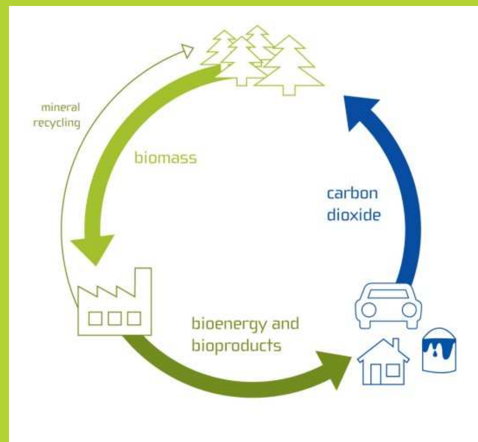
BIOSYNERGY

SIXTH FRAMEWORK PROGRAMME

Advanced physical/chemical fractionation

WP Coordinator: Robert Bakker

Workshop of the EU FP6
Integrated Project BIOSYNERGY

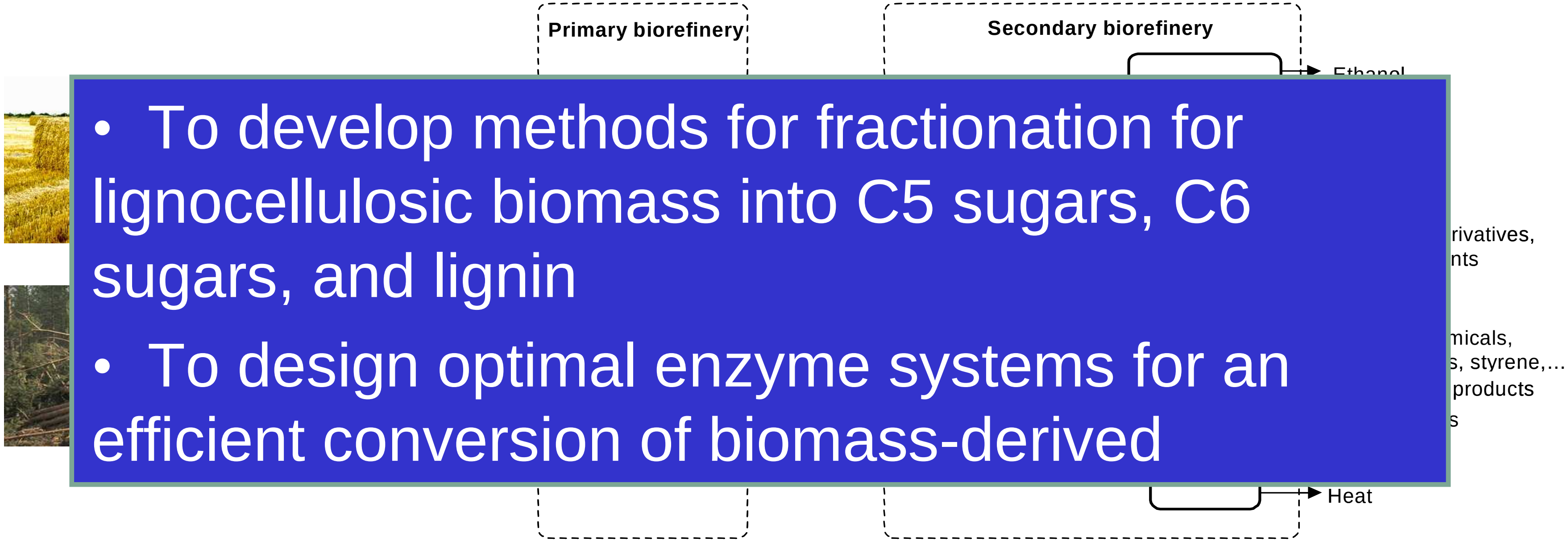


November 17th, Reims, France

Overview

- Objectives Fractionation work in BioSynergy
- Main processes studied
- Major accomplishments
- Assessment of fractionation routes
- Conclusions

Fractionation of lignocellulosic biomass



- To develop methods for fractionation for lignocellulosic biomass into C5 sugars, C6 sugars, and lignin
- To design optimal enzyme systems for an efficient conversion of biomass-derived

Objectives Fractionation:

- Fractionation of lignocellulosic biomass into its **composing fractions** with sufficient quality for production of (bio)chemicals (including lignin).
- **Enhancement (enzymatic) degradability** of cellulose to fermentable sugars.

Main routes studied; partners

- Ethanol/water organosolv
- Organic acid organosolv
- Mechanical/Alkaline fractionation
- Mild fractionation of hemicellulose
- HCl-based hydrolysis
- Enzymatic hydrolysis

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Activities

- Proof of concept for fractionation
  work on the basis of same lignocellulosic feedstocks
- Exchange of protocols
- Exchange of samples for enzymatic hydrolysis
- Supply of fractionised products to other WP
- Definition and application of technical benchmarks

Ethanol/H2O Organosolv, ECN

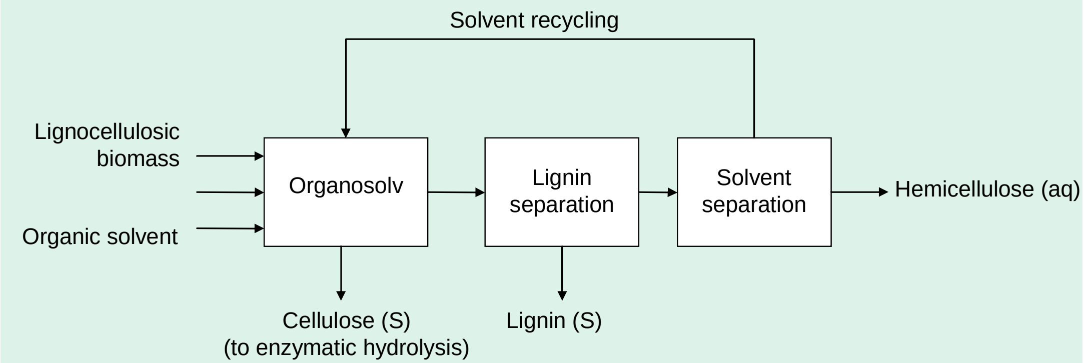
Mech./alk pretreatment A&

Acid organosolv Pilot plant ARD

Partners: WUR, ABNT, ARD, Bioref, ECN, TUD

Ethanol/water organosolv (ECN)

- Method
  - 160-200 ℃, 15-60 min, 5-30 bar.
  - Organic solvent: ethanol (/ acetone)
  - Catalyst: no or H_2SO_4



- Application in Biorefinery
  - Carbohydrates for 2nd generation biofuels or chemicals (furans)
  - High-purity Lignin for conversion into chemicals
  - Remaining solids for energy

Major Accomplishments EtOH/water organosolv

- Parameters established that govern organosolv fractionation.
- Suitability organosolv fractionation for various feedstocks assessed.
- Scale-up process to 20L batch reactor.
- Application tests of cellulose and lignin.
- Conceptual design completed

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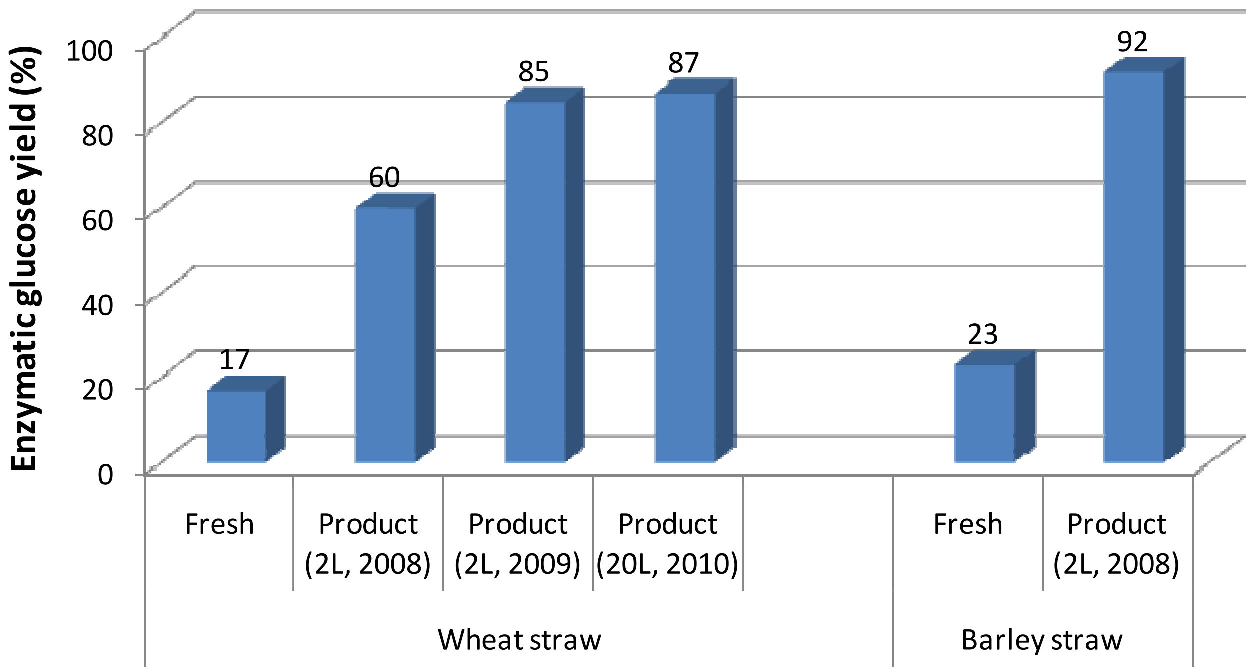
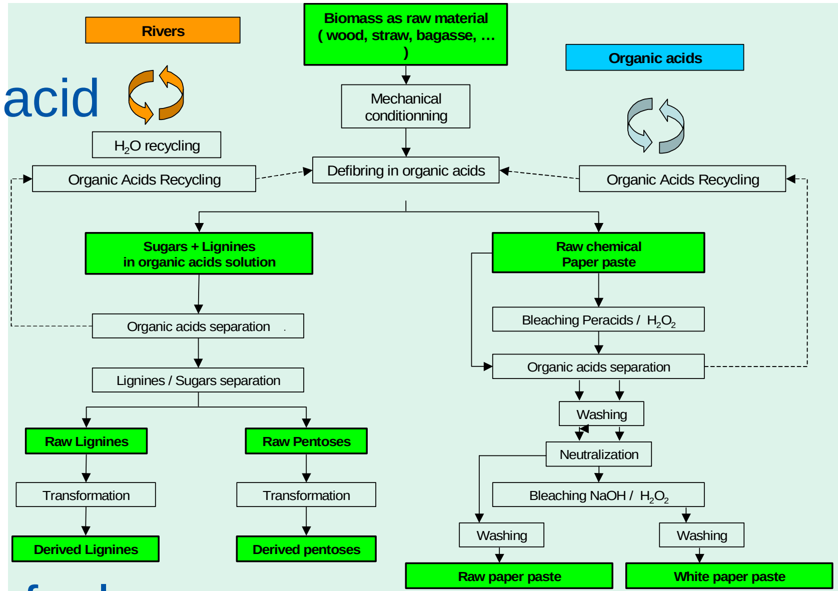
Enzymatic digestibility



Organic Acid Organosolv (ARD)

- Method
  - 105 ℃, atmospheric pressure
  - Organic solvent: acetic acid, formic acid



- Application in Biorefinery
  - Carbohydrates for 2nd generation biofuels
  - High-purity Lignin for conversion into chemicals
  - Remaining solids for energy

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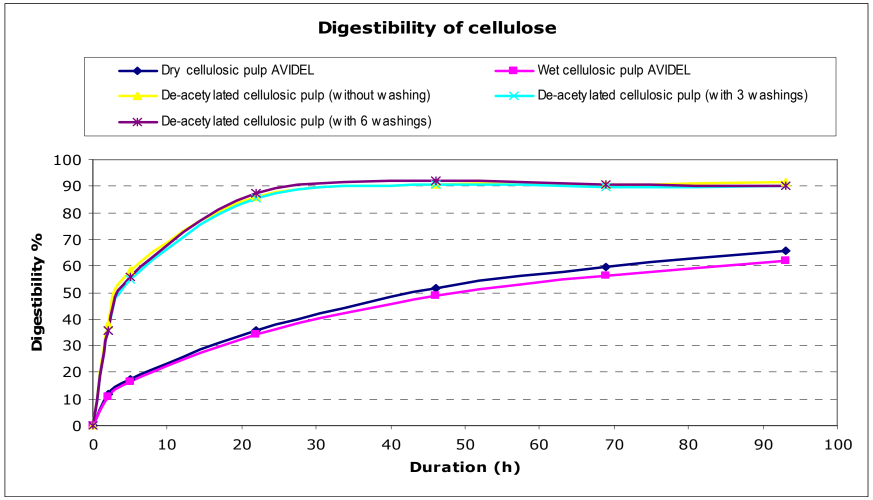
Major Accomplishments Org. Acid Organosolv

- Improved cellulose digestibility and purity of cellulose
  - By changing acid types
  - By de-acetylisation of cellulose pulp
- Experiments performed with woods
- Experiments performed at micro-pilot scale



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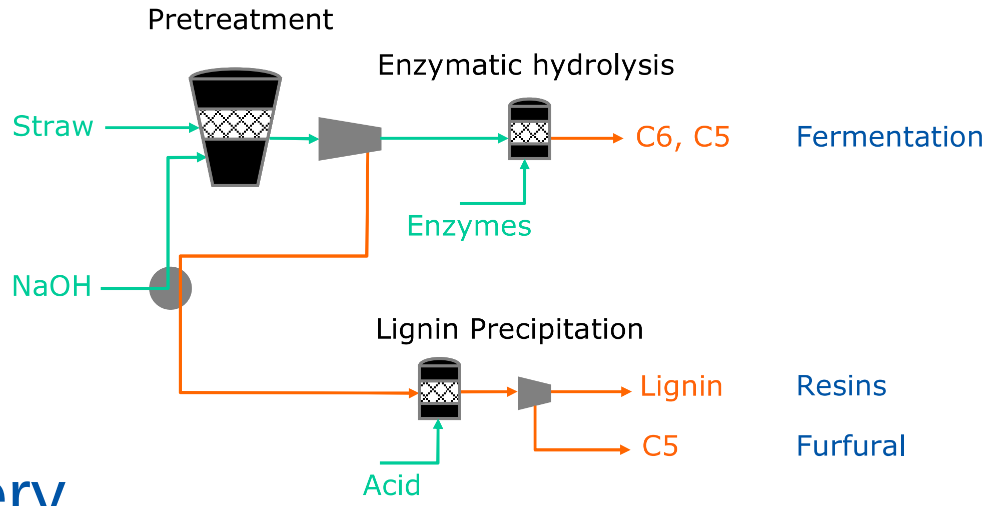
Mechanical-Alkaline Fractionation (WUR)

- Method
  - 75-100 ℃, 1 – 4 h, atmospheric pressure
  - Catalyst: NaOH



- Application in Biorefinery
  - Combined C5/C6 fermentation to alcohols, organic acids
  - Lignin application as phenolic resins
  - Remaining solids for energy

Major Accomplishments Alkaline Fractionation

- Effect of processing conditions on chemical composition of pretreated straw and yield
- Enzymatic hydrolysis
  - Effect of dry matter on hydrolysis yields
- Isolation of lignin
  - Effect of processing conditions on black liquor properties
  - Properties of isolated lignins established
  - Application tests of isolated lignin

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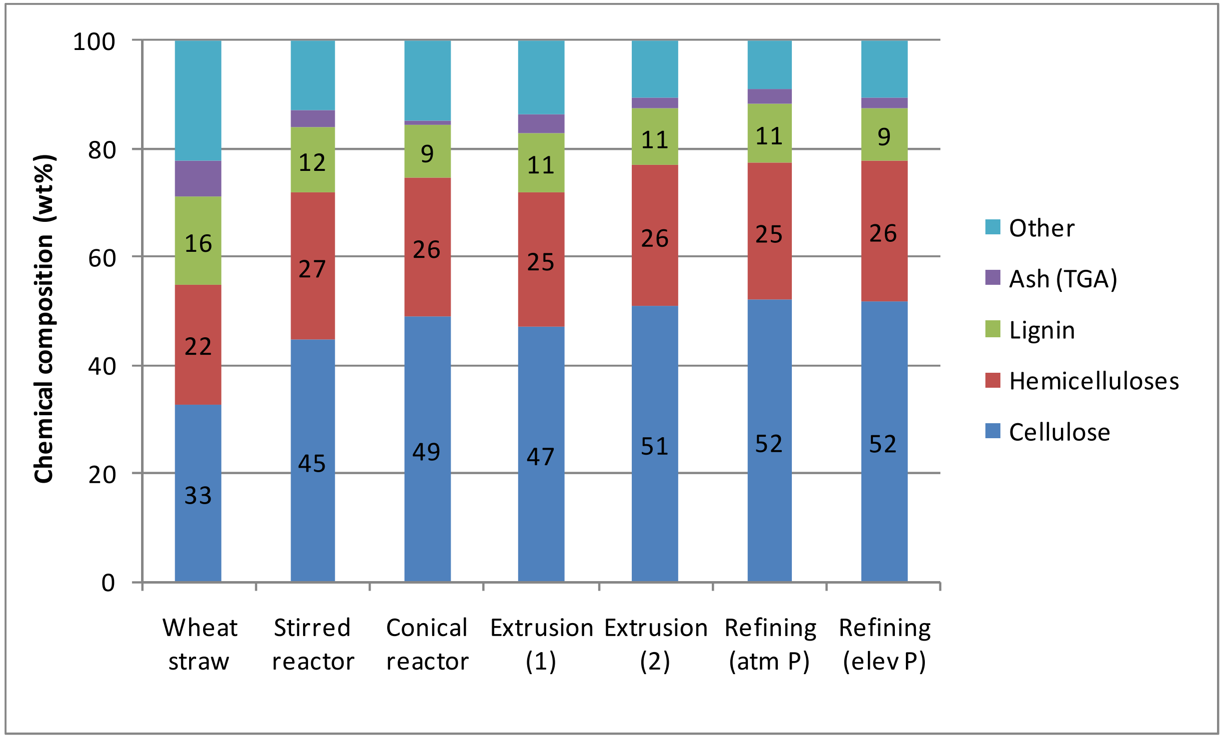
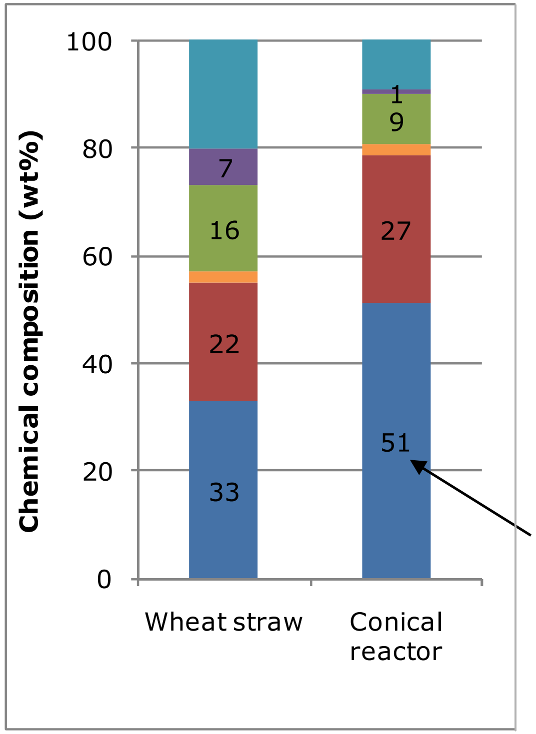
Pretreatment *Efficiency*

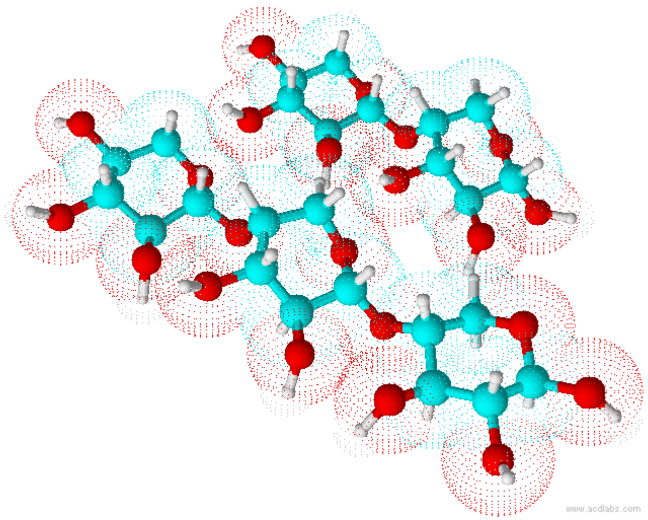
Lab scale



Semi-technical scale



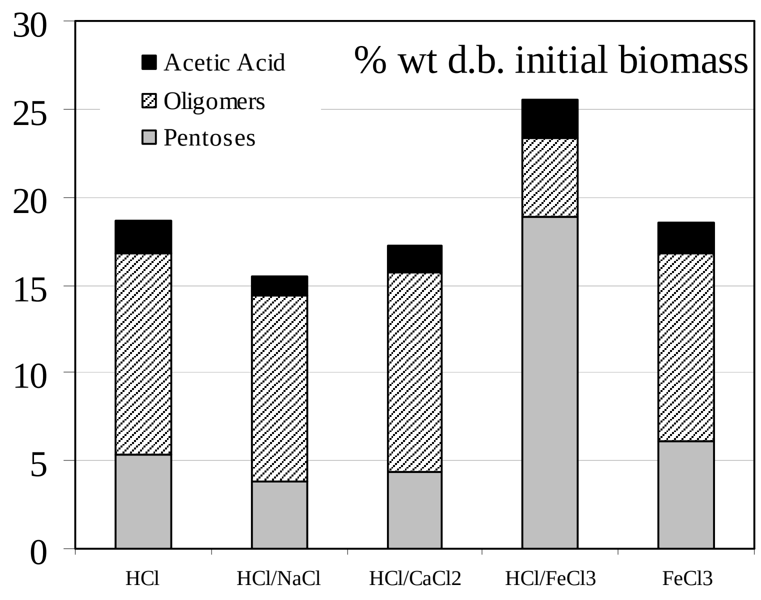
Mild fractionation of hemicellulose (TUDelft)



- Method
  - 120 ℃, 15-60 min, 5 bar.
  - Catalyst: HCl, FeCl3
- Application in Biorefinery
  - Selective production of hemicellulose-derived carbohydrates
    - – Further conversion into furfural, xylitol, surfactants etc
  - Solid residue for enzymatic conversion, or further separation routes
  - Remaining solids for energy

Major Accomplishments hemic. fractionation

- Proof of principle mild (T < 120 ˚C) fractionation of hemicelllulose
  - Relatively simple process, low-cost operation expected
  - Cellulose remains intact after C5 extraction and is free of minerals
  - Enzymatic degradability
    of cellulose needs improvement



HCl-based Acid hydrolysis (BioRef)

- Method
  - 32% - 37% HCl, room temperature

- Application in Biorefinery
  - Combined C5-C6 fermentation to alcohols
  - Applications of lignin products in hardboards
  - Remaining solids for electricity and heat

Major Accomplishments Acid hydrolysis

- Improved direct saccharification with a two-step strong hydrochloric acid application
  - No enzymes required
- Remaining lignin with good thermal properties
- Fractionation method is applicable for all feedstocks

Enzymatic hydrolysis (ABNT)

Objectives

- Achieve High productivity strains
- Increased enzyme effective activity which makes a reduction possible of enzyme dosage below 5mg/ g cellulose during enzymatic hydrolysis
- Production of enzymes at competitive cost

Major Accomplishments Enz. hydrolysis

- New supplemental enzymes developed
- Trials performed at 20% wt/wt
- Increased enzymatic activity of commercial enzyme mixes when supplemented
- Yield of SSF with new enzymes 44 g/L ethanol

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Benchmarks for evaluating Fractionation

- Delignification
- Lignin purity, quality
- Hemicellulose hydrolysis
- Enzymatic degradability of cellulose
- Fermentability of glucose obtained from cellulose

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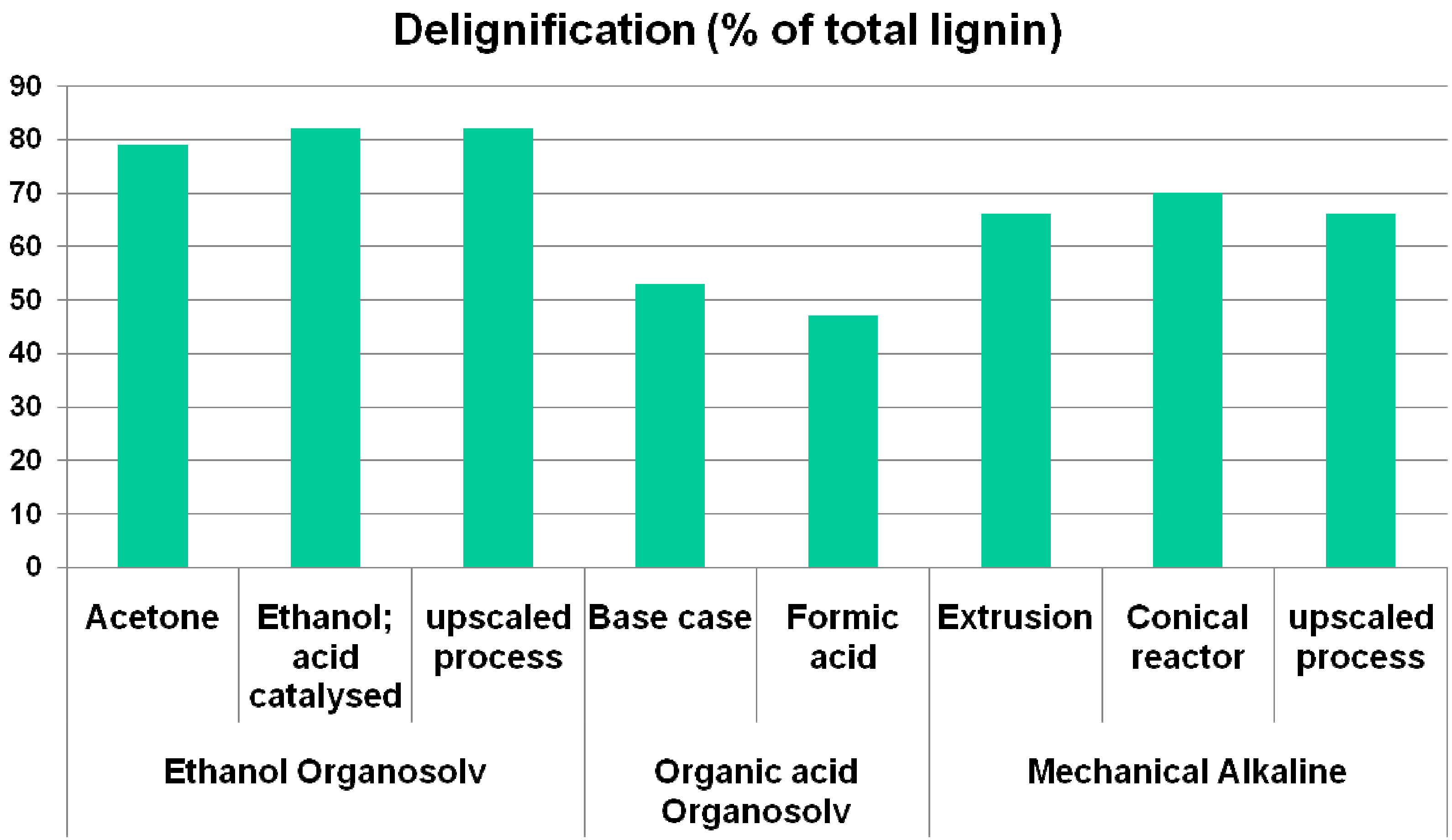
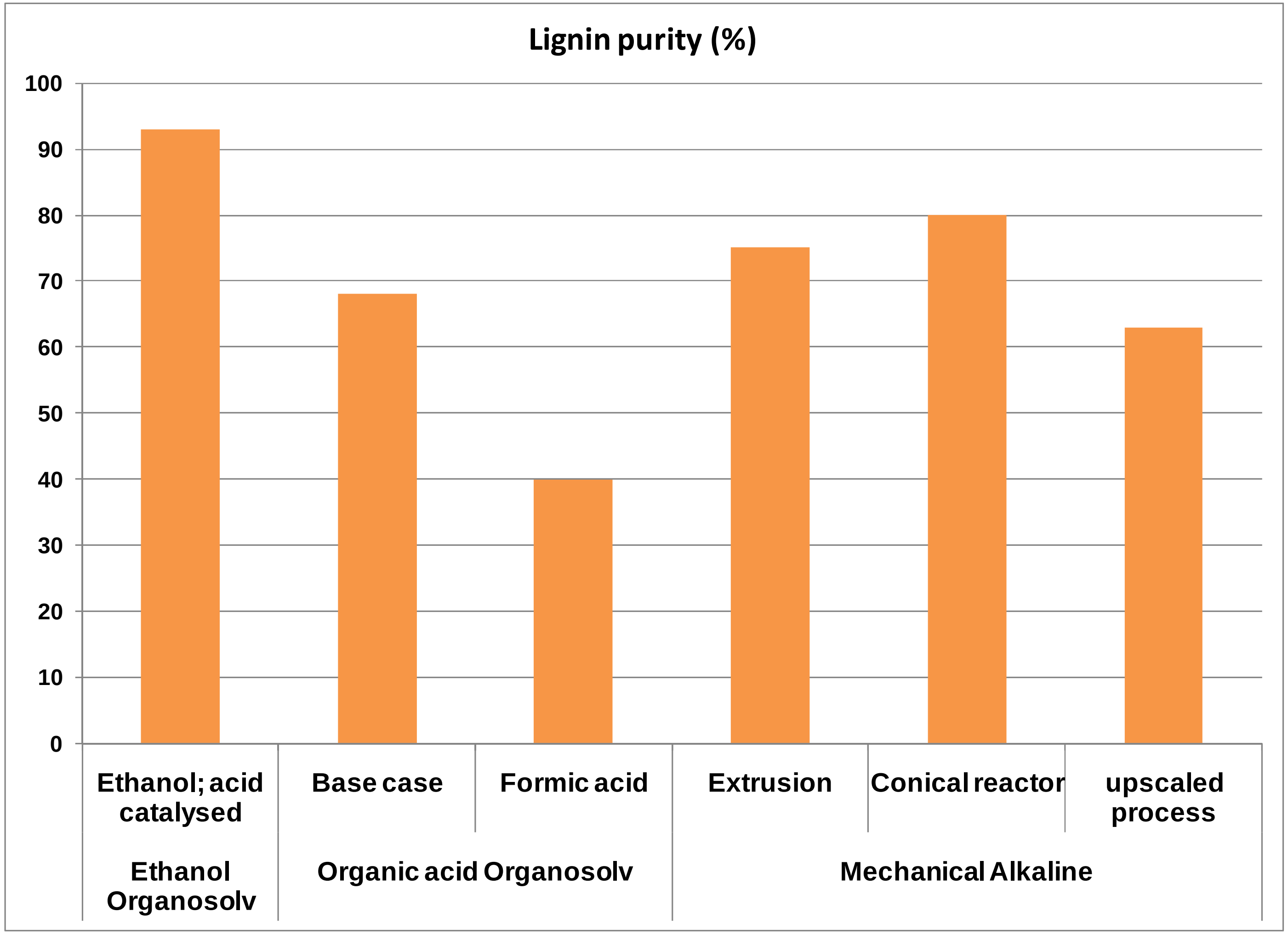
Results benchmarking (wheat straw)

		Delignification	Lignin purity	Hemicellulose hydrolysis	Cellulose degradability
EtOH Organosolv	Acetone	79		82	87
	Ethanol; acid catalysed	82	93	74	85
	upscaled process	82		82	87
Organic acid Organosolv	Base case	53	68	81	52
	Formic acid	47	40	63	76
	De-acetylisation			81	90
Mechanical Alkaline	Extrusion	66	75	39	100
	Conical reactor	70	80	38	89
	upscaled process	66	63	26	62
Hemicell fractionation	Mild hemicellulose fract.			98	40


Delignification (% of total lignin)
90
80
70
60
50
40
30
20
10
0
Acetone
Ethanol; acid catalysed
upscaled process
Base case
Formic acid
Extrusion
Conical reactor
upscaled process
Ethanol Organosolv
Organic acid Organosolv
Mechanical Alkaline


Lignin purity (%)
100
90
80
70
60
50
40
30
20
10
0
Ethanol; acid catalysed
Base case
Formic acid
Extrusion
Conical reactor
upscaled process
Ethanol Organosolv
Organic acid Organosolv
Mechanical Alkaline

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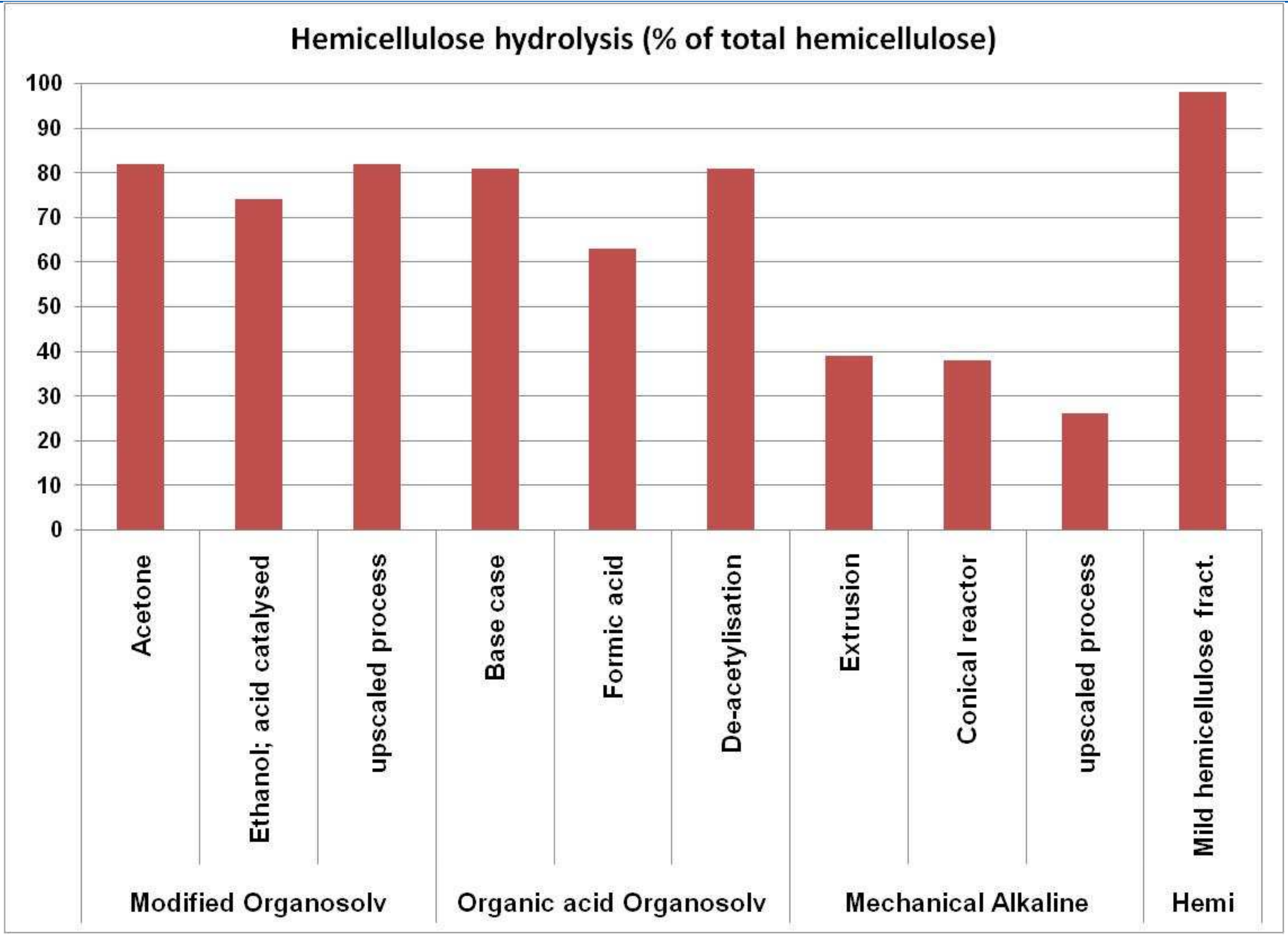

Hemicellulose hydrolysis (% of total hemicellulose)
100
90
80
70
60
50
40
30
20
10
0
Acetone
Ethanol; acid catalysed
upscaled process
Base case
Formic acid
De-acetylisation
Extrusion
Conical reactor
upscaled process
Mild hemicellulose fract.
Modified Organosolv
Organic acid Organosolv
Mechanical Alkaline
Hemi

Main conclusion

- **All technologies lead to significant fractionation into composing elements C5, C6 sugars and lignin**
  - **High cellulose degradability**
  - **Differences in hemicellulose hydrolysis, and lignin yield and – characteristics**
  - **Often trade-off between desired effects**
- **Fractionation technologies need to be optimized toward a particular goal**
  - An integrated approach feedstock-process-endproduct is therefore required!

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Remaining Issues

- Feedstock flexibility
- Development of large scale lignin applications
- Recycling of reactants
- Improving enzymes, esp. for upscaling
- Use of organic acids in stead of mineral acids
- Developing continuous reactor systems for fractionation

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