# Extraction of spruce hemicelluloses

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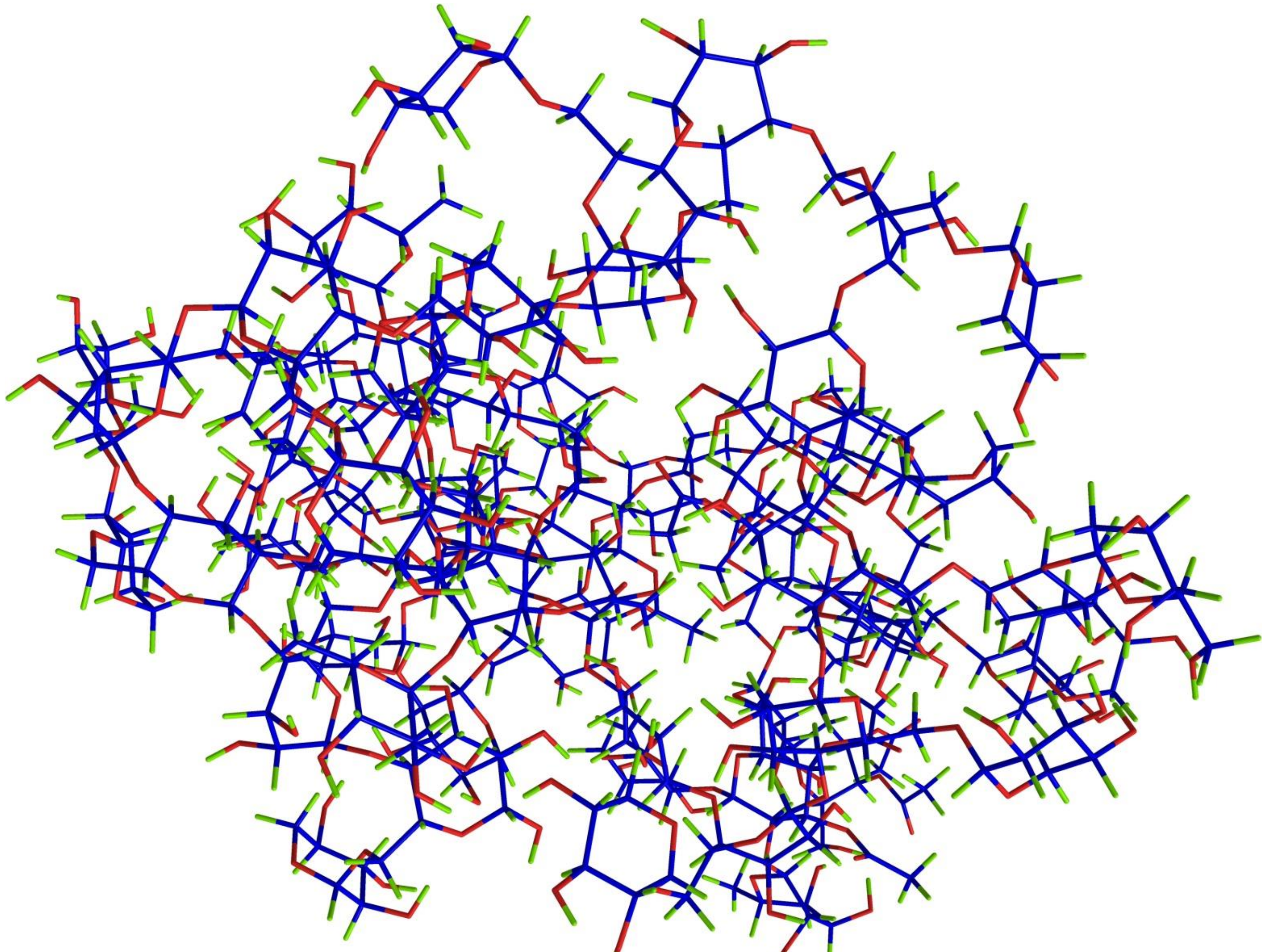
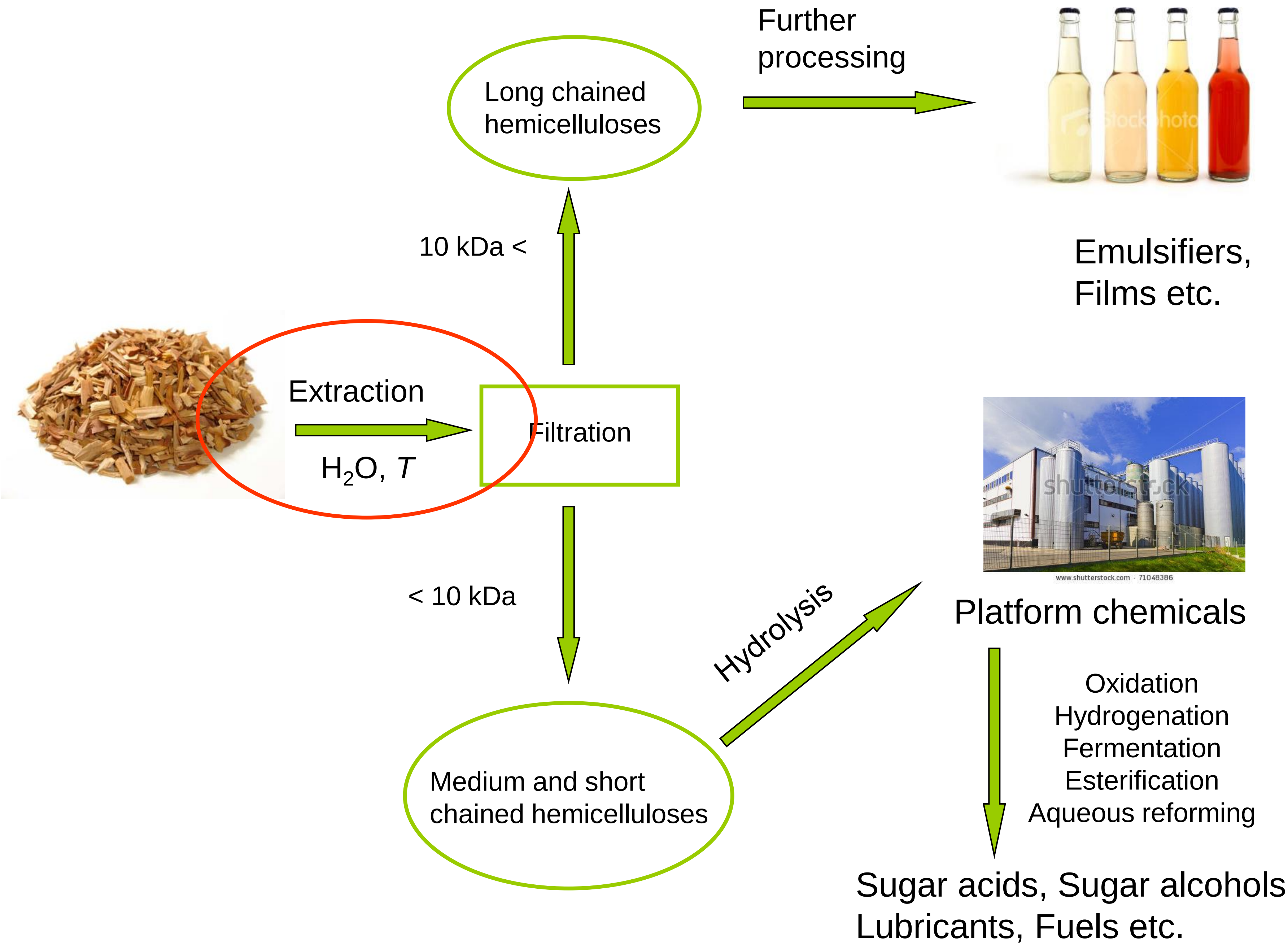
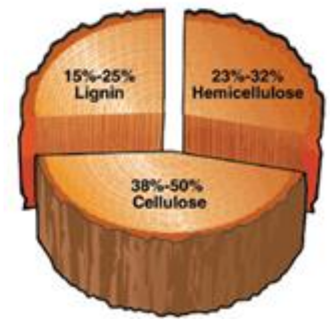
# Hemicellulose molecule



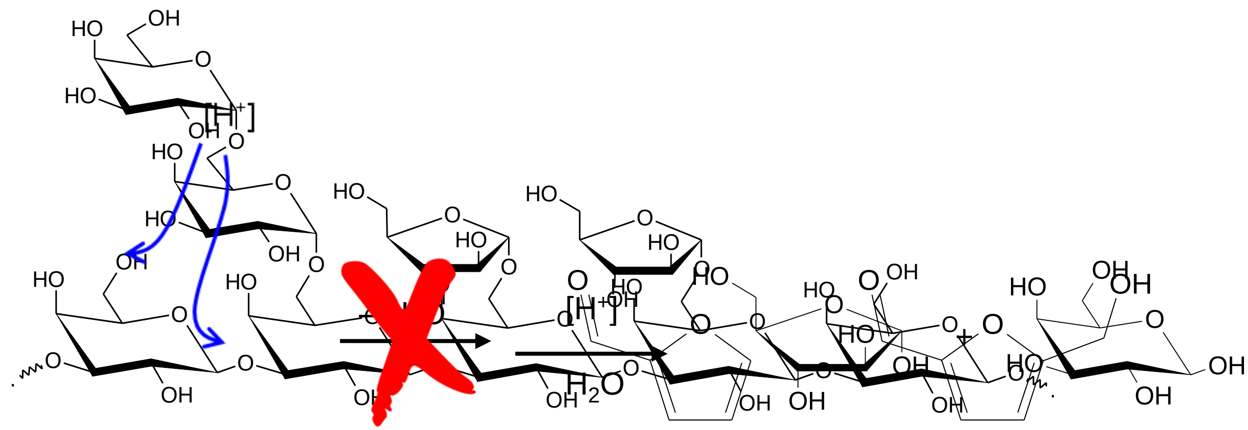

Long chained hemicelluloses
Further processing
Emulsifiers, Films etc.
10 kDa <
Extraction
$H_2O$, $T$
Filtration
< 10 kDa
Hydrolysis
www.shutterstock.com · 71048386
Platform chemicals
Oxidation
Hydrogenation
Fermentation
Esterification
Aqueous reforming
Medium and short chained hemicelluloses
Sugar acids, Sugar alcohols, Lubricants, Fuels etc.

# Background

- Protonation of glycosidic bonds




Wood

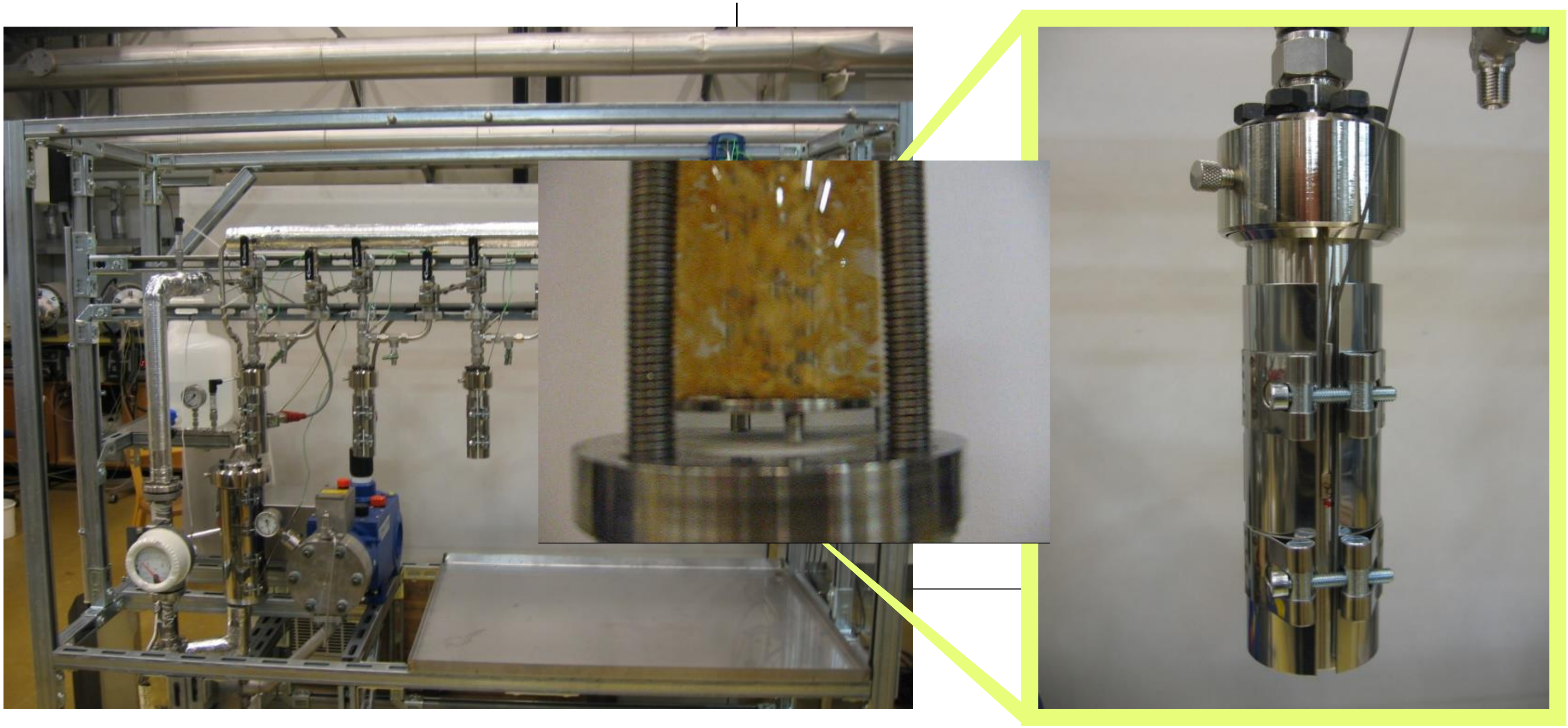


# Starting material

Non-extracted chips, 1.25 – 2 mm

Non-extracted cubic blocks, 10 mm

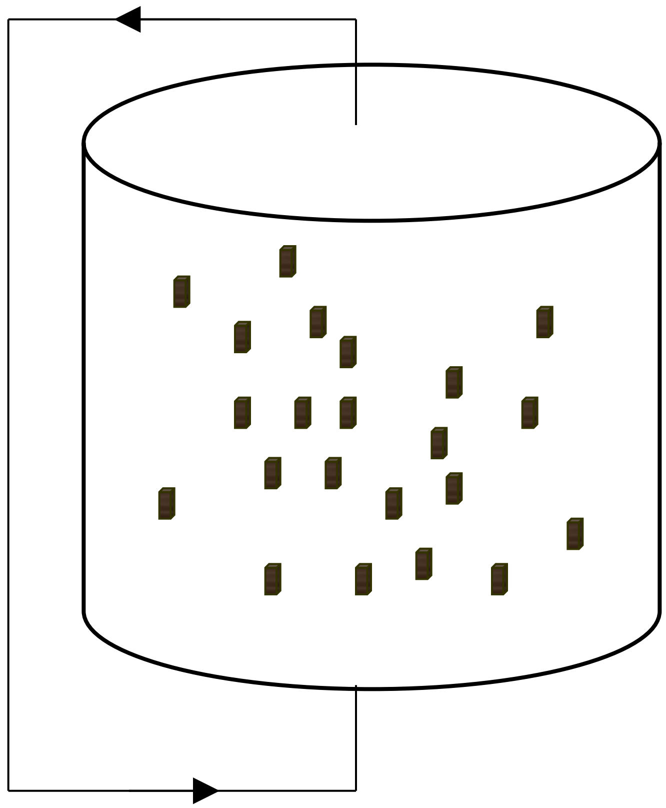
# Reactor system



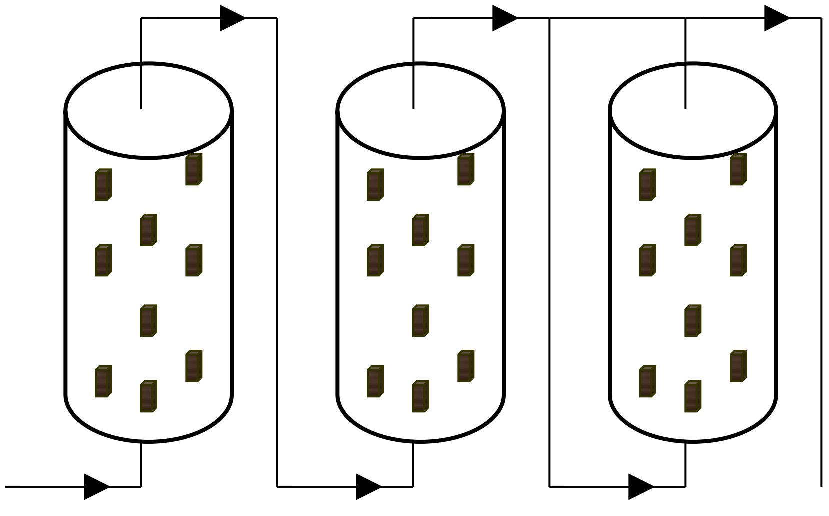
- Cascade reactor
- Flexible 5 point sampling of liquid and solid phases
- Accurate control and measurement of temperature, pressure and flow rate

# Batch reactor versus cascade reactor

## Traditional batch digester



## Cascade reactor



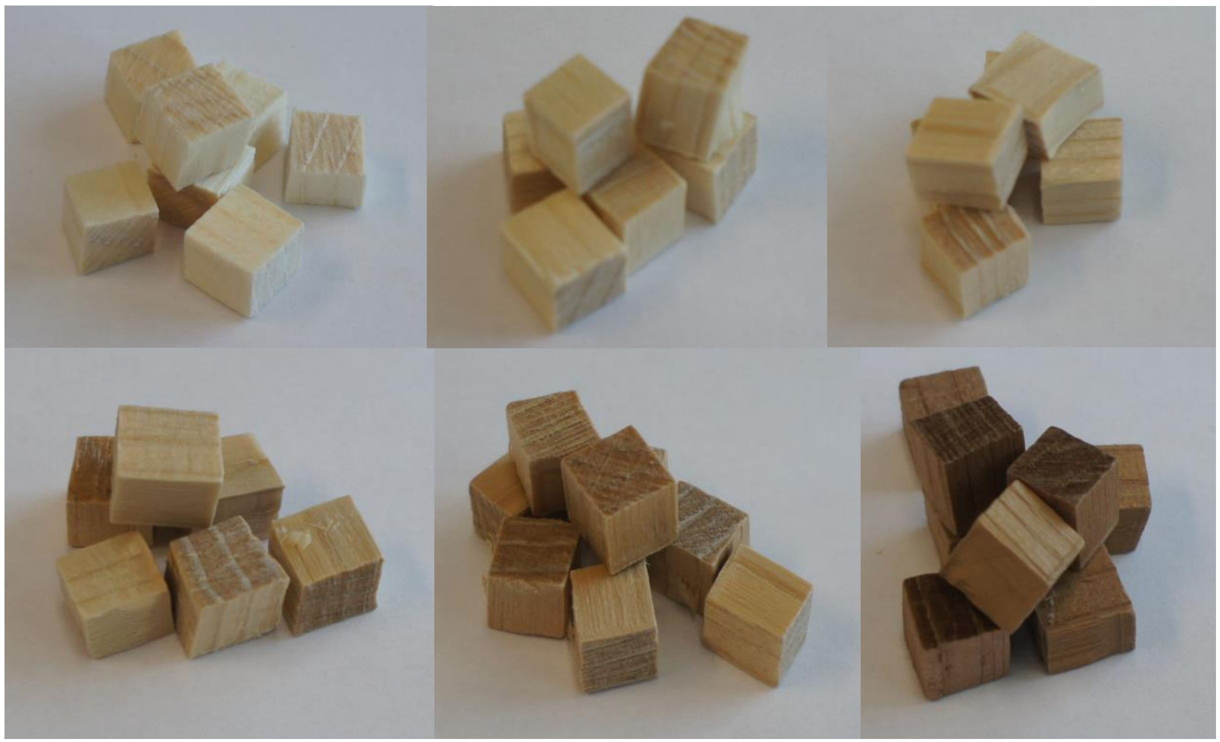
*The chips do not differentiate between reactor type*

# Liquid samples, 170°C, 0-60 min


- The viscosity of the extract increasing
- The color becomes brown

# Solid samples, 170°C, 0-60 min

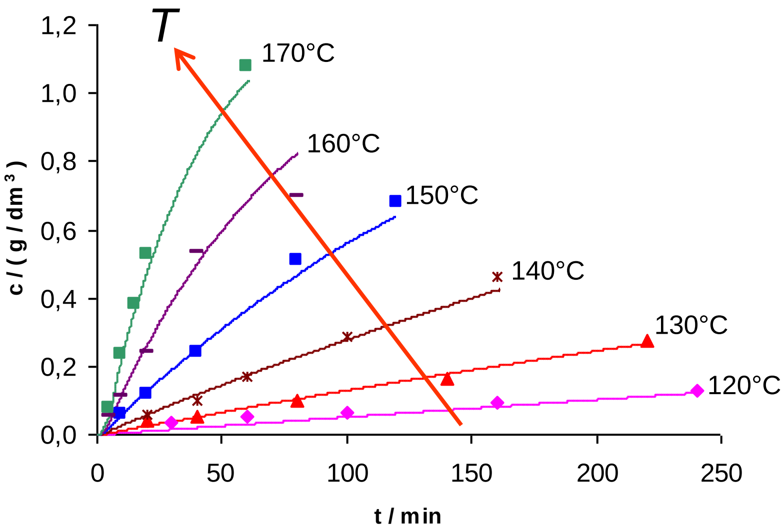
0 min 5 min 10 min



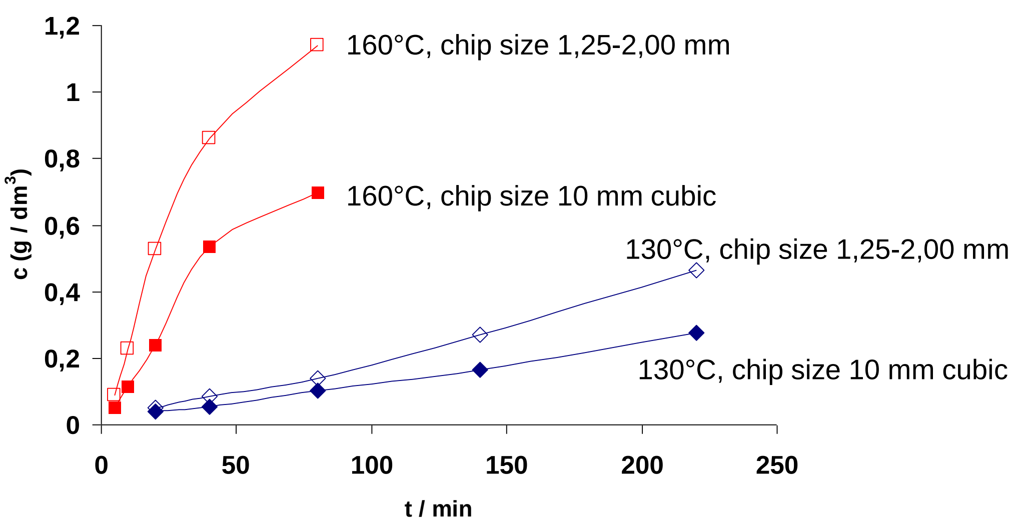
15 min 20 min 60 min

# Experimental results

The influence of temperature and chip size on the overall extraction rate

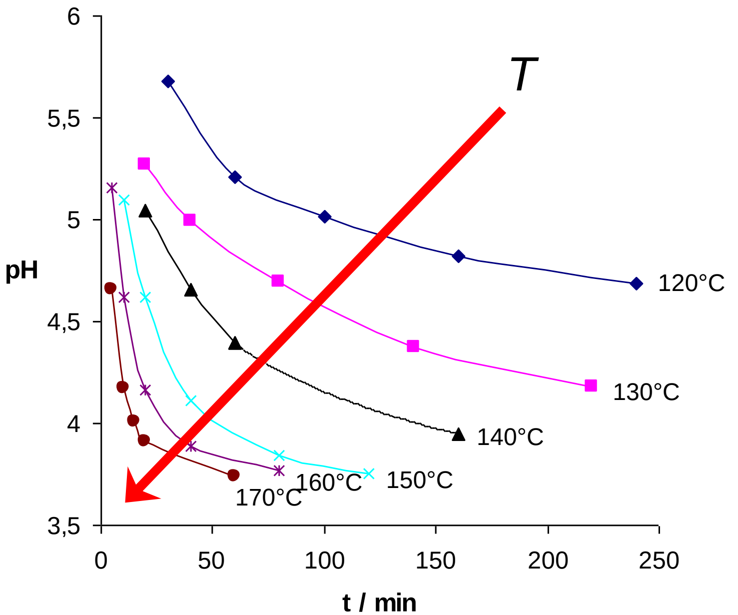



Concentration of hemicellulose as a function of time (10 mm cubic blocks).

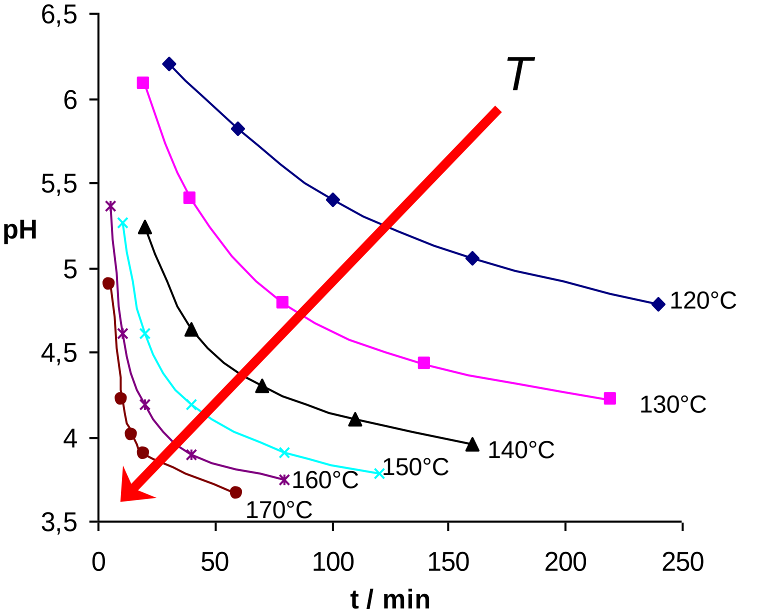



Liquid phase concentration as a function of time with different chip sizes.

# The behaviour of pH during extraction



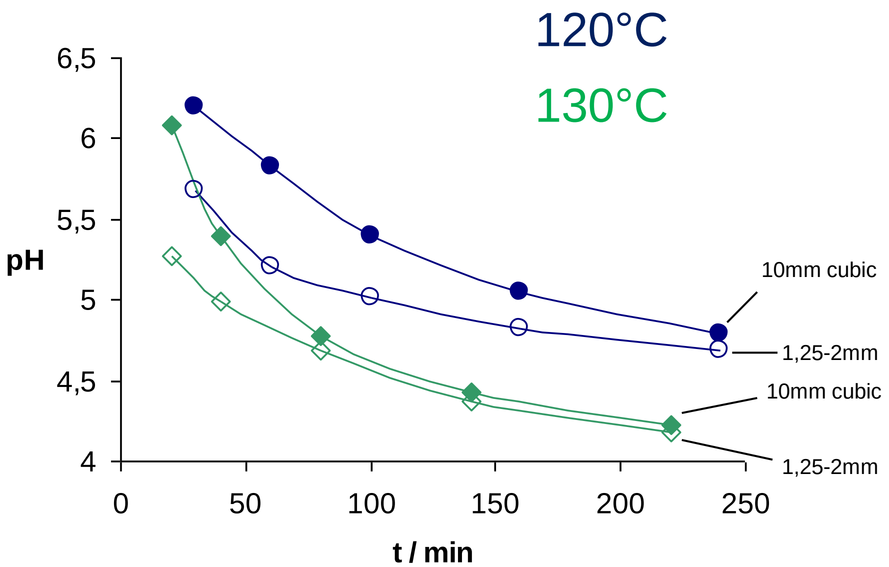

1,25 – 2,00 mm wood chips



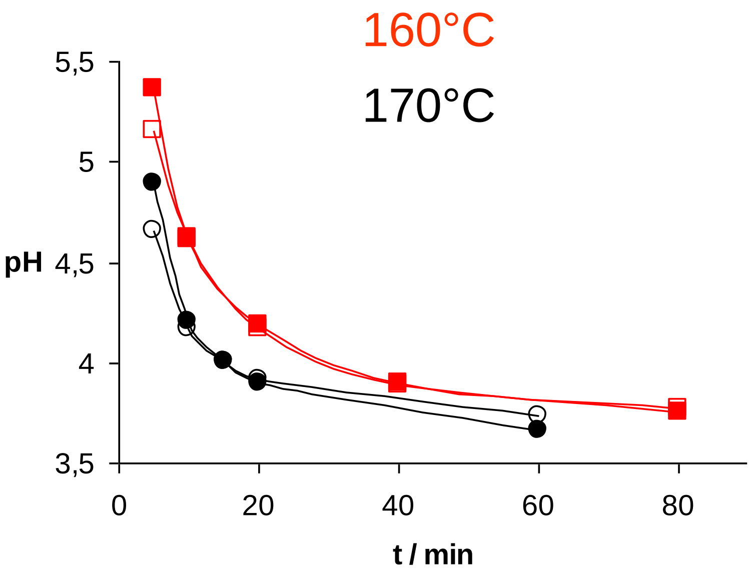

10 mm cubic wood blocks

# Influence of chip size on pH

The behavior of the pH during the reaction at four different temperatures

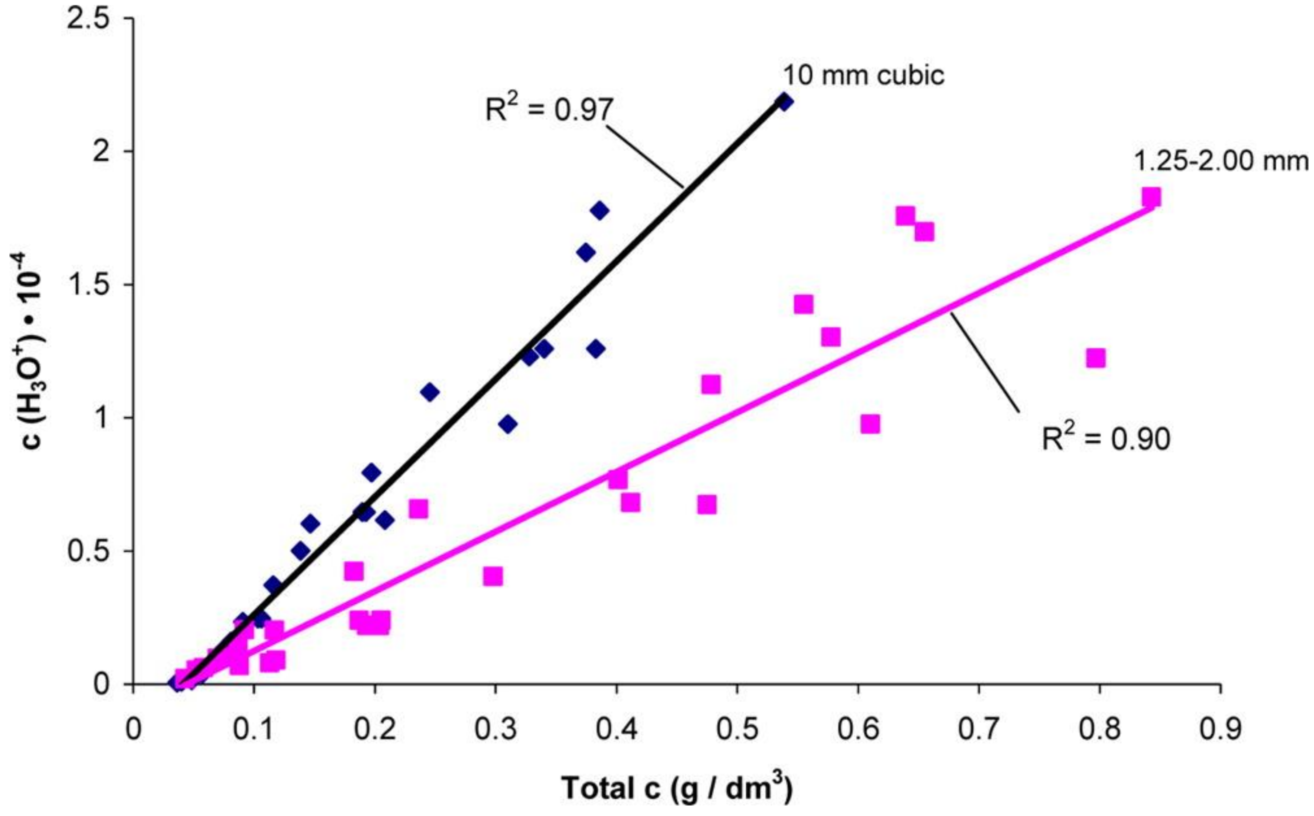



The pH with 1,25 – 2 mm chips (open symbols) and 10 mm cubic blocks (solid symbols).




The pH with 1,25 – 2 mm chips (open symbols) and 10 mm cubic blocks (solid symbols).

# $H_3O^+$ vs total hemicellulosic sugars




- The diffusion of the acetyl groups is clearly faster than for the hemicelluloses i.e. higher $cH_3O^+$ is obtained at the same conversion for the larger chips

# Modelling

$$rate = k_I \cdot c_{solid}^{n_1} \cdot (H^+)^{n_2}$$

$$n_1 = 1$$

$$n_2 = 0$$

$$rate = k_I \cdot c_{solid}$$

$$k_I = k_{0I} \cdot e^{\frac{-E_{a_I}}{RT}}$$

$$T = \frac{1}{T} - \frac{1}{T_{mean}}$$

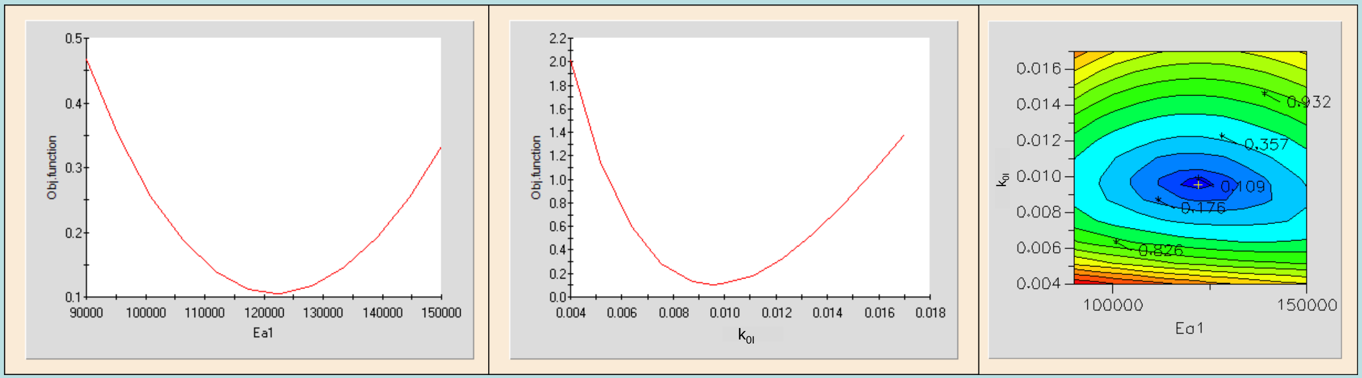
$$T_{mean} = 150°C$$

| | 1,25 - 2,00 mm chips | | 10 mm cubic blocks | |
|---|---|---|---|---|
| | Estimated parameters | Estimated Std Error (%) | Estimated parameters | Estimated Std Error (%) |
| $E_a$ [kJ / mol] | 122 | 0,3 | 120 | 0,2 |
| $k_{0I}$ [(L$^{(n_1+n_2)-1)}$ / (g$^{(n_1+n_2)-1}$ · min)] | $9{,}57 \cdot 10^{-3}$ | 0,3 | $5{,}55 \cdot 10^{-3}$ | 0,3 |

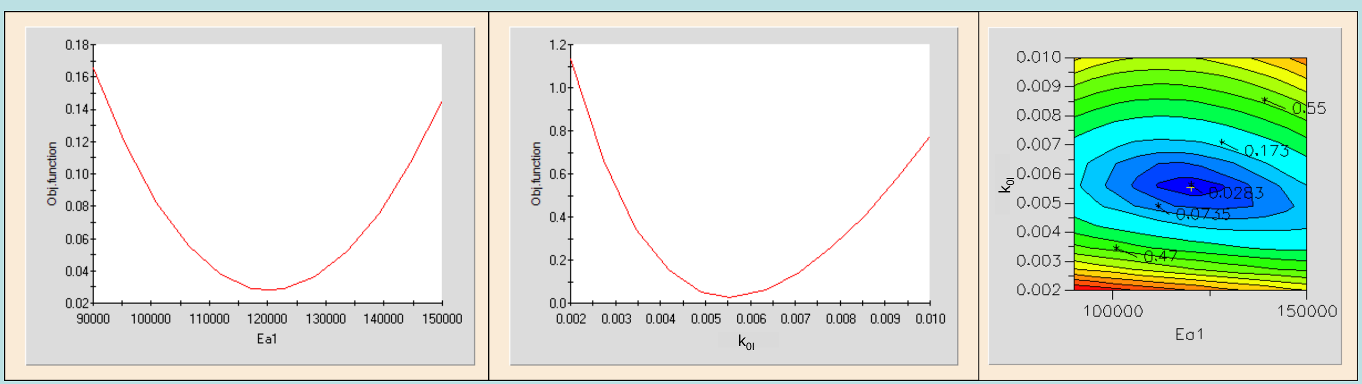
*The model of the complicated system can be simplified significantly*

# Sensitivity analysis and parameter correlations ($E_a$ *and* $k_{0l}$)

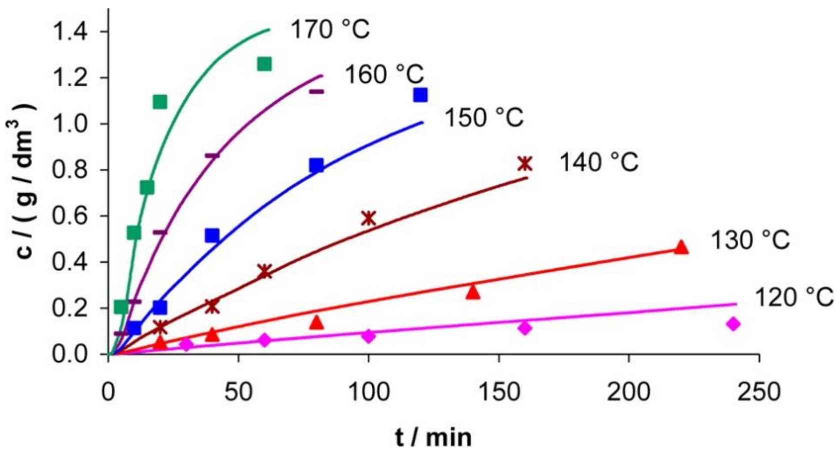
## 1,25 – 2,00 mm chips



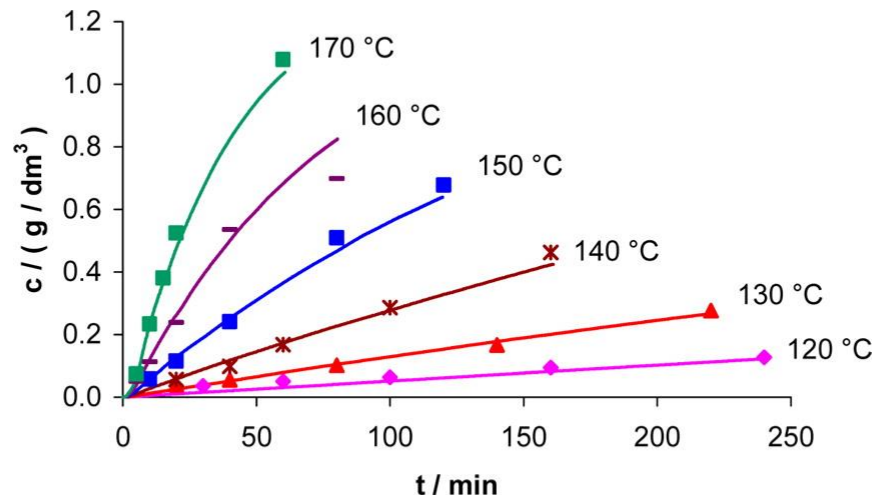

## 10 mm cubic blocks



# Modelling results




Fit of the model to experimental data (liquid-phase hemicellulose concentrations *c*) for the smaller chip size (1.25–2 mm).




Fit of the model to experimental data (liquid-phase hemicellulose concentrations *c*) for the larger chip size (10 × 10 mm).

# So what did we learn from modelling exercise?

- Extraction and hydrolysis rate very temperature sensitive
- The chip size influences the overall extraction rate and the molar mass of the obtained hemicelluloses
- The extraction rate is not significantly influenced by pH
- The mathematical model for the complex system could be simplified significantly
- A good fit of the model to the experimental data was achieved

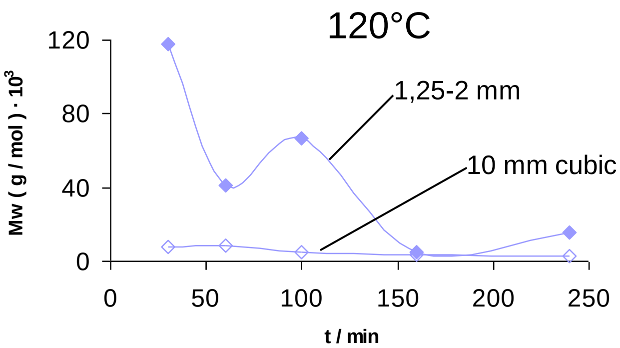
Rissanen, Grénman, Willfor, Murzin, Salmi, Industrial & Engineering Chemistry Research (2014), 53(15), 6341-6350.

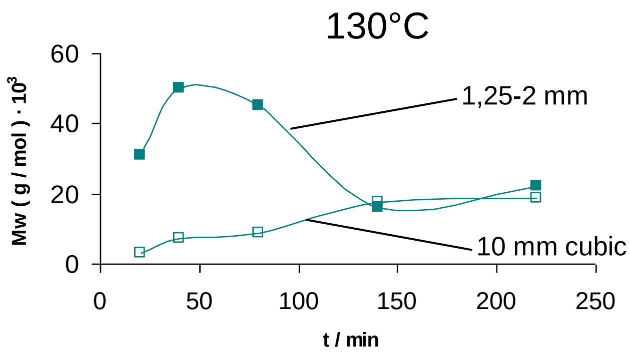
Rissanen, Grénman, Xu, Willför, Murzin, Salmi, ChemSusChem 2014, accepted, DOI 10.1002/cssc.201402282R1

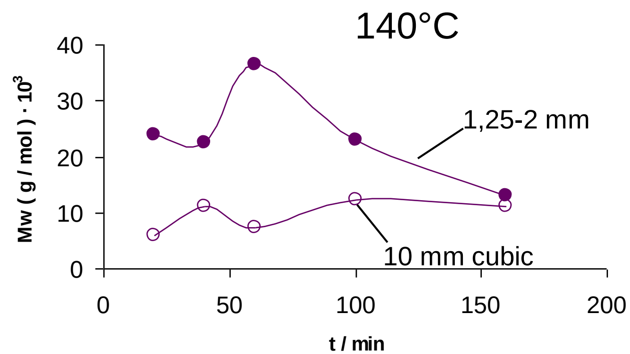
Rissanen, Grénman, Xu, Willför, Murzin, Salmi, Cellulose Chemistry and Technology, submitted after revision

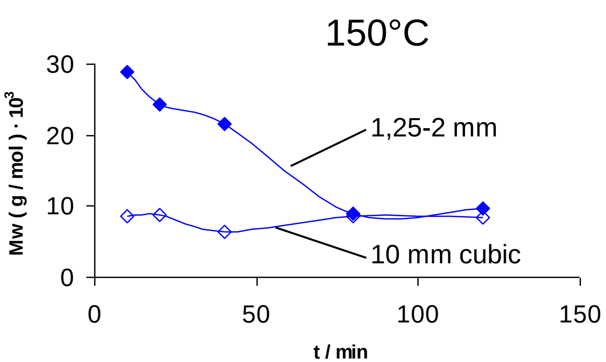
# Molar mass of extracted hemicelluloses

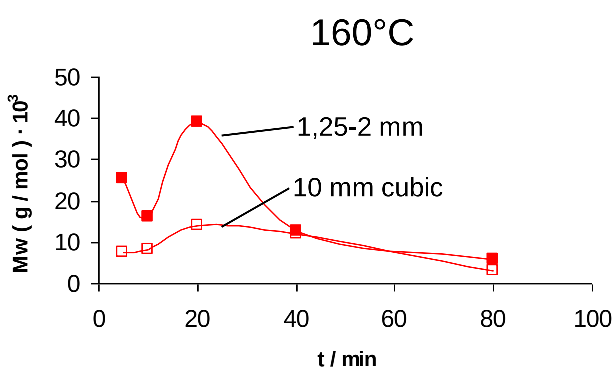
Molecular weight as a function of time for different temperatures and chip sizes

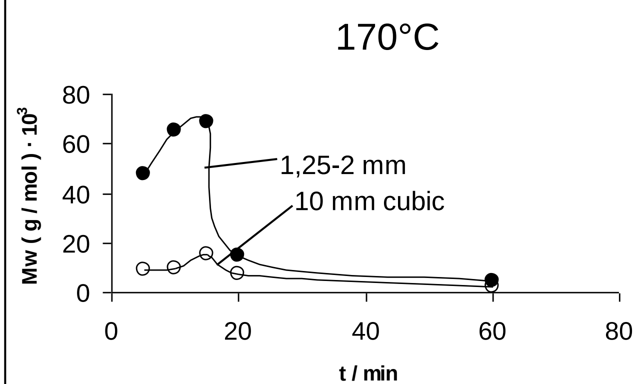


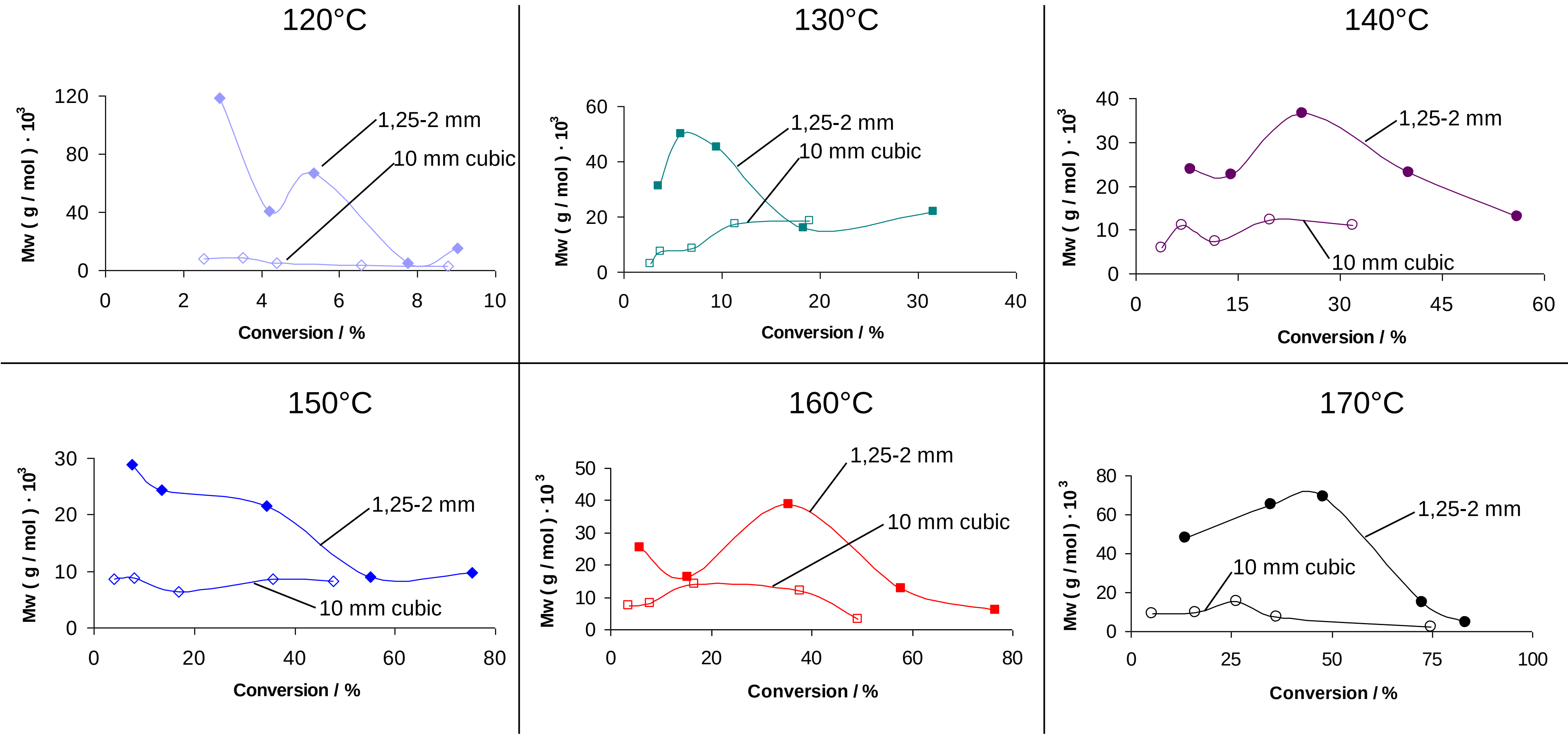



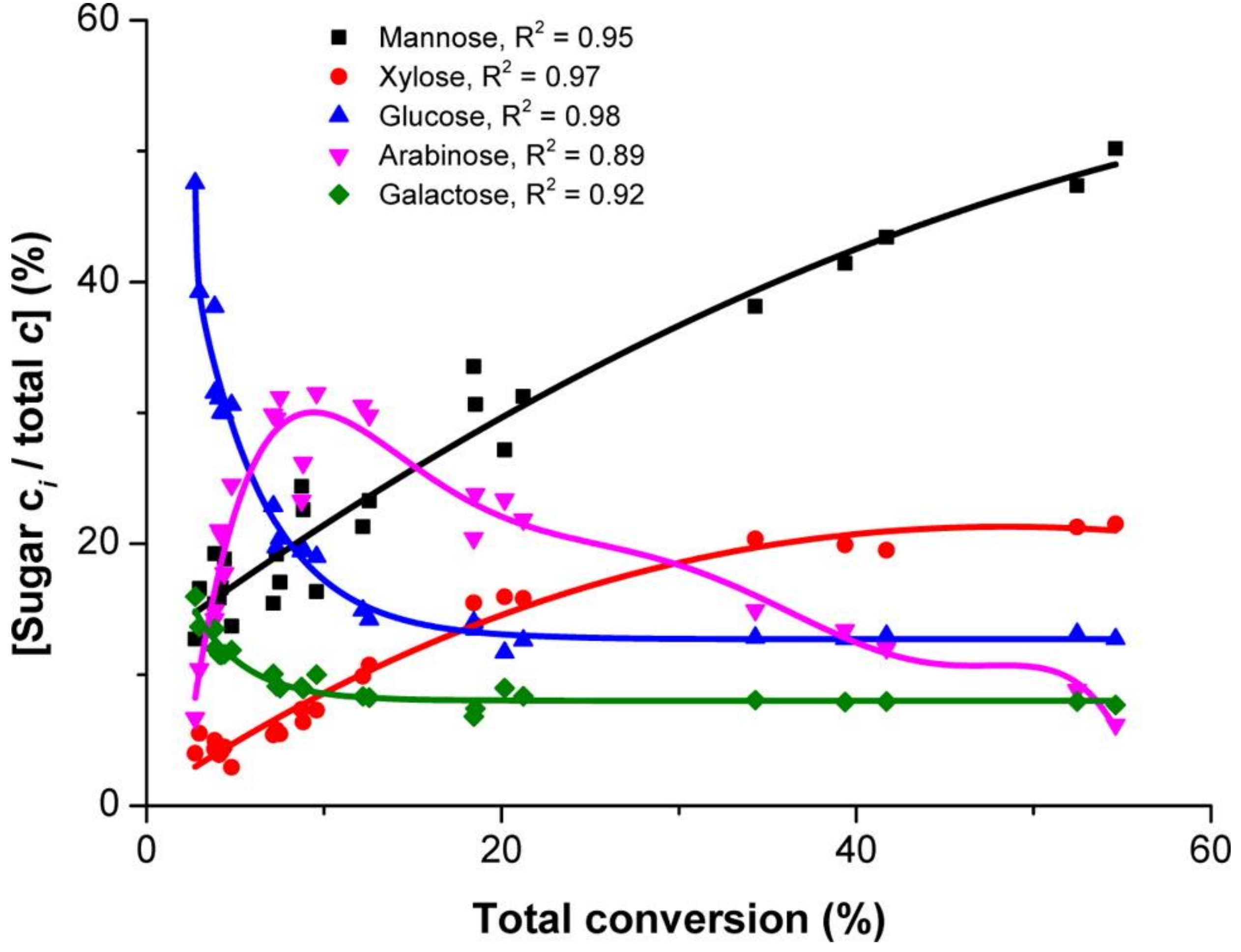



# Molecular weight as a function of conversion for different temperatures and chip sizes



# Percentage of sugars in the extract, 120–170° C



# Conclusions

- Industrial applications need long chained hemicelluloses and monomers
- The extraction kinetics is crucial in order to tailor the product as well as the production
- The overall extraction is influenced by several interlinked phenomena

Rissanen, Grénman, Willfor, Murzin, Salmi, Industrial & Engineering Chemistry Research (2014), 53(15), 6341-6350.

Rissanen, Grénman, Xu, Willför, Murzin, Salmi, ChemSusChem 2014, accepted, DOI 10.1002/cssc.201402282R1

Rissanen, Grénman, Xu, Willför, Murzin, Salmi, Cellulose Chemistry and Technology, submitted after revision

# Conclusion –

## The influence of the extraction parameters is complex and interlinked