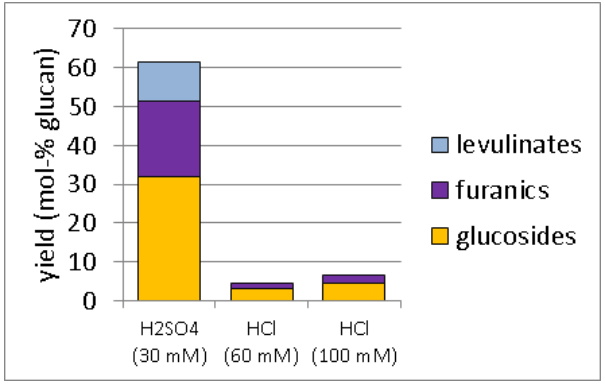
(consuming protons)





Milder conditions

Higher final pH
Higher pulp yield
Less soluble products
Furfural → xylosides



Conclusions

- Alcoholysis is a powerful tool to liquefy lignocellulosic biomass in one step, both in methanol and ethanol
- Alkyl-glucosides can be produced in high yield 56 % (of glucan), simultaneously with a high yield of furfural 55 % (of xylan) directly from lignocellulosic biomass at 175C
- Under tested conditions the alcoholysis is mainly Brønsted acid catalysed
  - The ANC of biomass is affecting the optimum acid dose
  - Chloride ($MgCl_2$, HCl) has a large neutralising effect due to chlorination of the solvent
- Lignin has no large detrimental effect on alcoholysis in the studied ranges
  - Delignification prior to alcoholysis does not change the product distribution much,
    allows higher glucan loadings and
    changes the ANC of the solid

Acknowledgement

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Thank you for your attention.

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