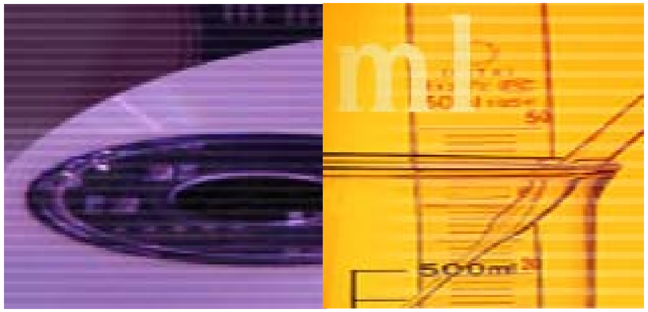
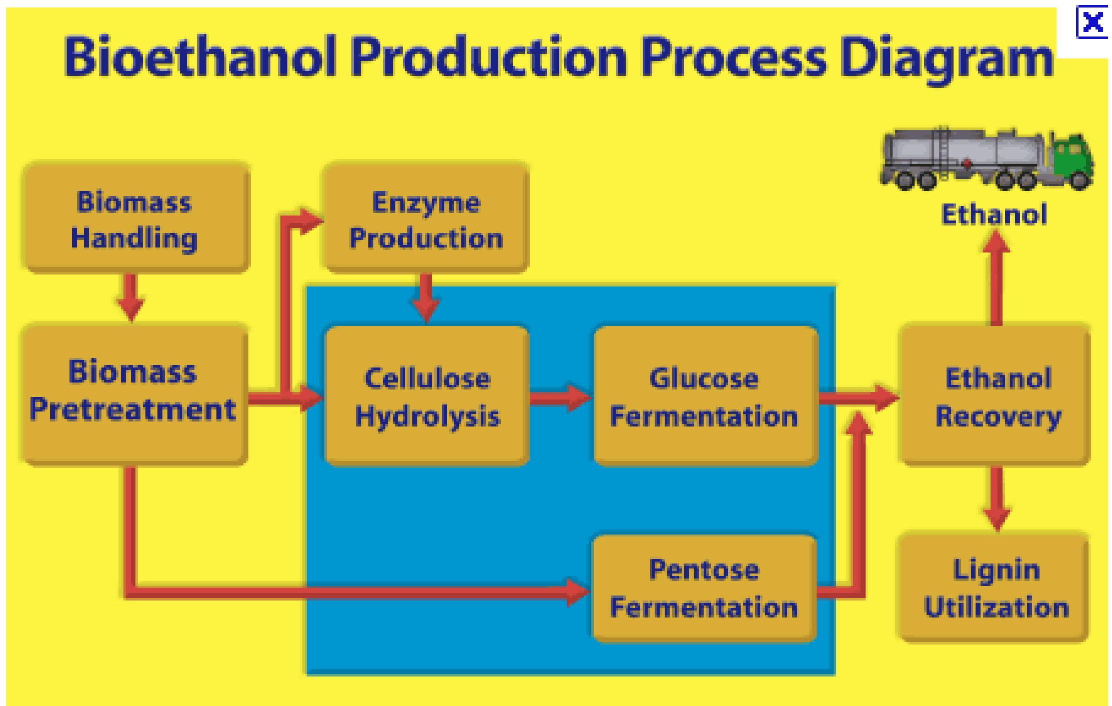
Dream CNU

Comparison of dilute mineral and organic acid pretreatment for enzymatic hydrolysis of wheat straw



Introduction

▪ Second generation bioethanol production uses relatively cheap, abundant, and renewable agricultural by-products, such as corn stover, wheat straw, or forestry residues.



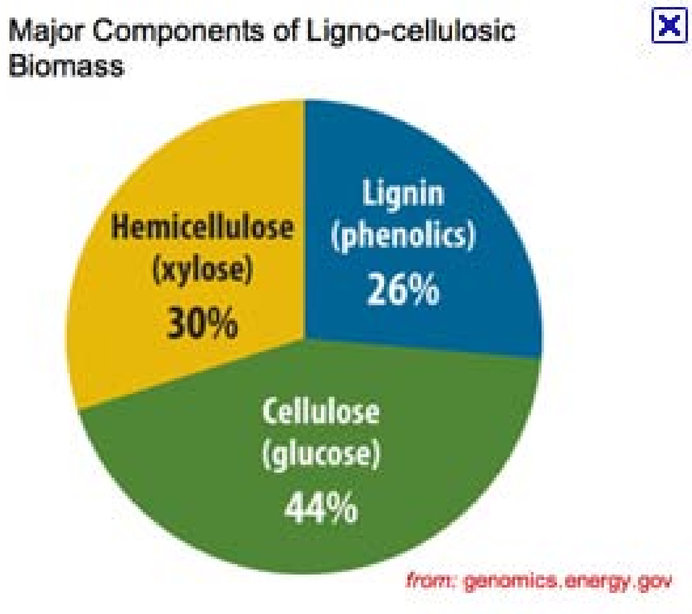
Introduction

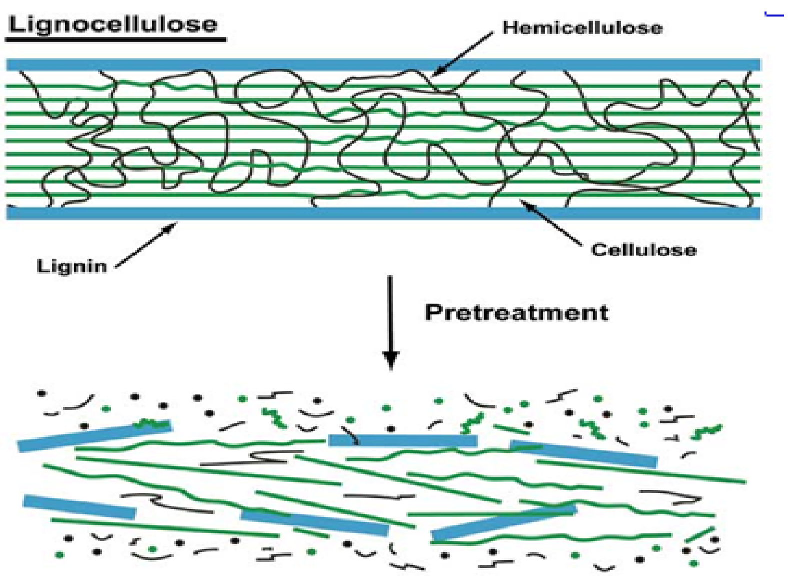
- Ligno-cellulosic biomass requires pretreatment to improve cellulose accessibility to cellulolytic enzymes.

- Usually this entails a heat treatment in water in presence of a catalyst (acid or base).

- A common pretreatment uses dilute sulfuric acid (50–300mM) at 100–200 ◦C.

- Maleic and fumaric acid have been suggested as alternatives for sulfuric acid in the pretreatment.



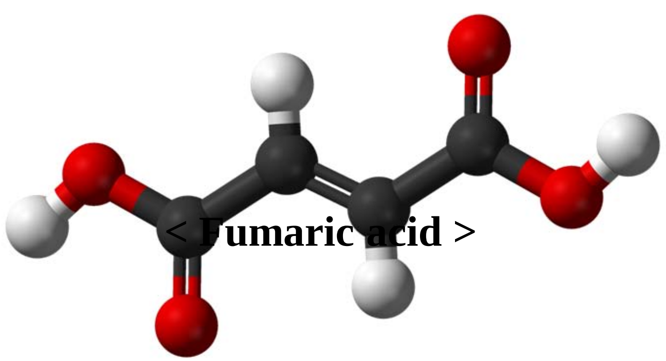


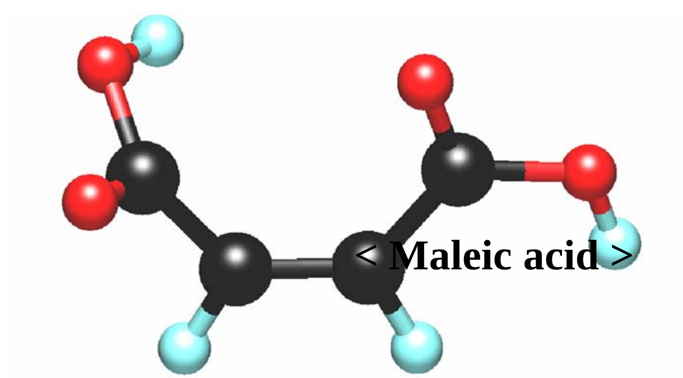
Objectives

▪The efficiencies of water, fumaric, maleic, and sulfuric acid in the pretreatment of wheat straw at various temperatures.

▪Investigation on whether the dilute organic acids can pretreat wheat straw with an efficiency comparable to that of dilute sulfuric acid, while producing significantly less sugar degradation products.

▪ Investigation on the effect of raising the solids loading, both on the efficiency of the pretreatment, as well as on the formation of sugar degradation products.





Materials and methods

Preparation and analysis of wheat straw

Table 1 Chemical composition (dry-weight basis) of the wheat straw used in this study.

Component	Content (%, w/w)
Glucan	36.3
Xylan	19.0
Arabinan	2.1
Galactan, mannan, rhamnan	<0.6 each
Uronic acids	2.1
Lignin	25.5
Extractives	7.8
Protein	3.3
Ash	6.7

- Wheat straw was milled twice; first in a Pallmann mill (4mm×30mm sieve) and then in a Retsch mill (1mm sieve). Milled straw was kept in a sealed plastic barrel at room temperature until used.

- Chemical composition was analyzed as described by TAPPI methods, with minor modifications.

- Monomeric sugars were measured by HPAEC-PAD (High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection).

Materials and methods

Experimental setup for wheat straw pretreatment

- All acids were of research grade and used as received (maleic acid: Aldrich M153; fumaric acid: Aldrich F19353; sulfuric acid: Fluka 84721).

- Milled wheat straw (8.0 g; 7.34 g dry matter) was mixed in poly-ethylene containers with 65.5mL of acid solution (50mM) or with de-ionized water, resulting in 10% (w/w) dry straw solids loading.

- The straw/acid mixture was soaked for 20–24 h at room temperature and then transferred to 316L stainless steel reactors (inner height × diameter: 90.0mm×40.0mm; 5.0mm wall), fitted with thermocouples.

- Pretreatments were performed at 130, 150, and 170 ◦C. Holding time was 30 min, starting from when desired core temperature was reached.

- After the reaction time, the reactors were cooled by quenching in ice water.

- All experiments were conducted in duplicate.

Materials and methods

Enzymatic hydrolysis of pretreated wheat straw

- After pretreatment, reactor contents were transferred to 250mL baffled shake flasks.

- Flasks were left overnight for the pH to equilibrate.

- After pH fine tuning and enzyme addition, flasks were closed with airtight plugs and placed in an Innova 44 incubator shaker (50 ◦C, 150 rpm, 2 in. stroke; NBSC, Edison, NJ).

- Samples were stored at −20 ◦C until analysis.

- The glucose yield from cellulose was calculated as follows:

$$\text{Glucose yield}(\%) = \frac{GH}{GS} * 100$$

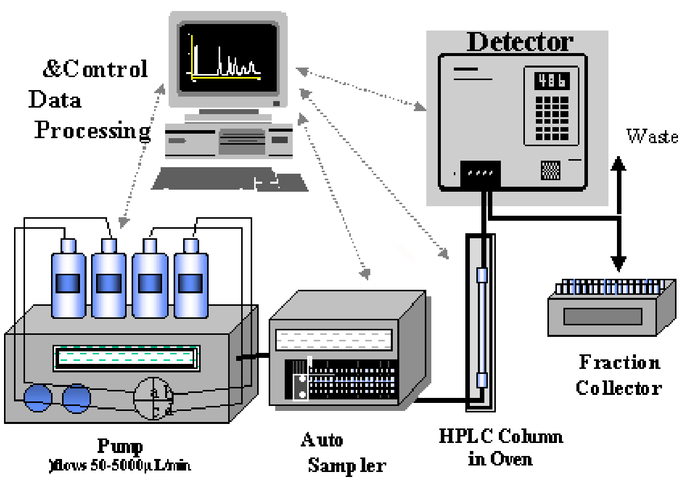
- GS : the amount of glucose present in the sample of dry straw,
- GH : the amount of glucose (g) present in the aqueous phase of the sample
  : after pretreatment or enzymatic hydrolysis.

Materials and methods

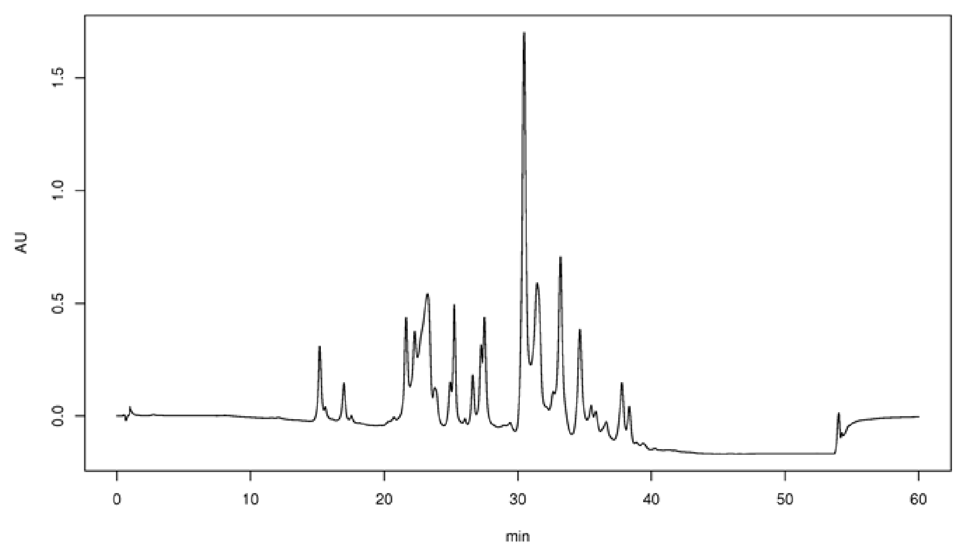
HPLC analytical method for organic acids and sugar degradation products

- Maleic acid, fumaric acid, furfural, and 5-HMF concentrations after pretreatment were measured by HPLC.

- Measurements were performed in the liquid phase prior to starting the enzymatic treatment.



< HPLC >



Results and discussion

1. Influence of pretreatment temperature

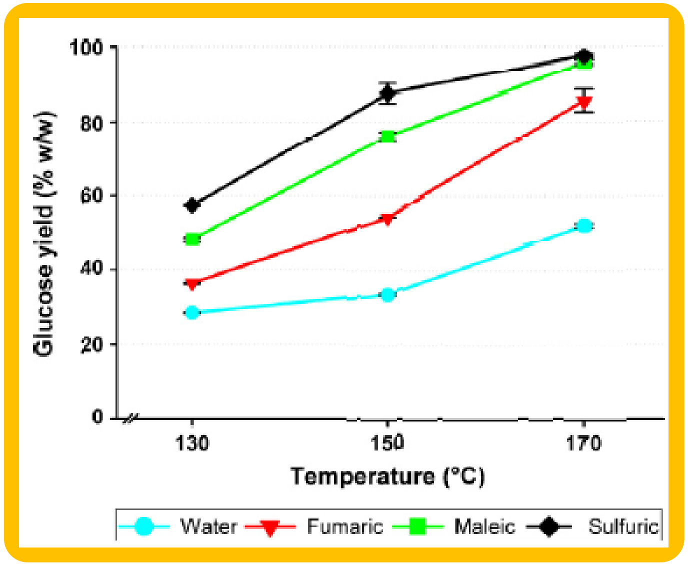


Fig. 1. Glucose yield as function of pretreatment temperature, measured after enzymatic hydrolysis (72 h, 50 ◦C). 100% = 0.40 g glucose/g dry matter straw. Error bars represent standard deviation.

- Organic acids can pretreat wheat straw with high efficiency (Fig. 1).
- at 150 ◦C, maleic acid pretreatment is very effective with close to 80% glucose yield after enzymatic digestion.
- Fumaric acid is less effective than maleic acid.
- In general, increasing the temperature and lowering the pH are known to increase the pretreatment efficiency.

- The trends as illustrated in Fig. 1 (water < fumaric <maleic < sulfuric)

Results and discussion

Influence of pretreatment temperature

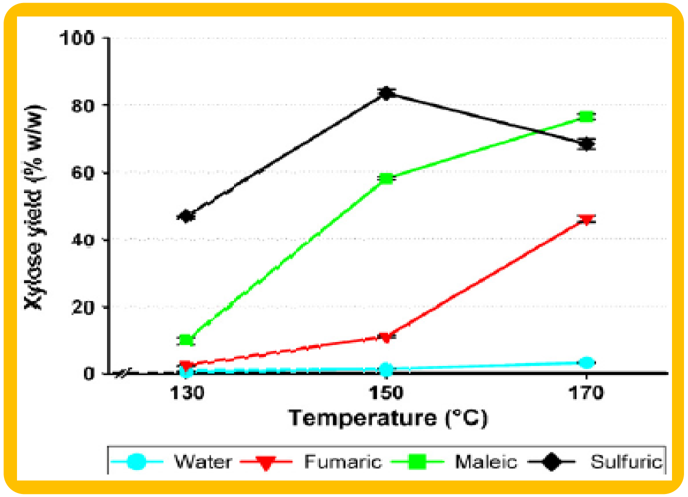


Fig. 2. Xylose yield as function of pretreatment temperature, measured after pretreatment. 100% = 0.21 g xylose/g dry matter straw. Error bars represent standard deviation.

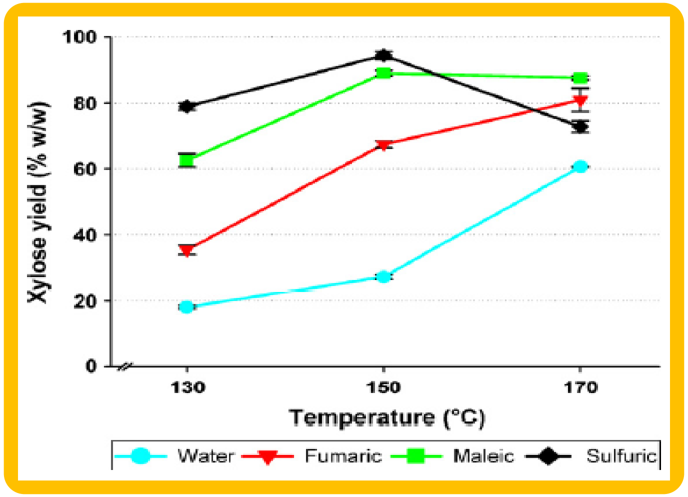


Fig. 3. Xylose yield as function of pretreatment temperature, measured after enzymatic hydrolysis (72 h, 50 ◦C). 100% = 0.21 g xylose/g dry matter straw. Error bars represent standard deviation.

- As opposed to cellulose, a large portion of the hemicellulose (up to ca. 80% of total) was converted to monomeric sugars during the pretreatment, most notably when maleic or sulfuric acid was used at 150 or 170 ◦C (Fig. 2).

Results and discussion

Influence of pretreatment temperature

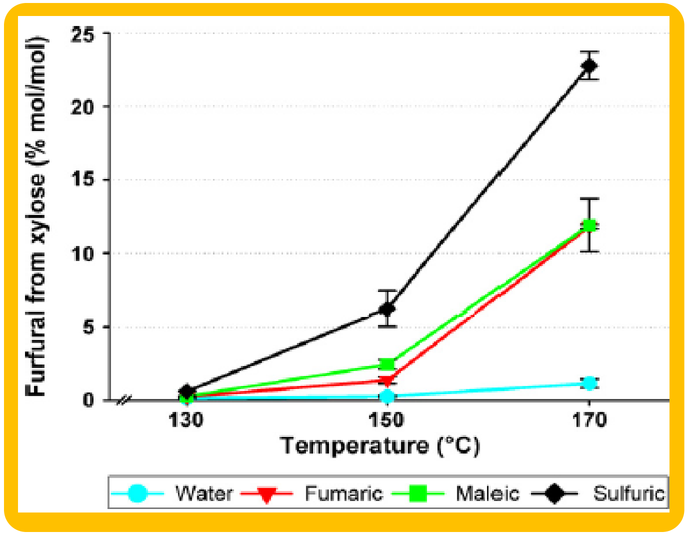


Fig. 4. Furfural formation from xylose as function of pretreatment temperature. Error bars represent standard deviation.

- Pretreatment with sulfuric acid at 170 ◦C resulted in less free xylose than at 150 ◦C.
 Reason : due to more extensive degradation of xylose to furfural (Fig. 4).

•A somewhat unexpected result is that similar amounts of furfural were produced during the 170 ◦C maleic and fumaric acid pretreatments.

•furfural production was expected to be higher during the maleic acid pretreatment than when fumaric acid was used.
 Reason : due to the presence of more free xylose in the case of maleic acid(Figs. 2 and 4).

Results and discussion

2. Solids loading

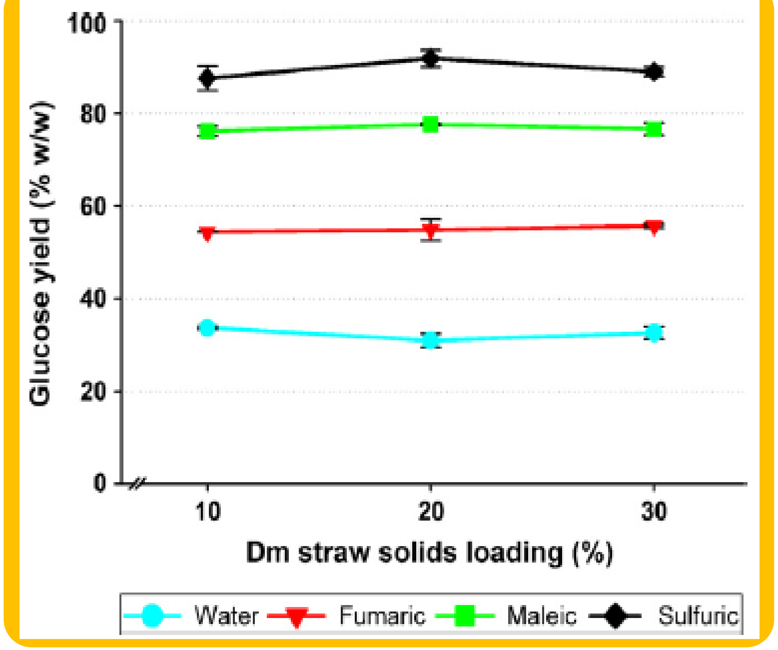


Fig. 5. Glucose yield as function of dm straw loading, measured after enzymatic hydrolysis (72 h, 50 ◦C). Pretreatment temperature 150 ◦C. 100% = 0.40 g glucose/g dry matter straw. Error bars represent standard deviation.

- Raising the solids loading in the pretreatment would decrease process cost, both by lowering reactor size and heating requirements during the pretreatment.

- With constant acid-to-straw ratio, raising the solids loading in 150 ◦C pretreatment from 10 to 20 and 30% (w/w) did not lower glucose yield from cellulose, measured after the enzymatic hydrolysis (Fig. 5).

Results and discussion

Solids loading

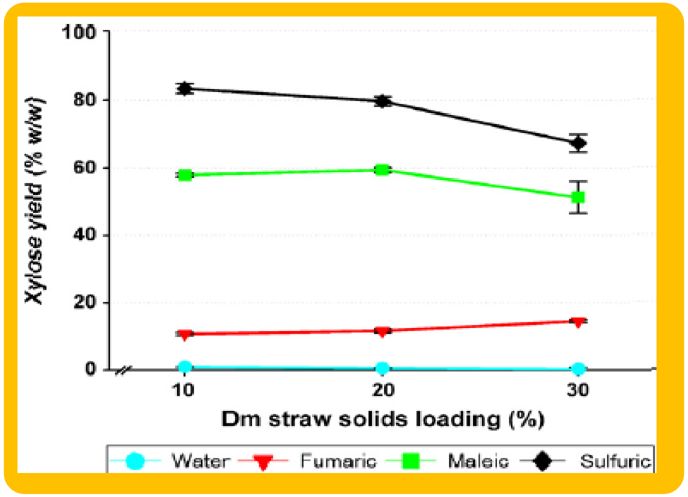


Fig. 6. Xylose yield as function of dm straw loading, with equal acid:straw ratio, measured after pretreatment. Pretreatment temperature 150 ◦C. 100% = 0.21 g xylose/g dry matter straw. Error bars represent standard deviation.

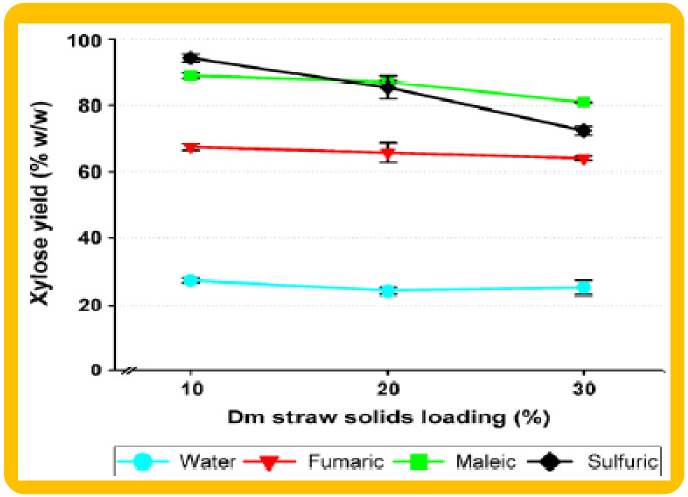


Fig. 7. Xylose yield as function of dm straw loading, with equal acid:straw ratio, measured after enzymatic hydrolysis (72 h, 50 ◦C). Pretreatment temperature 150 ◦C. 100% = 0.21 g xylose/g dry matter straw. Error bars represent standard deviation.

- For the xylose yield from hemicellulose, the effect of raising the solids loading was somewhat different (Figs. 6 and 7).

- When water or fumaric acid were used, it was clear that higher solids loading pretreatment did not reduce xylose yield after enzymatic hydrolysis.

Results and discussion

Solids loading

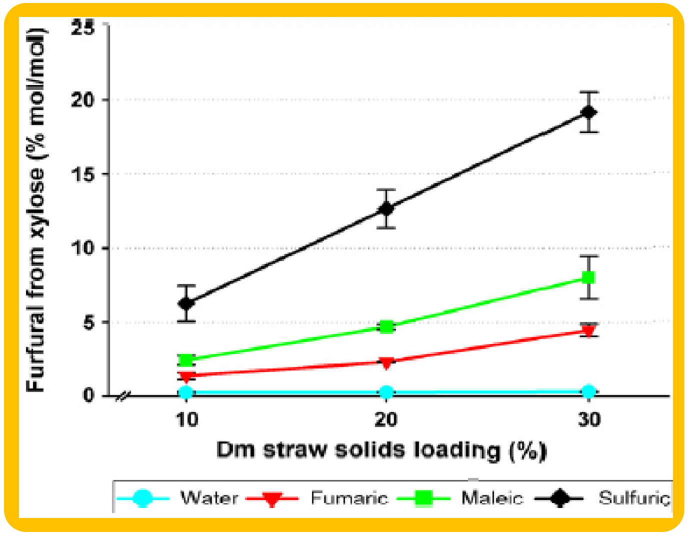


Fig. 8. Furfural formation from xylose as function of dm straw loading. Pretreatment temperature 150 ◦C. Error bars represent standard deviation.

- after sulfuric acid pretreatment, enzymatic xylose yield decreased by more than 20%. This was largely caused by formation of ca. 15% more furfural (Fig. 8).

- Also illustrated in Fig. 8 is that the effect of the organic acids causing much less furfural formation during the pretreatment than sulfuric acid does, persists at high solids loading.

- However, furfural formation does increase when raising the solids loading, and for the maleic acid pretreatment.

Conclusions

- During the organic acid pretreatment, much less furfural is formed from xylose than when using sulfuric acid, and this effect persists when the solids loading is raised.

- This study shows that the application of dilute organic acids in the pretreatment of lignocellulosic biomass like wheat straw can be effective and thus a serious alternative for the dilute sulfuric acid pretreatment.

- It has been made clear that efficient pretreatment of wheat straw is possible using maleic and fumaric acid.