Lignocellulosic biomass fractionation as a pretreatment step for production of fuels and green chemicals

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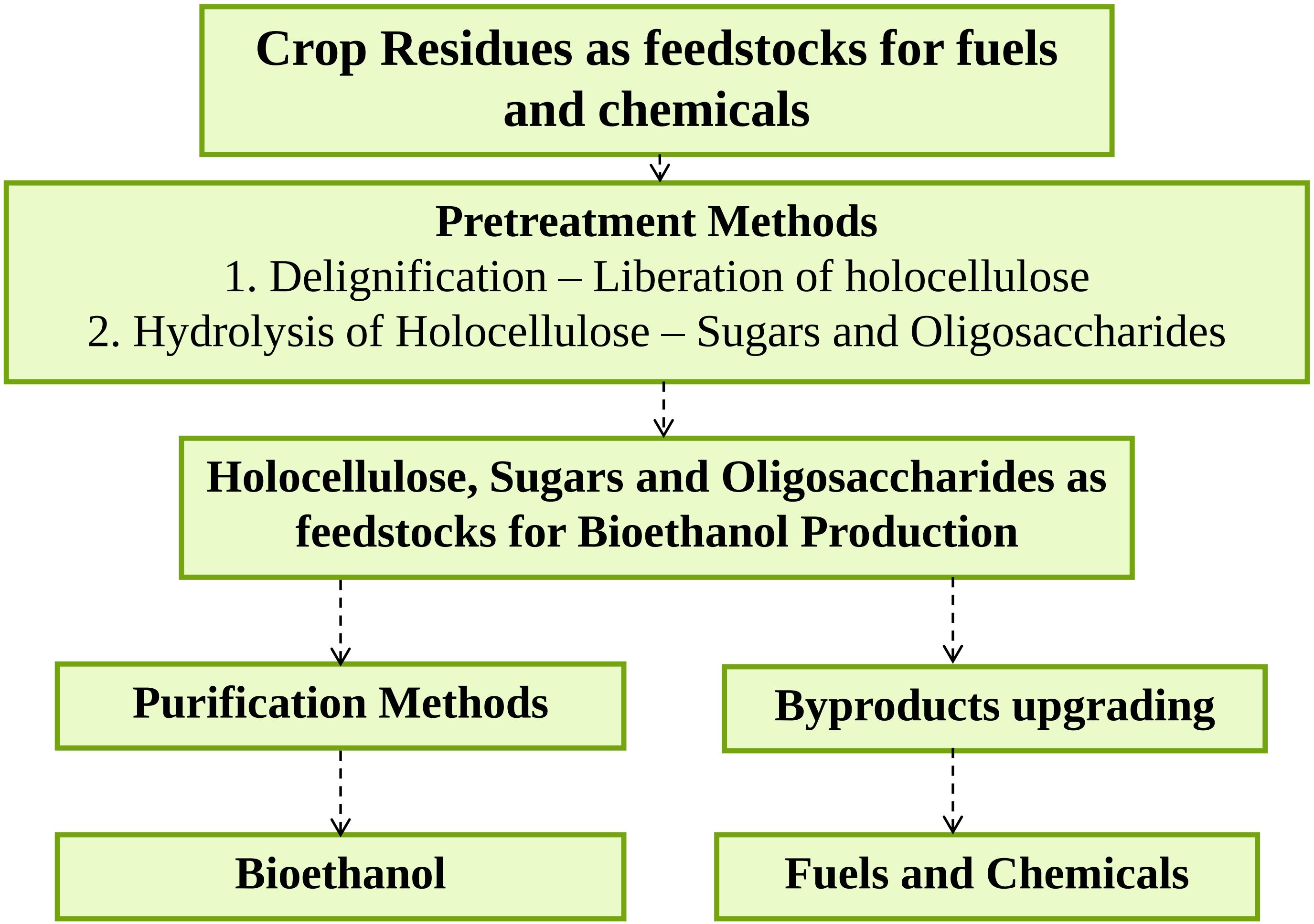
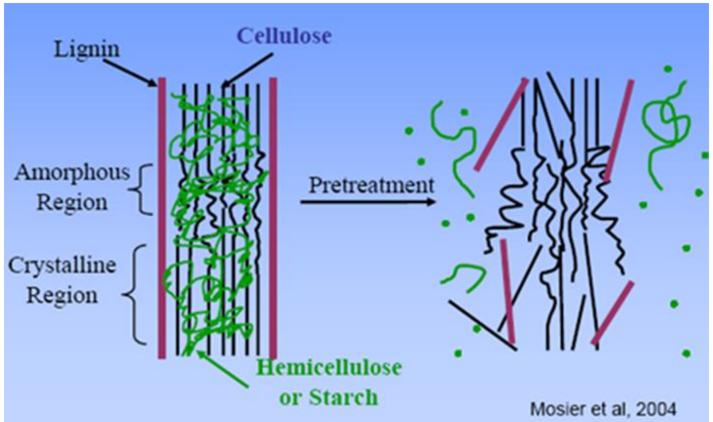
Outline

- **S**ustainable **I**ntegrated **M**ethod for the **P**roduction of **L**ignocellulosic **E**thanol (SIMPLE) Project
- Focus of this work
- Delignification Pretreatment Method
- Hydrothermal Pretreatment Method

SIMPLE Project



1. Focus of this work



Biomass → Pretreatment → Lignin byproduct

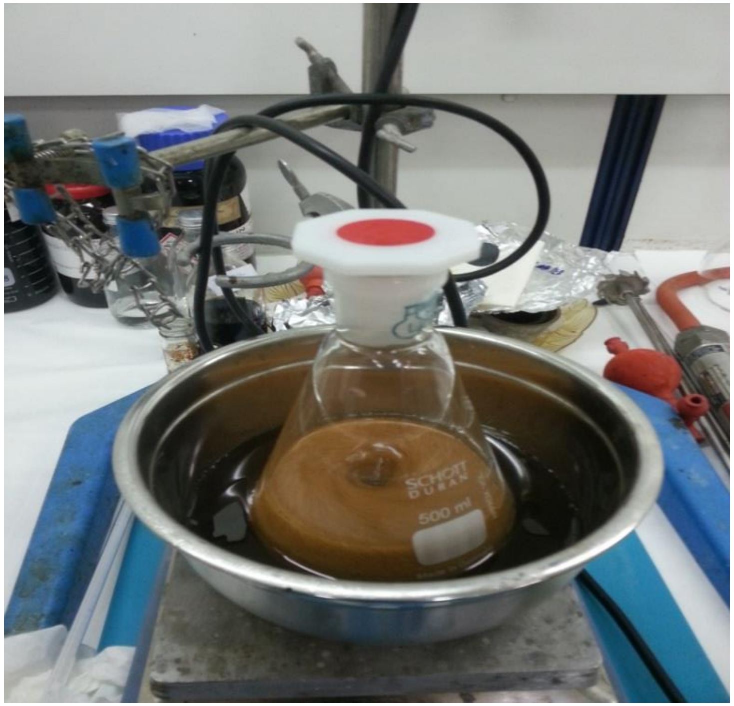
Pretreatment → Cellulose Hydrolysis → Hexose Fermentation

Pretreatment → Pentose Fermentation

Hexose Fermentation / Pentose Fermentation → Distillation → Ethanol

Distillation → Lignin byproduct

2. Delignification Pretreatment Method



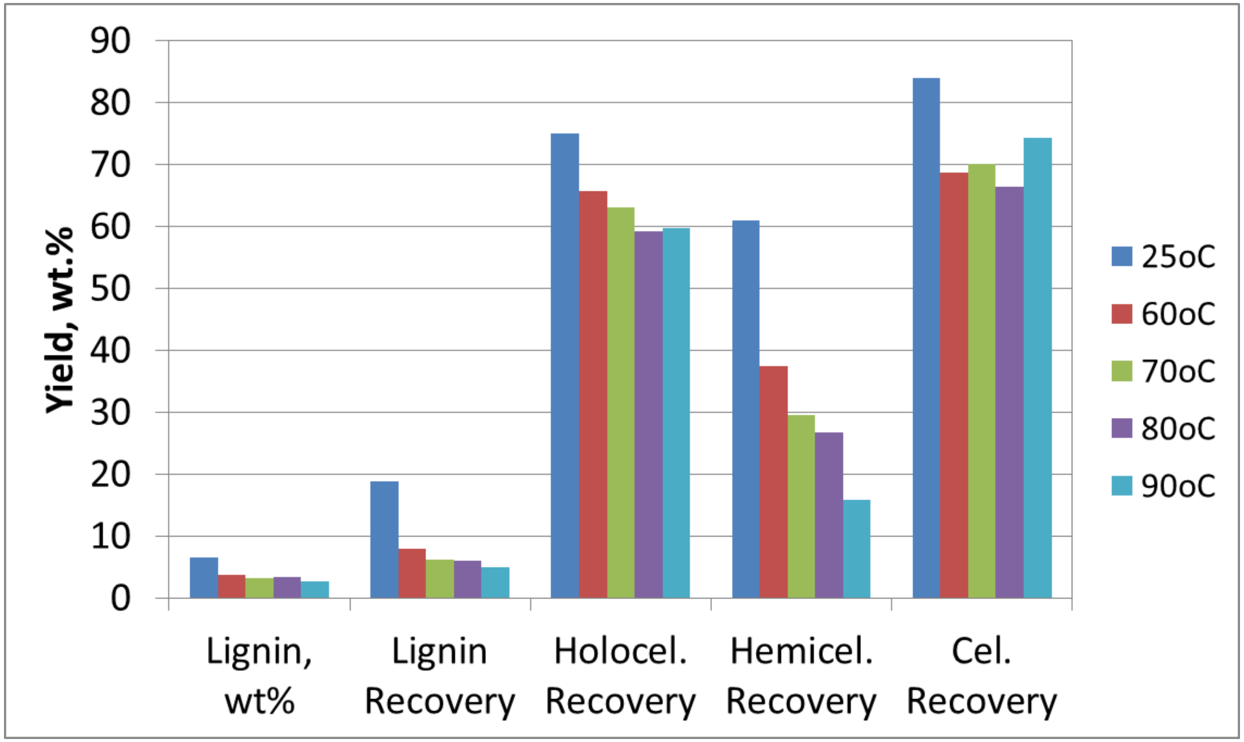
Milox Process

Treatment of biomass with an organic acid, typically Formic acid (FA) or Acetic acid (AA) or their mixtures, wherein the addition of H_2O_2 results in lignin depolymerization and subsequent dissolution in the organic acid.

Parameters studied

- Temperature
- Type of acid – Org. acid ratio
- H_2O_2 concentration
- Time
- Type of biomass

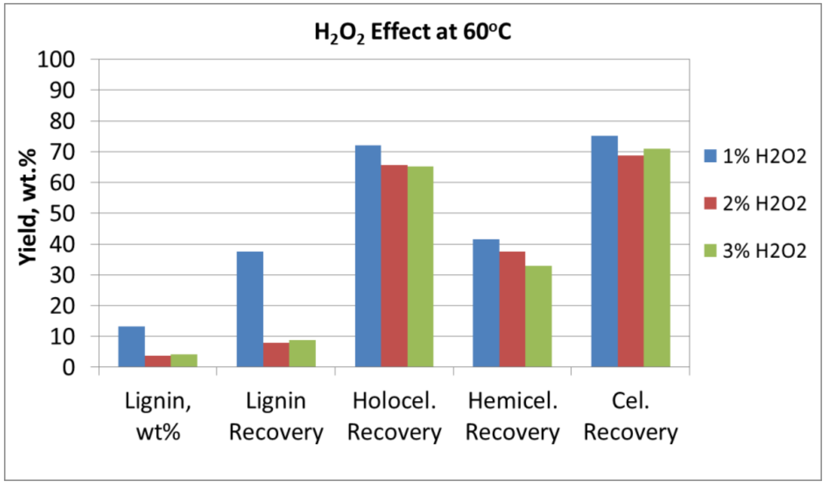
Temperature effect

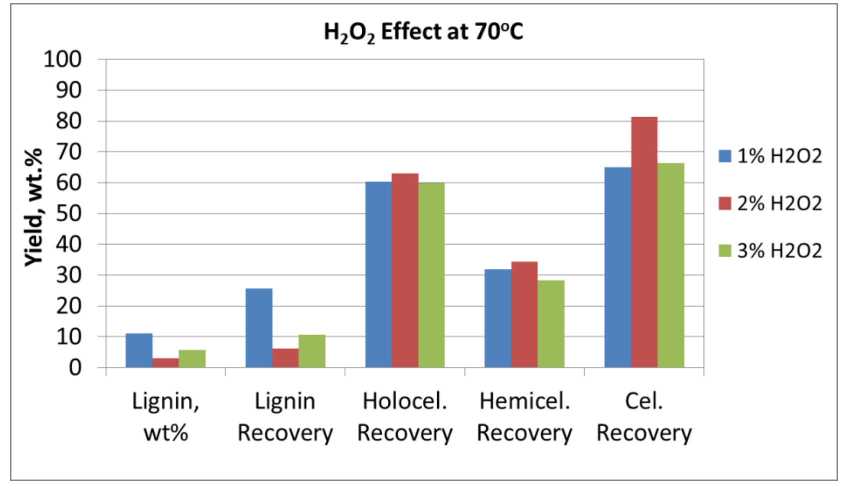


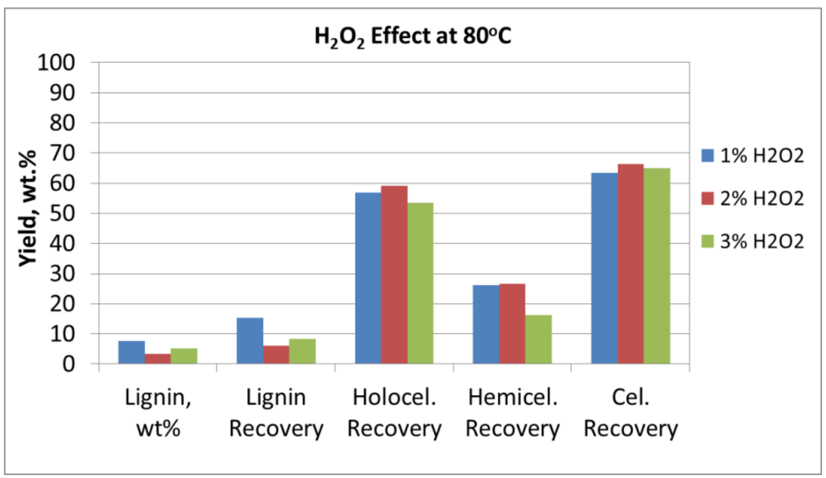
- **Time 1 h at 60-90 ºC and 7 h at 25 ºC**
- **100 % FA + 2 wt.% H_2O_2**
- **Beechwood sawdust**

- Increasing T results in more efficient lignin removal
- Cellulose is unaffected, hemicellulose is dissolved with increasing T
- Small overall differences for T between 60 and 80 ºC
- At 25 ºC more time is needed, less lignin is removed, more holocellulose received as solid

H_2O_2 concentration effect

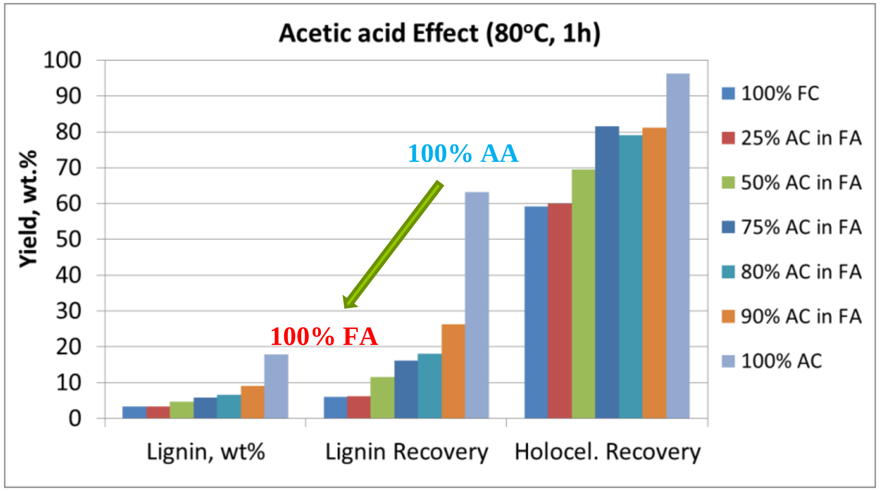


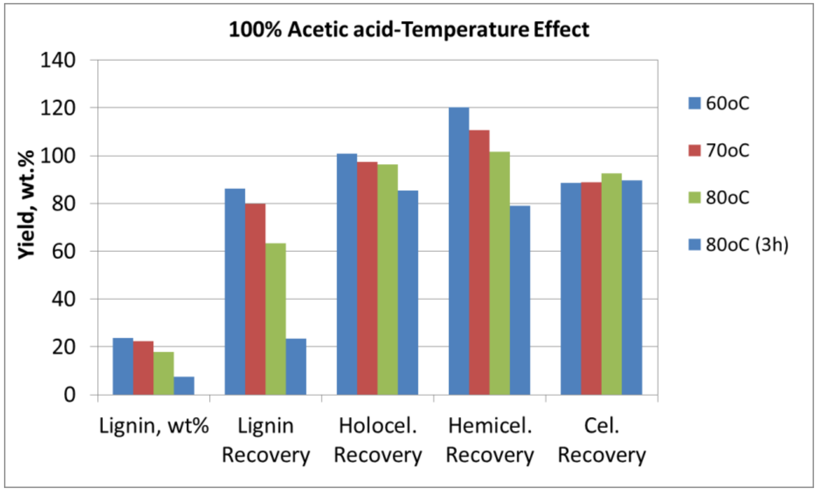




- At all T, 2 wt.% H_2O_2 achieves high delignification
- Increasing H_2O_2 results in higher hemicellulose dissolution
- Cellulose is more or less stable
- High T (80 ºC) required to achieve pulp lignin content below 10% for 1 wt.% H_2O_2

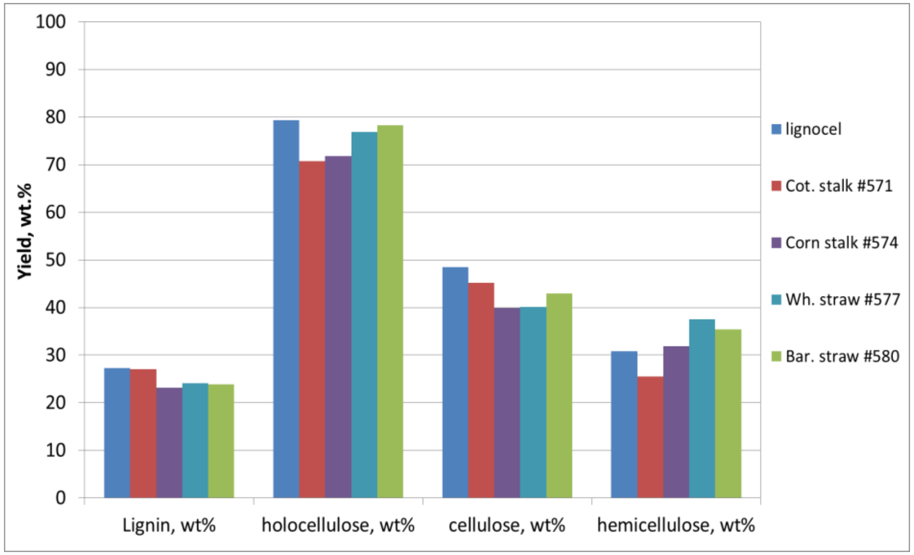
Organic acid effect

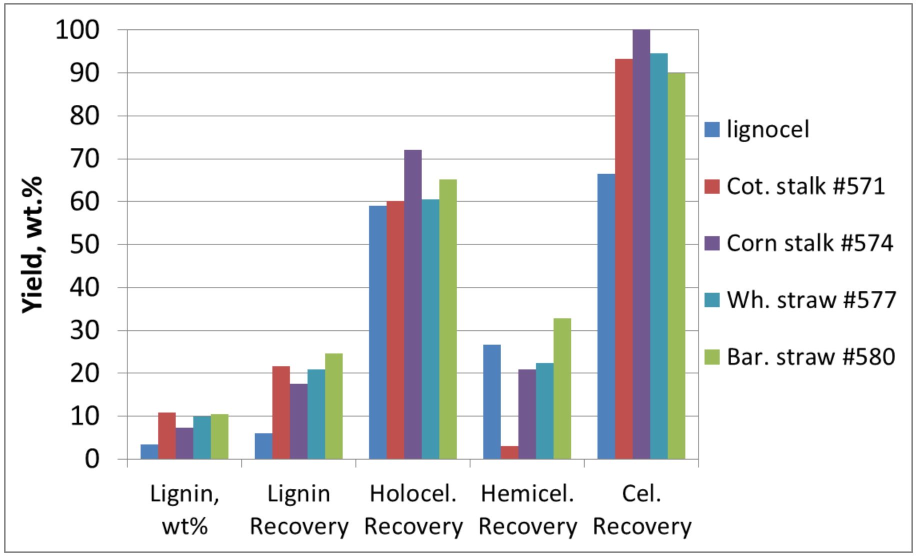




- Acetic acid (AA) less reactive than Formic acid (FA)
- 10 wt.% FA enough to decrease pulp lignin content below 10%
- Increasing FA results in Lignin and Hemicellulose dissolution
- AA requires more time (3h) but more cellulose and hemicellulose retrieved in pulp
- AA active at higher T (80 ^{o}C)

Agricultural residues – Type of biomass





- **1 h at 80 °C**
- **100 % FA + 2 wt.% H_2O_2**

- Depending on type of biomass, different pulp lignin contents are achieved
- Low density of biomasses results in entrainment of solid particles and poor mixing with FA, hence the higher lignin compared to woody biomass
- Corn stalk had the lowest lignin content

MILOX Process - Conclusions

- Significant delignification achieved at various experimental conditions
- Delignification makes the holocellulose more accesible to enzymes and therefore its sugars are easily fermented towards bioethanol
- AA was less reactive but increasing time allowed for the efficient removal of lignin accompanied by high holocellulose recovery, therefore allowing for more sugars to be fermented downstream increasing the overall process efficiency
- Agricultural residues were successfully delignified, making them a potential feedstock for Bioethanol production

3. Hydrothermal Pretreatment Method

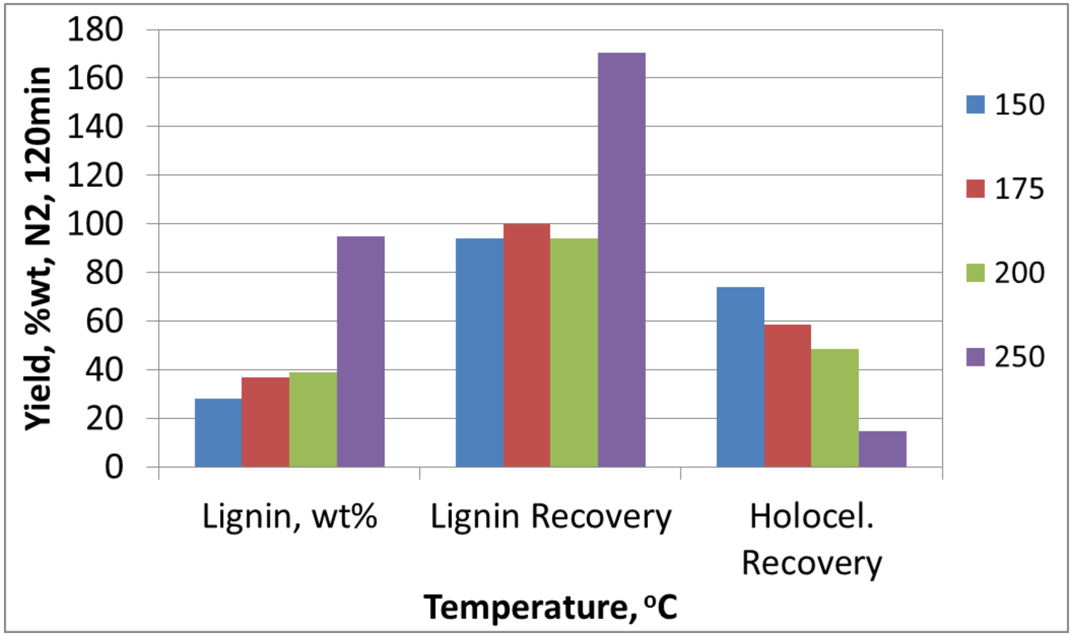
Hydrothermal treatment

Treatment with water under mild temperatures (150-250 ^oC) and low pressures, with or without catalysts (typically inorganic acids e.g. H_2SO_4) to achieve hydrolysis of holocellulose towards sugars and oligosaccharides.

Parameters studied

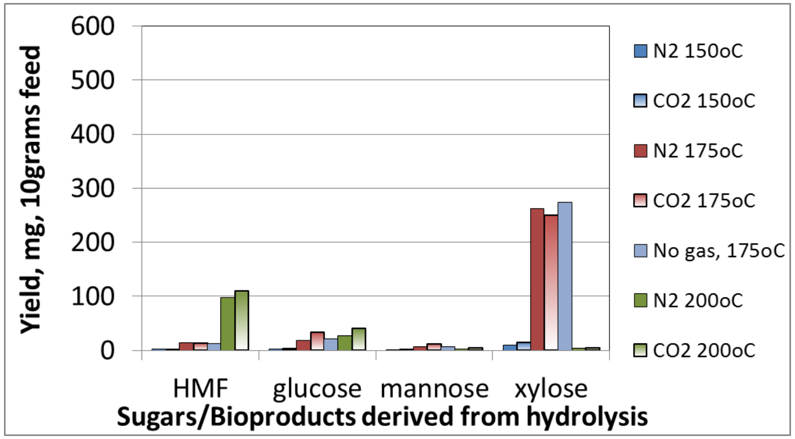
- Temperature
- Catalysis
- Type of biomass

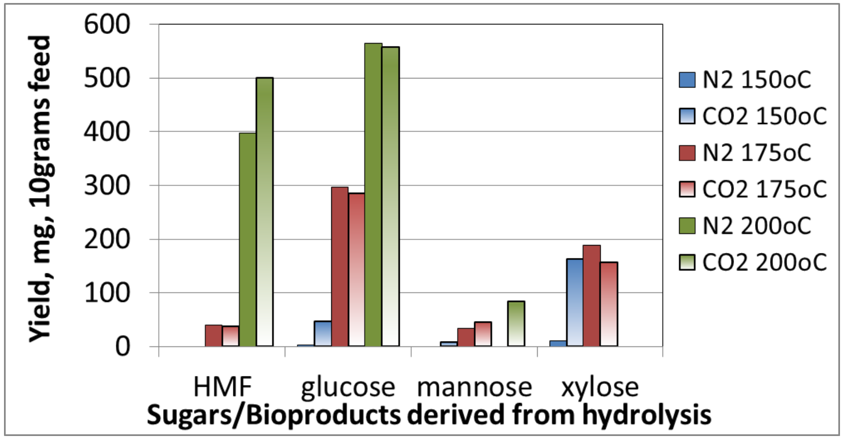
Temperature effect



- Increasing T results in holocellulose dissolution
- Lignin recovery as solid very high with hot water treatment
- At 250 °C holocelluloses is mostly hydrolysed/converted. Lignin recovery above 100% (170%) indicates that holocellulose is converted to insoluble degradation products (humins) due to high T

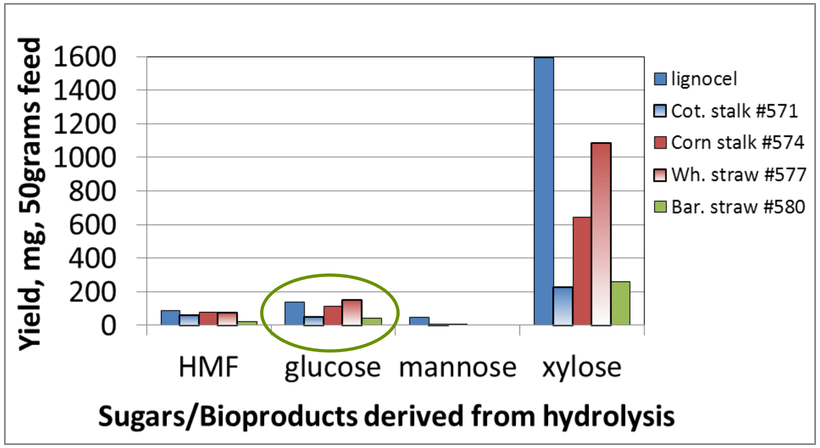
Delignification effect

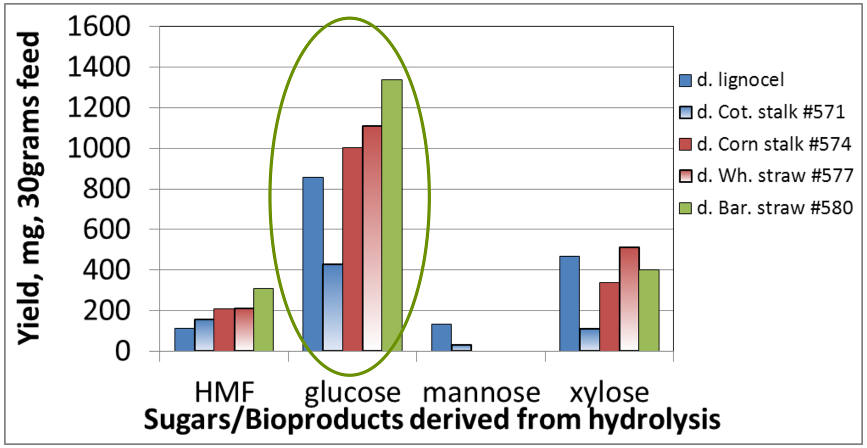




- Increasing T from 150°C to 175°C results in dissolved sugars increase
- At 200 °C mostly xylose and glucose in part are converted to HMF
- Delignified biomass yields higher sugars compared to untreated biomass
- CO_2 effect is clear at the low T of 150 °C, glucose and mostly xylose are increased simultaneously avoiding the production of HMF due to the low T treatment

Hydrolysis of agricultural residues





- Hydrolysis is strongly dependent on type of biomass
- For untreated biomass, woody biomass (Lignocel) yielded most sugars
- Corn stalk and Wheat straw produced highest sugar yields for the agricultural residues
- Delignification effect was significant, glucose yield was increased tenfold
- Barley straw yielded very high glucose, impressive increase compared to the minimal glucose yield of the untreated barley

Hydrothermal treatment - Conclusions

- Hemicellulose more easily dissolved than cellulose
- For increased conversion of holocelluloses either a catalyst is needed or harsher conditions (temperature, time)
- Glucose and Xylose were the main hydrolysis products while HMF was a degradation product mostly of Xylose
- Delignification of biomass upstream proved to be of pivotal importance, increasing sugars production by hydrolysis up to 10 times
- CO_2 addition increased sugars production at low temperatures (150 ^oC) without production of byproducts (HMF) – No acidic wastes were produced

Thank you for your attention

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