Effects of Catalysts on Organosolv Fractionation of Willow Wood and Wheat Straw

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Introduction

The development of cost-effective lignocellulose based biorefineries requires optimum valorisation of all main biomass constituents, i.e. both sugar polymers and lignin. Most pretreatment technologies, developed to increase the enzymatic hydrolysis of the cellulose fraction for the fermentative production of second generation biofuels or platform chemicals, produce a lignin-rich residue containing minerals and non-converted sugars, which is only suited for heat and power generation. By separating lignin prior to conversion of the cellulose fraction, a high quality lignin may be produced with suitable characteristics for higher-value applications such as the production of phenolics for resins. A pretreatment process that is capable of effective separation of lignin from lignocellulose is the organosolv process [1,2]. ECN is developing an organosolv fractionation technology with the aim to separate all lignocellulose constituents including lignin with sufficient quality for further conversion into fuels and chemicals [2,3].

The poster will discuss a study performed at ECN on the effects of catalysts on organosolv fractionation of willow wood and wheat straw. For more extensive information on this study we refer to [3]. First a screening of a wide range of catalysts (acids, bases, and salts) was made. Based on pulp yield and required catalyst dose, three catalysts were selected (H_2SO_4, HCl and $MgCl_2$). These catalysts were used in a more detailed study in which their effect on the fractionation (lignin yield, pulp composition, etc) and pre-treatment (enzymatic digestibility of the cellulose fraction) was studied.

Results

The use of catalysts was found to improve fractionation and enzymatic digestibility of both feedstocks (example shown in Figure 1). Acid catalysts particularly promoted xylan hydrolysis (besides delignification). For acid catalysts it was found that their effect was directly correlated to the pH. HCl was found to be the most effective catalyst tested. For wheat straw, optimum results were obtained at 0.02M HCl (0.8% w/w dry biomass) leading to 96% glucan recovery, 83% xylan hydrolysis, and 68% delignification.

The enzymatic digestibility of wheat straw was found to increase from 15% (raw material) to 44% (non-catalytic organosolv) and 99% (HCl-catalysed organosolv) (glucose yield based on glucan content raw material, enzyme dose: 35 FPU/gr substrate) (Figure 2). The application of catalysts in organosolv pretreatment was found to be particularly effective for wheat straw. The use of $MgCl_2$ was less effective than that of

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the acid catalysts, but it seems to more selectively improve delignification of willow wood.

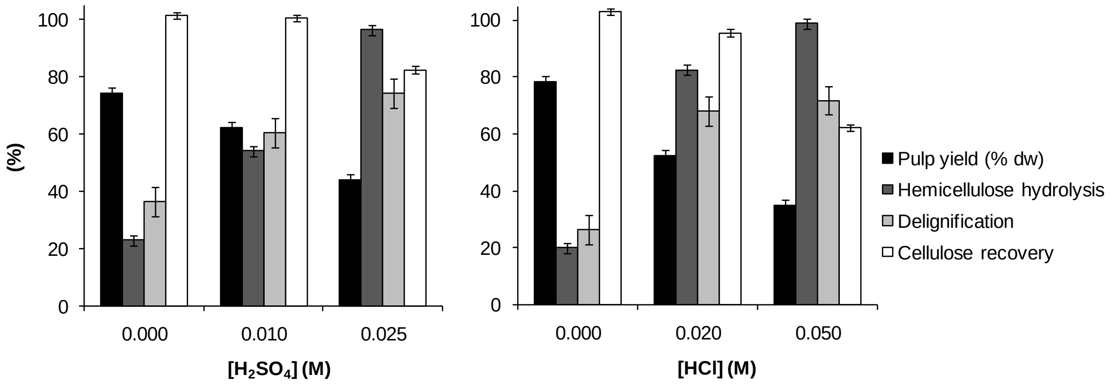

Fig. 1 Effect of acid catalysts on fractionation of wheat straw [3].

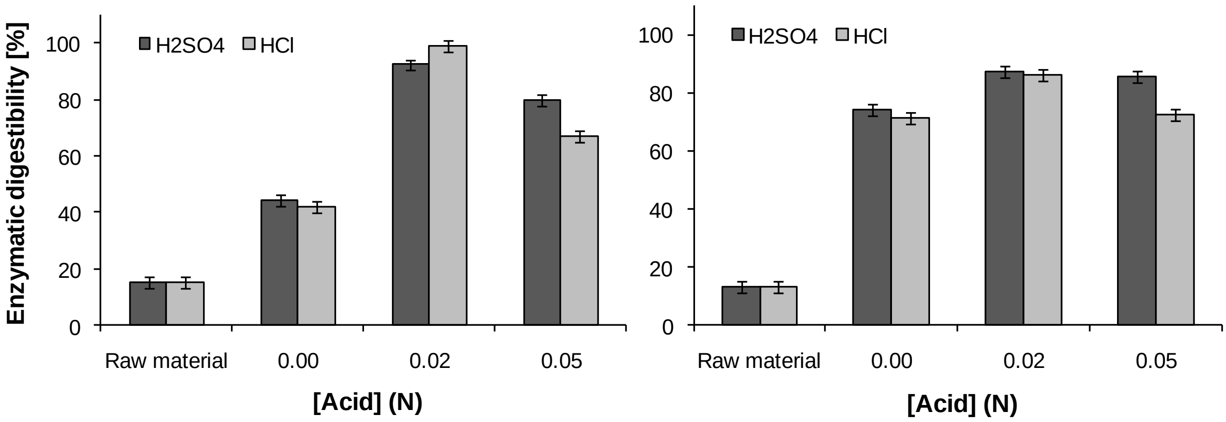

Fig. 2 Enzymatic digestibility of wheat straw (left) and willow wood (right) [3].

Conclusions

Application of catalysts in organosolv pretreatment of willow wood and wheat straw was found to substantially improve fractionation and enzymatic digestibility. The use of catalysts could contribute to achieve maximum utilisation and valorisation of lignocellulosic biomass in organosolv-based biorefineries.

Acknowledgements

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References

1. Zhao X, Cheng K and Liu D. (2009) Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. Appl Microbiol Biotechnol 82:815-27.
2. Huijgen W J J, Reith J H, Den Uil H (2010) Pretreatment and Fractionation of Wheat Straw by an Acetone-based Organosolv Process, Ind. Eng. Chem. Res. 49, pp. 10132-10140.
3. Huijgen W J J, Smit A T, Reith J H, Den Uil H (2011): Catalytic Organosolv Fractionation of Willow Wood and Wheat Straw as Pretreatment for Enzymatic Cellulose Hydrolysis (submitted).

[3] For more information about the LignoValue project, see www.lignovalue.nl and the oral presentation at this conference by R.J.A. Gosselink et al. 'Valorisation of lignin – Achievements of the LignoValue project'.

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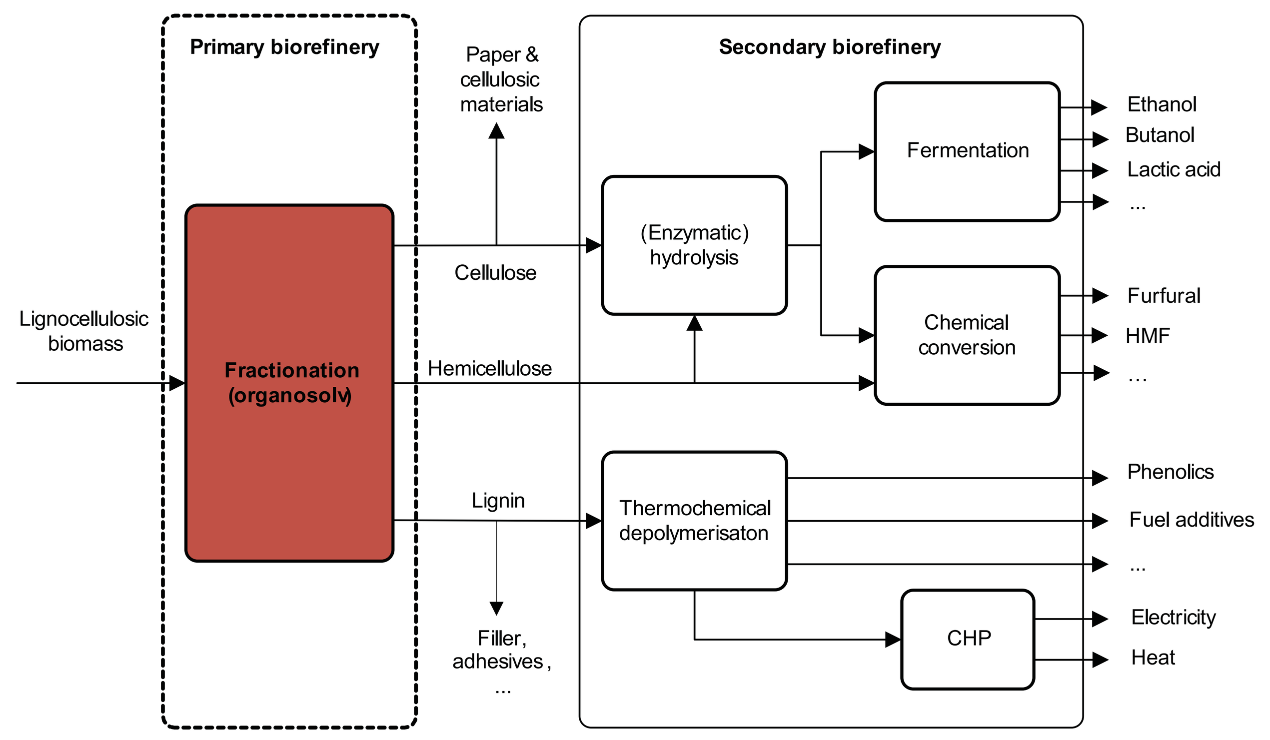
1. Lignocellulosic Biorefinery

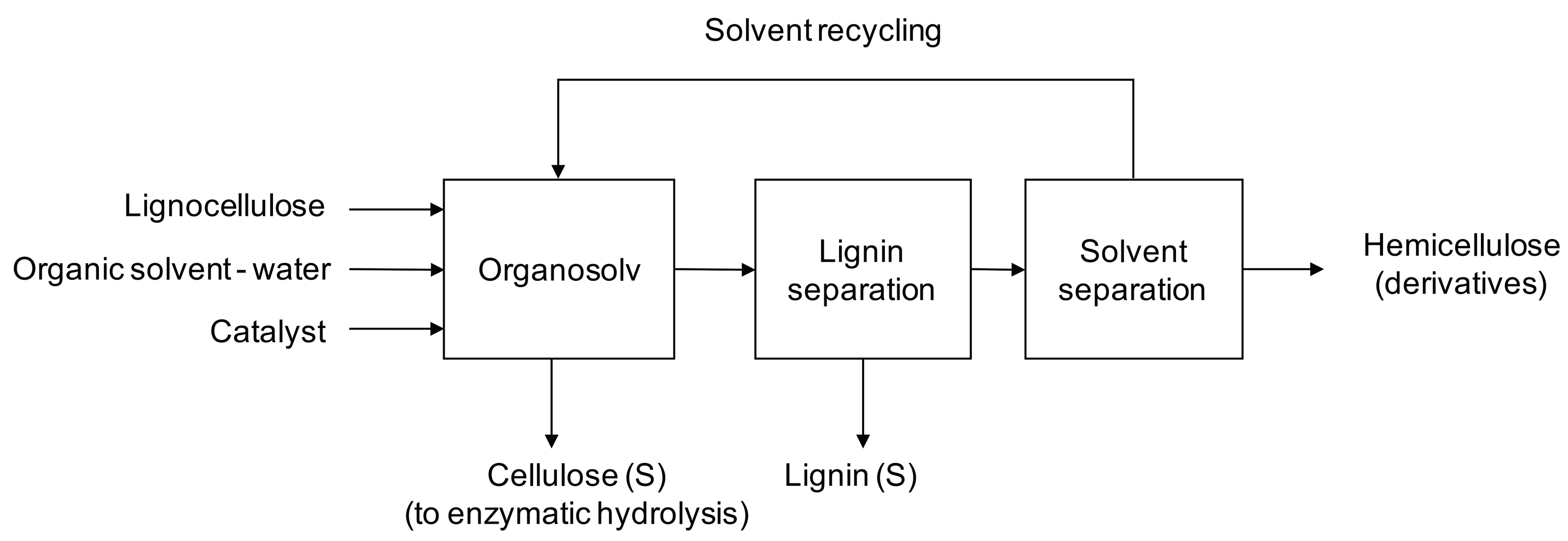
Organosolv fractionation:

- Biorefinery of lignocellulose for materials, fuels and chemicals.
- Extraction of high-quality lignin prior to enzymatic hydrolysis.
- Enhancement enzymatic hydrolysis cellulose to fermentable sugars.



Schematic view of a multi-product lignocellulose biorefinery.

2. ECN Organosolv Process



- Lignocellulosic biomass: focus on straw and hardwood.
- Solvents: ethanol, acetone, …
- Catalyst: H_2SO_4, ...
- Typical process conditions: 160-200 °C, 30-120 min.

3. Background Study

Study on effect of catalysts on organosolv treatment of lignocellulosic biomass, in particular:

- Fractionation (pulp composition, lignin yield, …).
- Pre-treatment (enzymatic digestibility of the cellulose fraction).

Selected catalysts: H_2SO_4, HCl & $MgCl_2$. Selection based upon:

- Literature study.
- Screening of a wide range of catalysts (acids, bases, and salts).

Study submitted for journal publication [1].

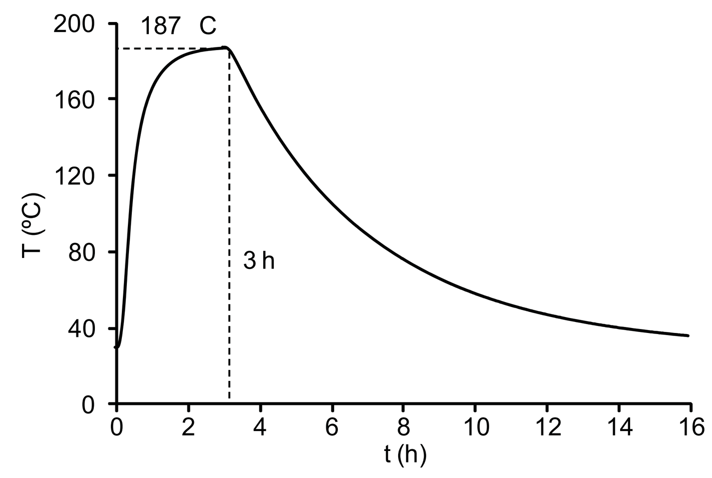
4. Experimental

Organosolv experiments:

- Feedstocks: willow wood & wheat straw.
- Solvent: aqueous ethanol (60% w/w).
- Reactor: 6*125 mL parallel.

		Willow wood	Wheat straw
Extractives		5.5	10.4
Polysaccharides	Arabinan	1.1	1.9
	Xylan	11.7	19.9
	Mannan	1.4	0.2
	Galactan	1.1	0.7
	Glucan	32.9	36.9
Lignin	AIL	28.5	16.7
	ASL	2.1	1.1
Ash		4.1	6.1

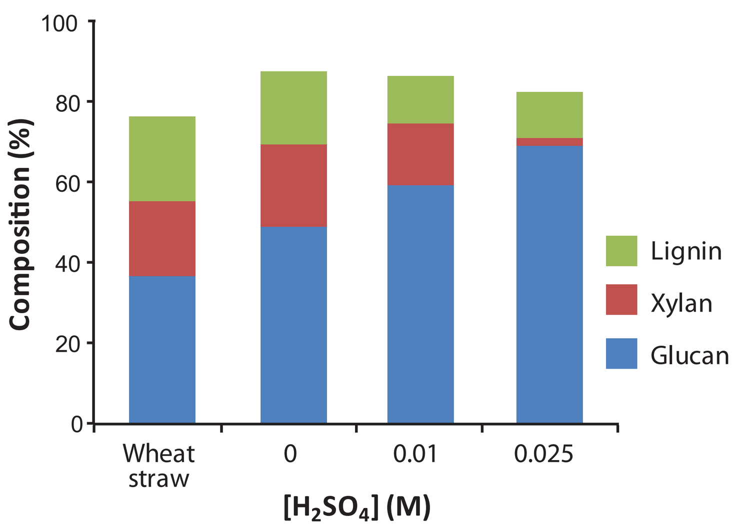
Biochemical composition of raw materials.



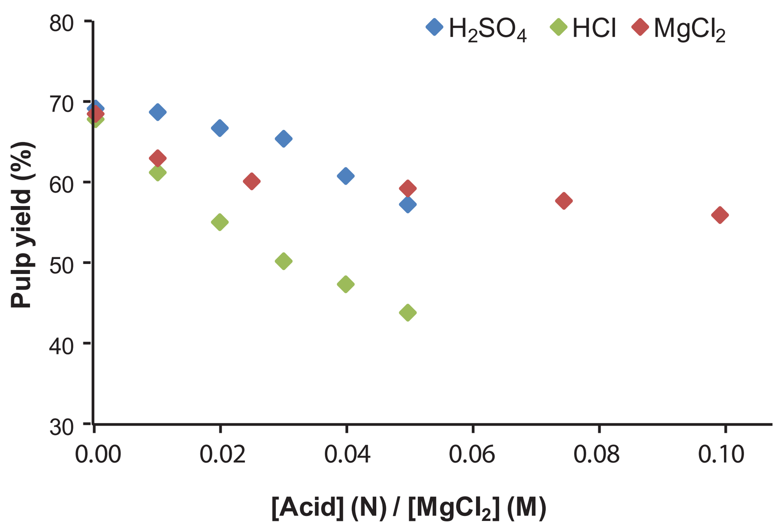
Experimental set-up and temperature profile.

5. Pulp Yield & Composition

Addition of catalysts lowers pulp yield (both for willow wood and wheat straw).



Biochemical composition (pretreated) wheat straw.

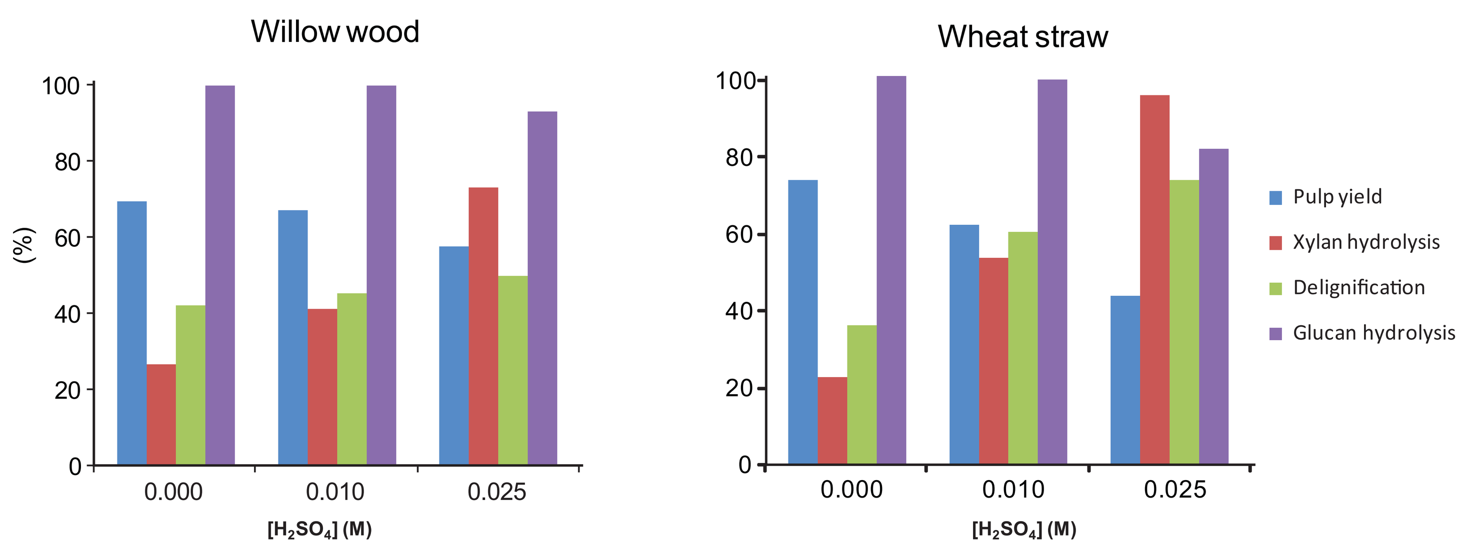


Influence of catalysts on pulp yield (willow wood).

Pretreated biomass: enrichment in glucan due to lignin removal and hemicellulose hydrolysis.

6. Acid Catalysts - Fractionation

- Improvement xylan hydrolysis and delignification.
- Glucan hydrolysis only at high acid doses (pH <3.5).
- Example wheat straw (0.02M HCl): 96% glucan recovery, 83% xylan hydrolysis, and 68% delignification.



Influence of H_2SO_4 on fractionation of willow wood and wheat straw.

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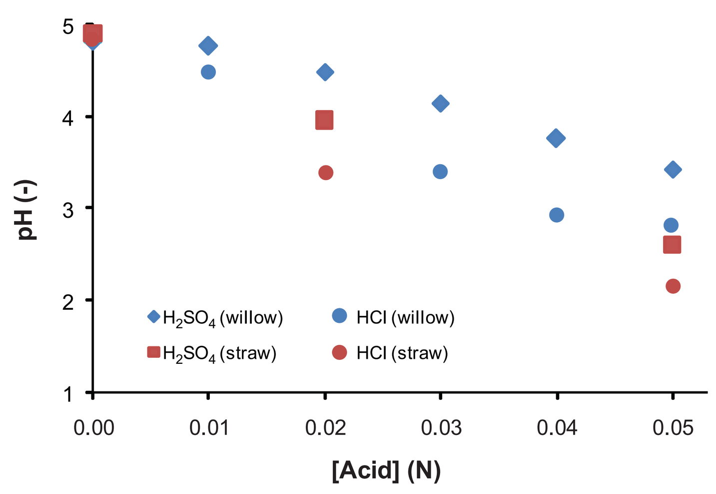
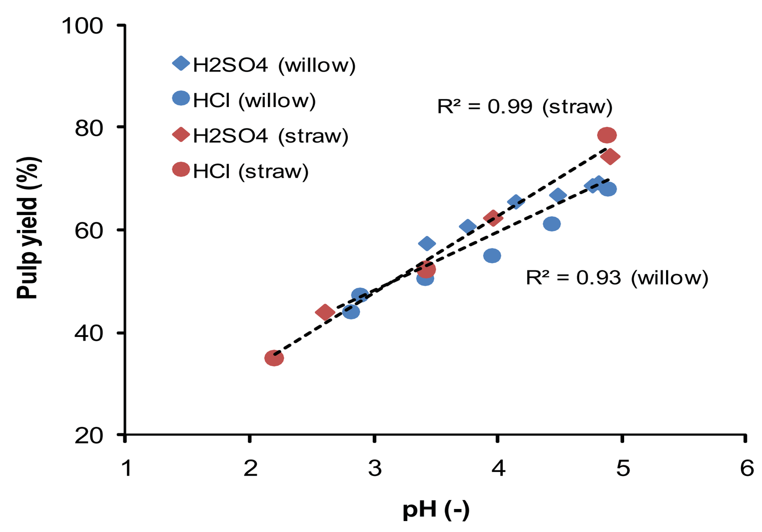
7. Acid Catalysts - Comparison

Influence acid catalysts:
- Primarily due to their effect on pH of organosolv liquor.
- Anion seems to play minor role.



Effect of acid catalyst on pH organosolv liquor.



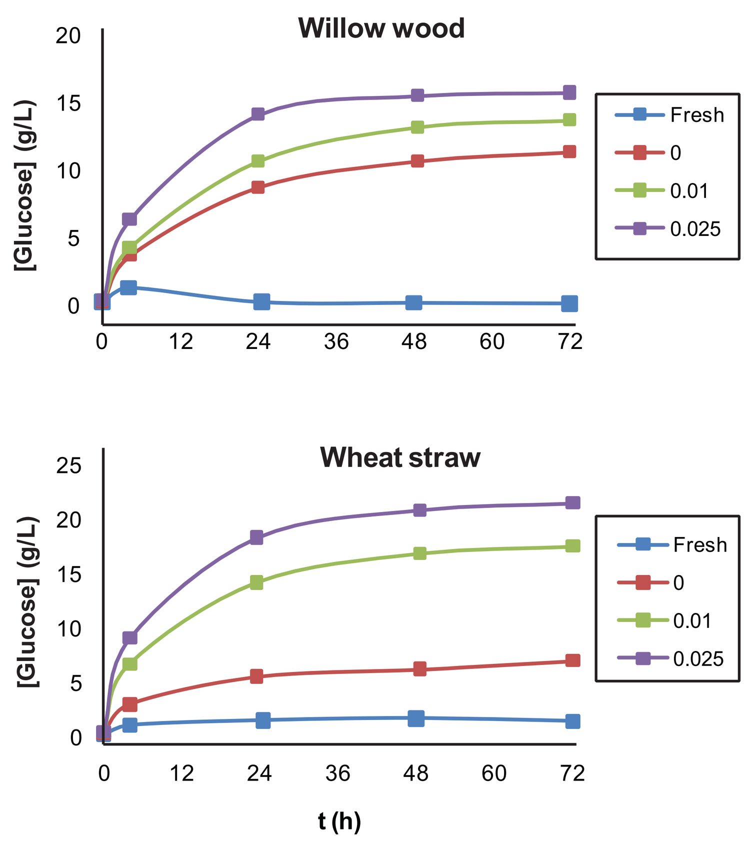
Influence pH organosolv liquor on pulp yield.

- HCl stronger acid than H2SO4 in aqueous ethanol.
- Acid neutralization capacity willow larger than for wheat straw.

9. Enzymatic Hydrolysis

Methodology:
- Genencor Accellerase 1500.
- 35 FPU/gr substrate.
- 3% w/v substrate, 50 °C, pH 4.8.

Results:
- Increase glucose concentration in hydrolysate due to organosolv fractionation.
- Use of catalysts especially beneficial for wheat straw.
- Maximum glucose concentrations obtained at 0.05M HCl:
  - 17 g/L willow wood.
  - 23 g/L wheat straw.



Influence of H_2SO_4 catalyst dose on enzymatic hydrolysis .

11. Conclusions

Application catalysts organosolv pretreatment of willow wood and wheat straw improves fractionation and enzymatic digestibility.

Maximum enzymatic digestibility obtained:
- Willow wood: 87% using 0.01M H_2SO_4 (1.1% w/w biomass) (73% xylan hydrolysis, 51% delignification).
- Wheat straw: 99% using 0.02M HCl (0.8% w/w biomass) (83% xylan hydrolysis, 68% delignification).

Acid catalysts: effect primarily due to their influence on the pH than type of anion. $MgCl_2$ less effective than acids, but possibly more selective in delignification of willow wood.

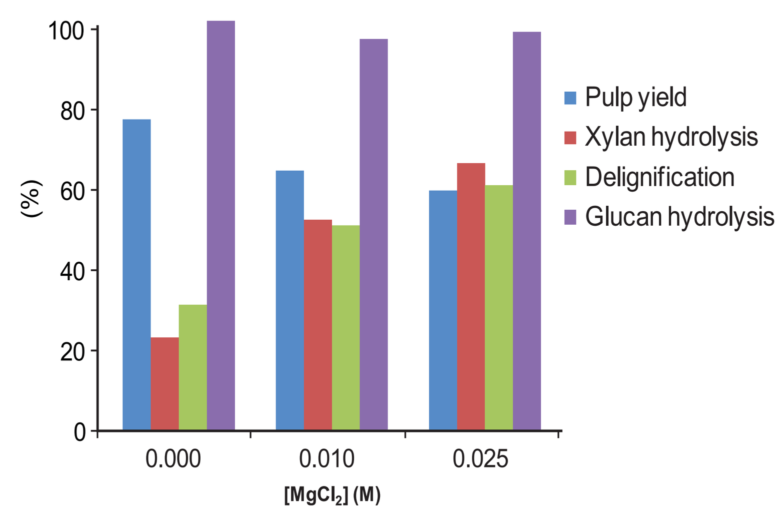
Use of catalysts: contribution to maximum utilisation and valorisation of lignocellulosic biomass in organosolv-based biorefineries.

8. Magnesium Chloride

Observations addition of $MgCl_2$:
- Improvement xylan hydrolysis and delignification.
- Lower pH organosolv slurry at start experiment (by ~1 unit at 0.025M $MgCl_2$)..

Catalytic mechanism $MgCl_2$ not entirely clear. Literature:
- Release of protons due to absorption of Mg^{2+} on carboxylic acid groups in biomass.
- Effect of anion including ionic strength of organosolv liquor.

$MgCl_2$ less effective than acid catalysts in doses applied. However, somewhat more selective in delignification of willow wood.



Effect of $MgCl_2$ on fractionation wheat straw.

10. Enzymatic Digestibility

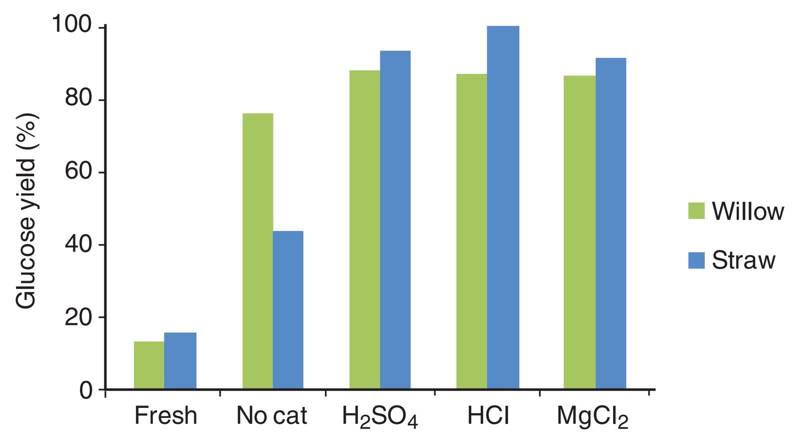
Substantial increase of enzymatic digestibility due to organosolv fractionation.

Maximum enzymatic digestibility:
- Willow wood: 87% (0.01M H_2SO_4).
- Wheat straw: 99% (0.02M HCl).

Similar results willow wood with all catalysts.

Enzymatic glucose yield lower at high acid doses due to cellulose hydrolysis during organosolv.

$MgCl_2$: enzymatic digestibility willow wood higher at equal xylan hydrolysis degree compared to acids.



Glucose yield by enzymatic hydrolysis based on composition raw material. For catalysts results at optimum dose are presented.

12. More Information & Acknowledgements

More information:
- Huijgen WJJ, Smit AT, Reith JH, den Uil H (2011): Catalytic organosolv fractionation of willow wood and wheat straw as pretreatment for enzymatic cellulose hydrolysis (submitted).
- http://www.ecn.nl/units/bkm/biomass-and-coal/

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http://www.lignovalue.nl/