Hydrolysis of model hemicellulose extracts catalyzed by sulfur dioxide (SO_2)

Rory Jara, Grad student (UMaine)

James Grundy, Undergrad student (Harvard)

Adriaan van Heiningen, Advisor (UMaine)

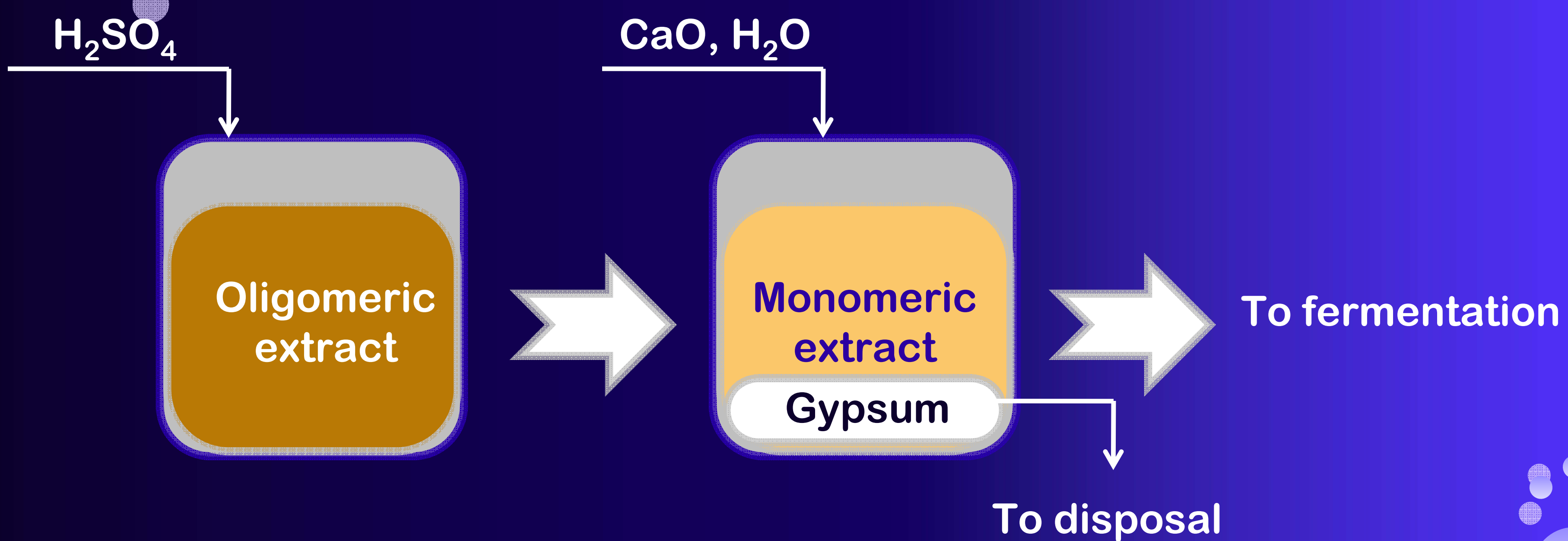
Outline

- Background
- Experimental methods
- Results and discussions
- Preliminary conclusions
- Current work

Background

- Hemicellulose extracts are a mix of sugar oligomers and monomers.
- Fermentation requires monomers to convert sugars into ethanol.
- Hydrolysis breakdown oligomers into monomers.
- Problems with traditional dilute sulfuric acid hydrolysis process.
  - H_2SO_4 is not recovered
  - Gypsum is produced
- Sulfur dioxide (SO_2) may be used as catalyst for the hydrolysis of hemicellulose oligomers.
  - SO_2 may be recovered and then recycled

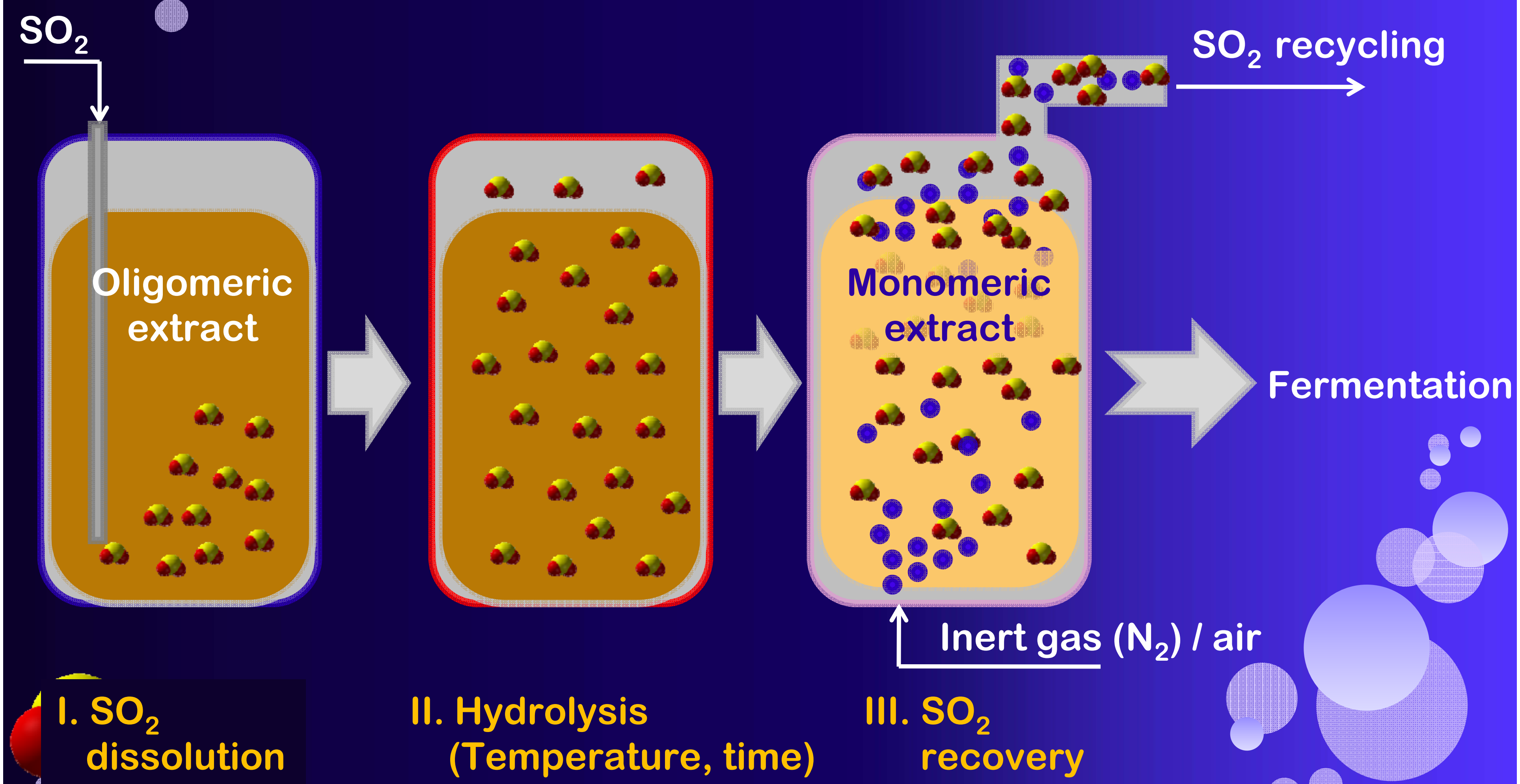
Conventional dilute H_2SO_4 hydrolysis



Hydrolysis: 0.5 – 4% H_2SO_4
120 – 126° C

Neutralization:
$H_2SO_4 + CaO + H_2O \rightarrow CaSO_4 \cdot 2H_2O$

Proposed SO_2 hydrolysis



Experimental methods

Simulated hemicellulose extracts

Composition in weight %

Hot water extract (HWE)	Birch xylan Acetic acid Water	1% 1% 98%
Near Neutral extract (NNE)	Birch xylan Sodium acetate Water	1% 2% 97%

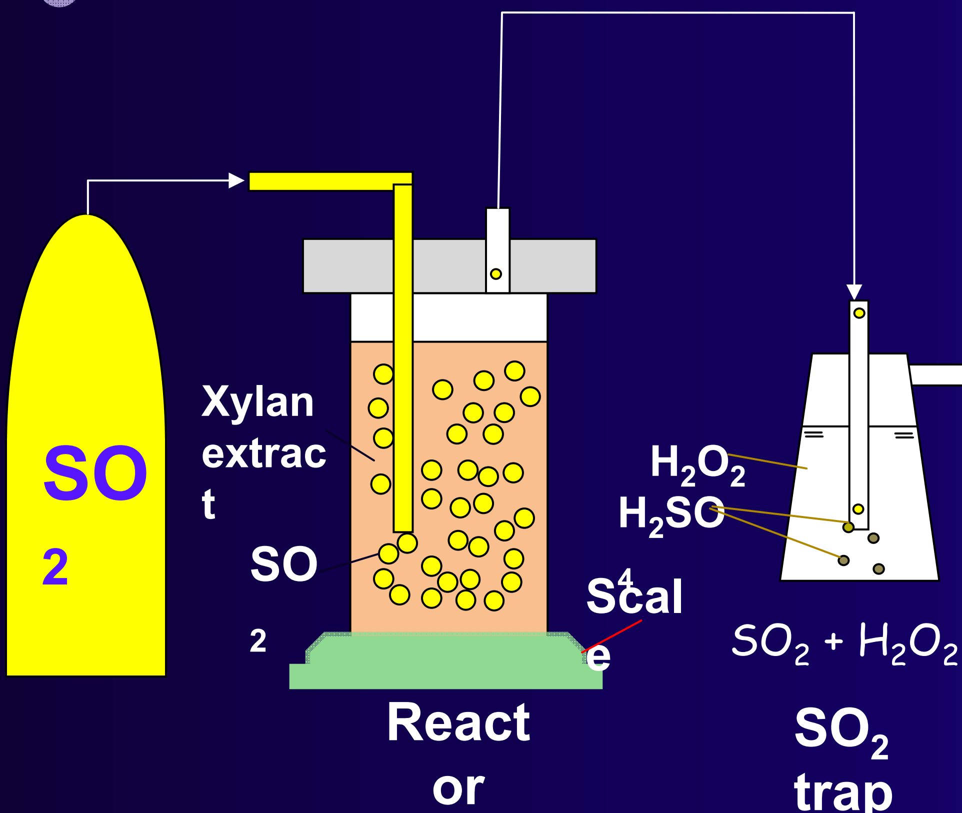
Near Neutral Extraction Process

$$Na_2CO_3 + H_2O \longrightarrow CO_2 + 2NaOH$$

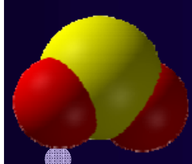
$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

Experimental methods

Sulfur dioxide dissolution



$SO_2 + H_2O_2 \rightarrow H_2SO_4$

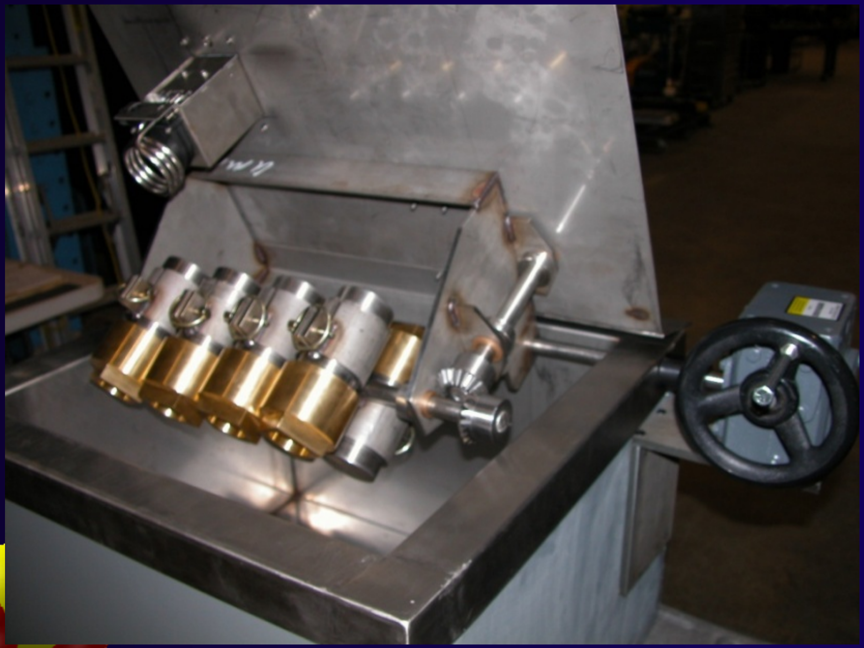


Final SO_2 concentration by difference on reactor weight

Experimental methods

Hemicellulose hydrolysis

Temperature	130 – 160 C
Time	30 and 60 min



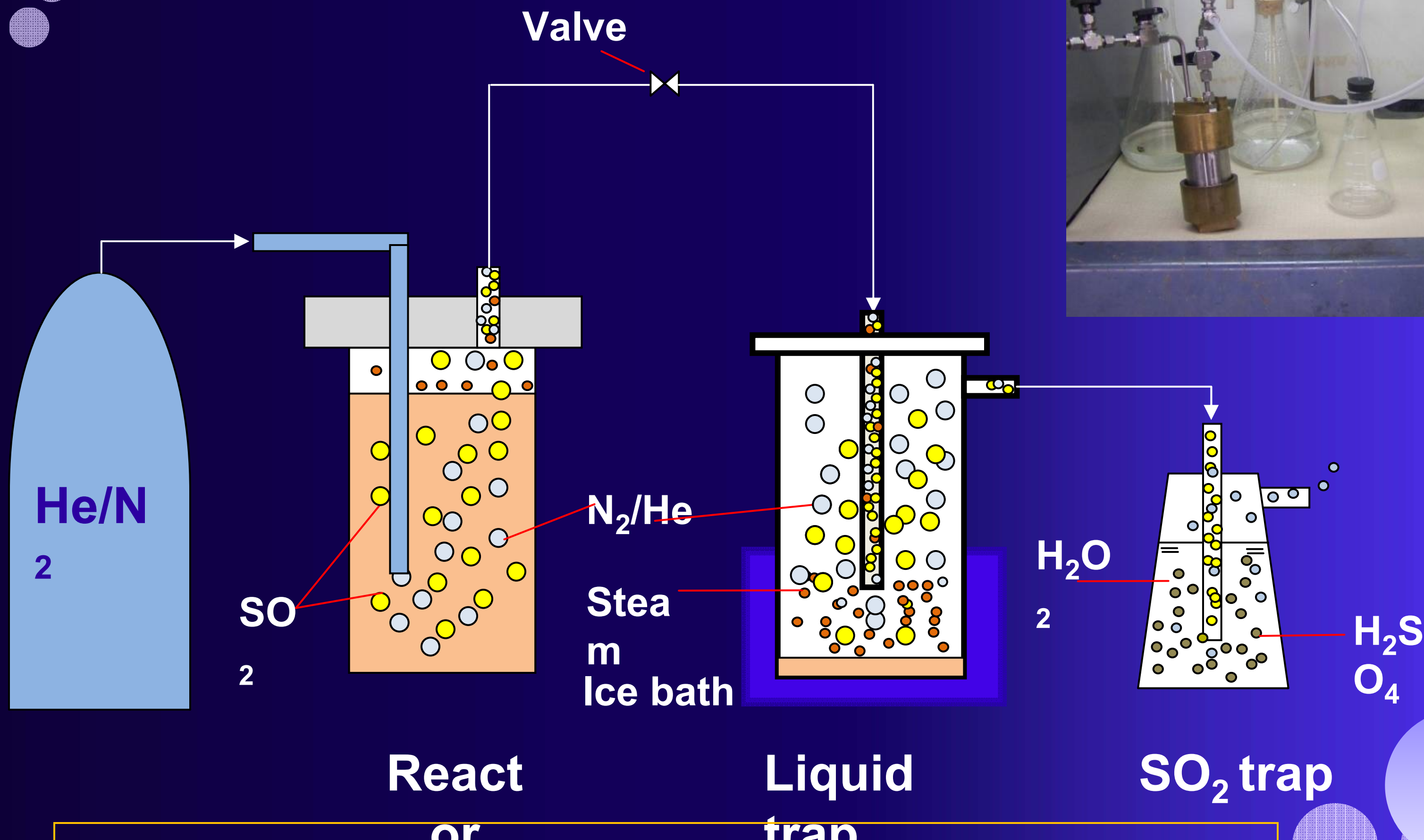
Analysis of monomeric xylan by HPAEC-PAD

$$\text{Xylose yield (\%)} = \frac{\text{Xylose hydrolyzate}}{\text{Max. xylose in Birch-xylan}} \times 100$$

$$\frac{\text{76.8 mg Xylose}}{\text{100.0 mg Birch-xylan}}$$

Experimental methods

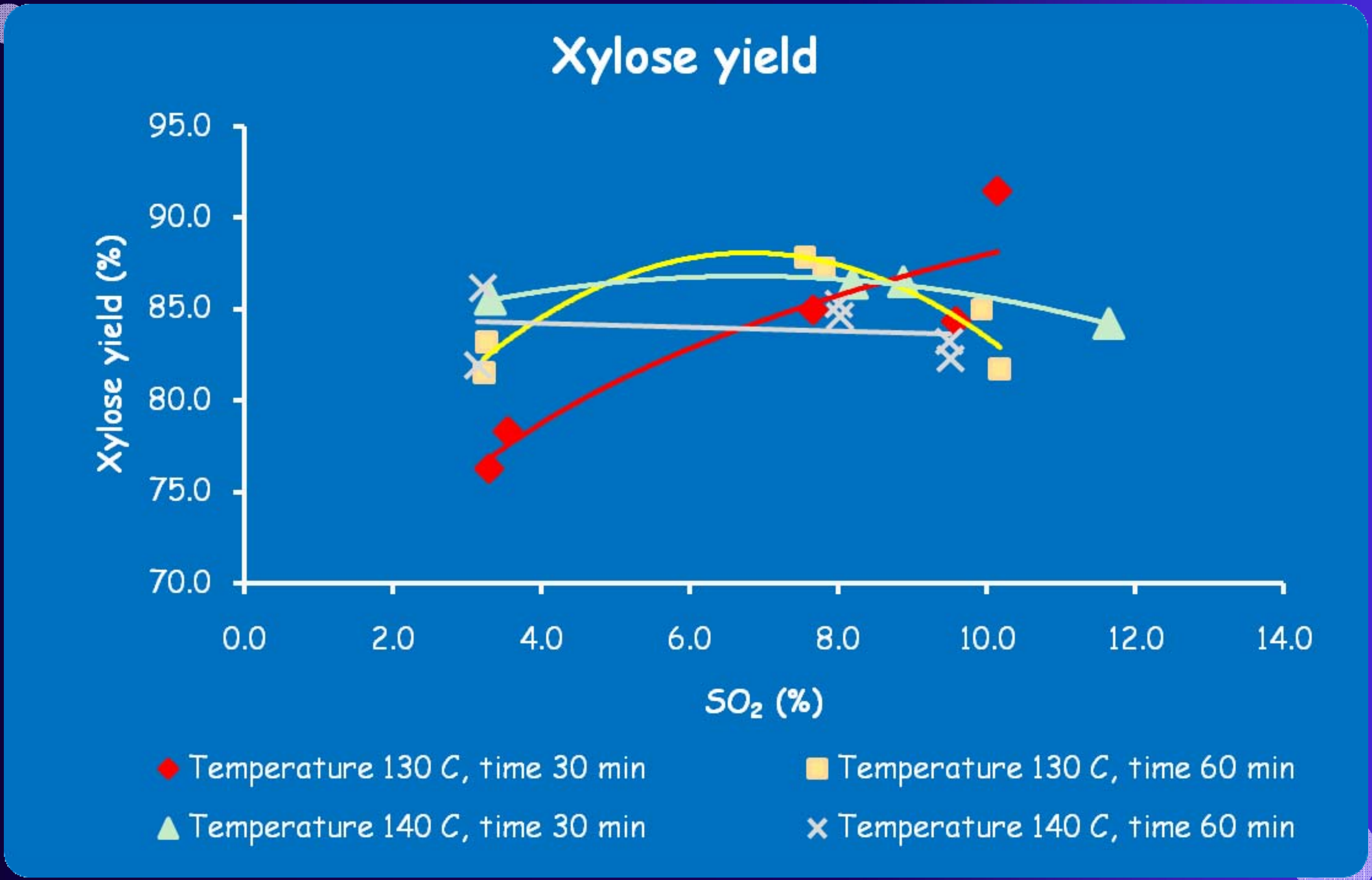
SO_2 recovery



SO_2 mass balance by analysis of SO_4^{2-} using IC

Results: Hydrolysis HWE

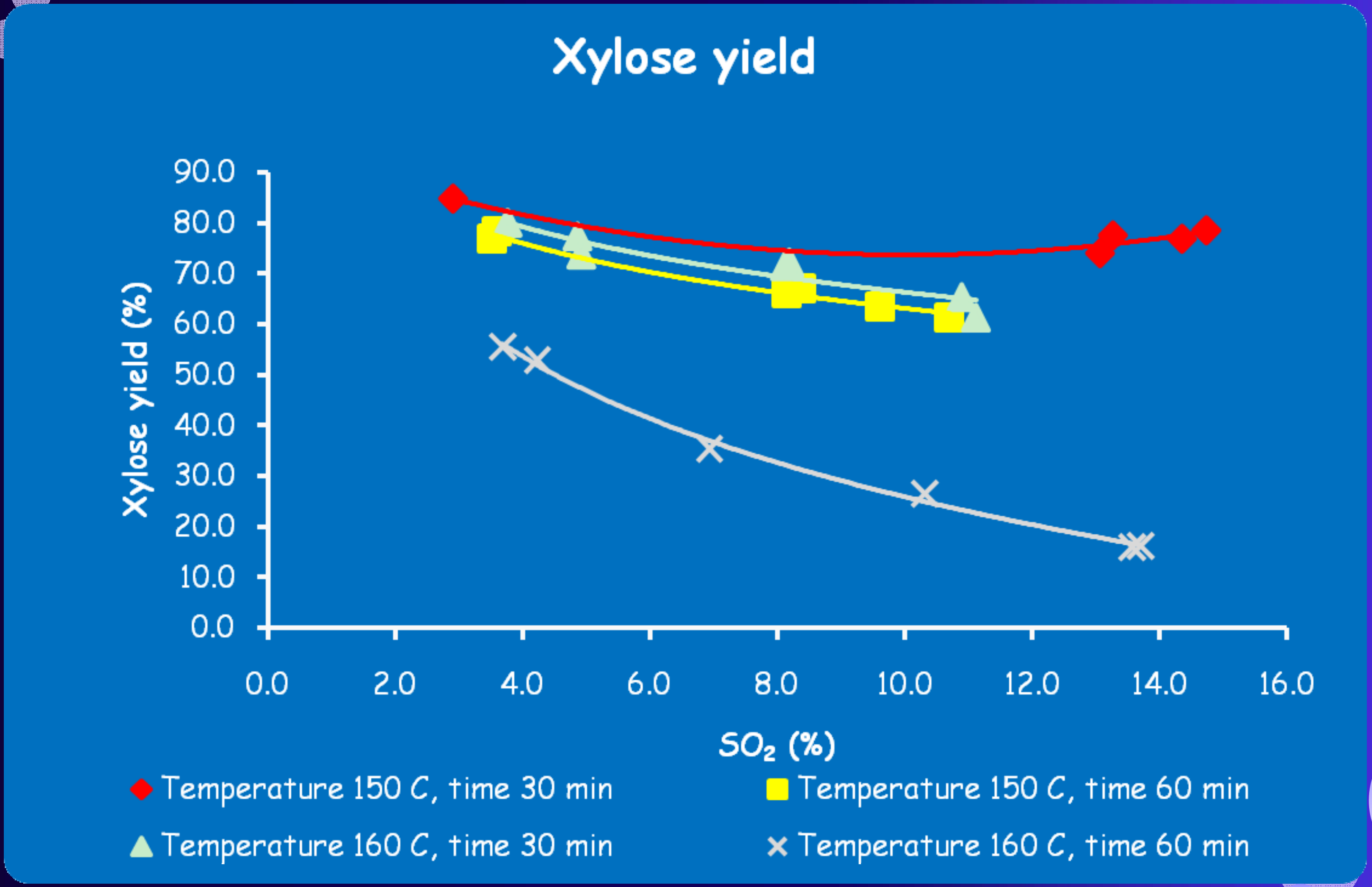
130 & 140 C



Max. Xylose yield close to 80%

Results: Hydrolysis HWE

150 & 160 C



Xylose yield higher in the lower temperature range

Modified Severity factor by Lloyd and Wyman[1]:

$$Mo = t \cdot nA \cdot \exp\left[\frac{\left(T_H - T_R\right)}{14.75}\right]$$

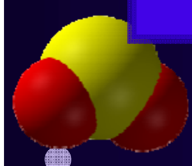
n: assuming a value of 10

Proposed modified P-factor based on Tunc and van Heiningen[2]:

$$MP = t \cdot nA \cdot \exp\left(40.48 - \frac{15106}{T_H}\right)$$

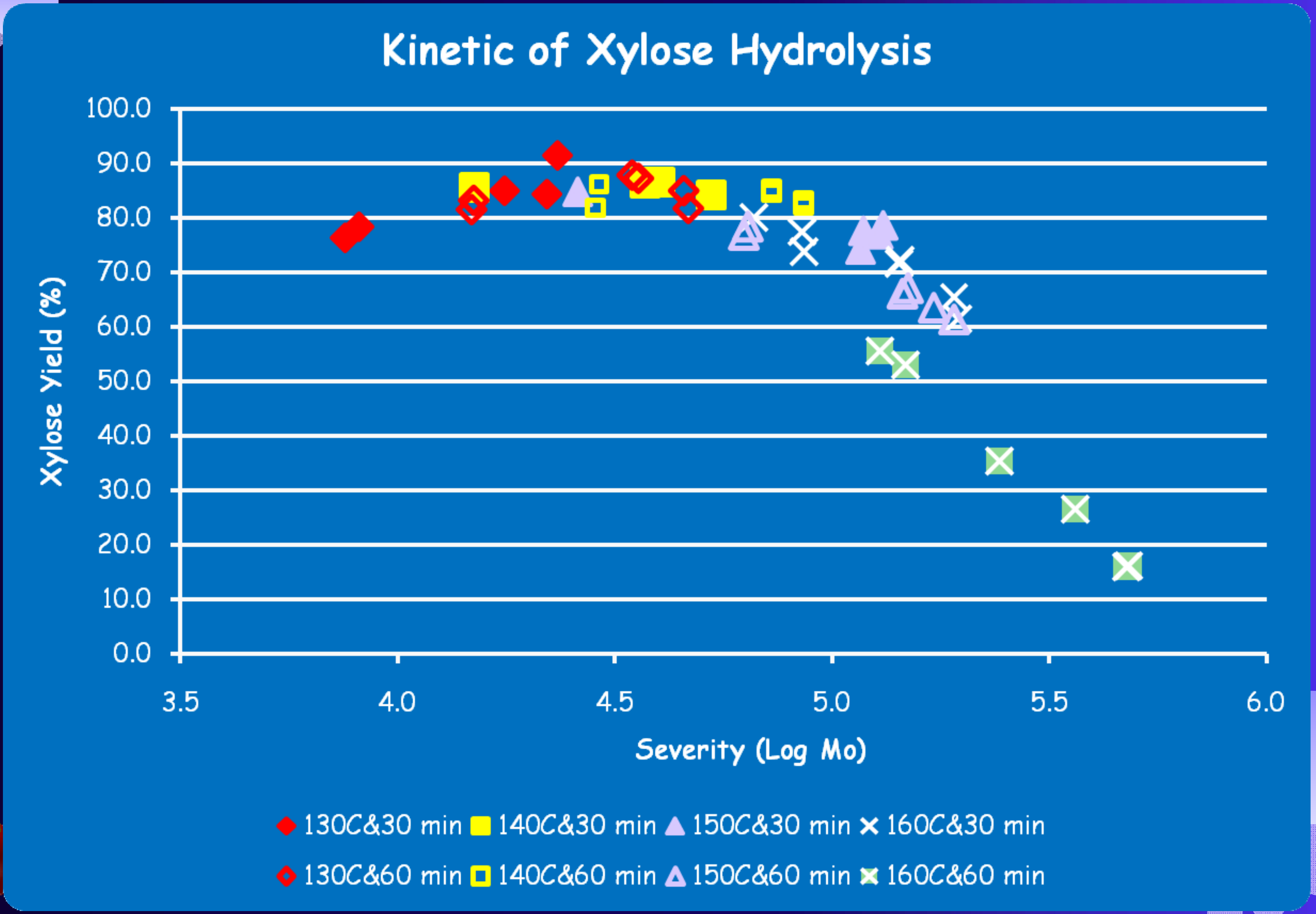
n: assuming a value of 1

t : time
n : proportionality constant
A :acid concentration in weight percent
T_H : hydrolysis temperature
T_R : reference temperature

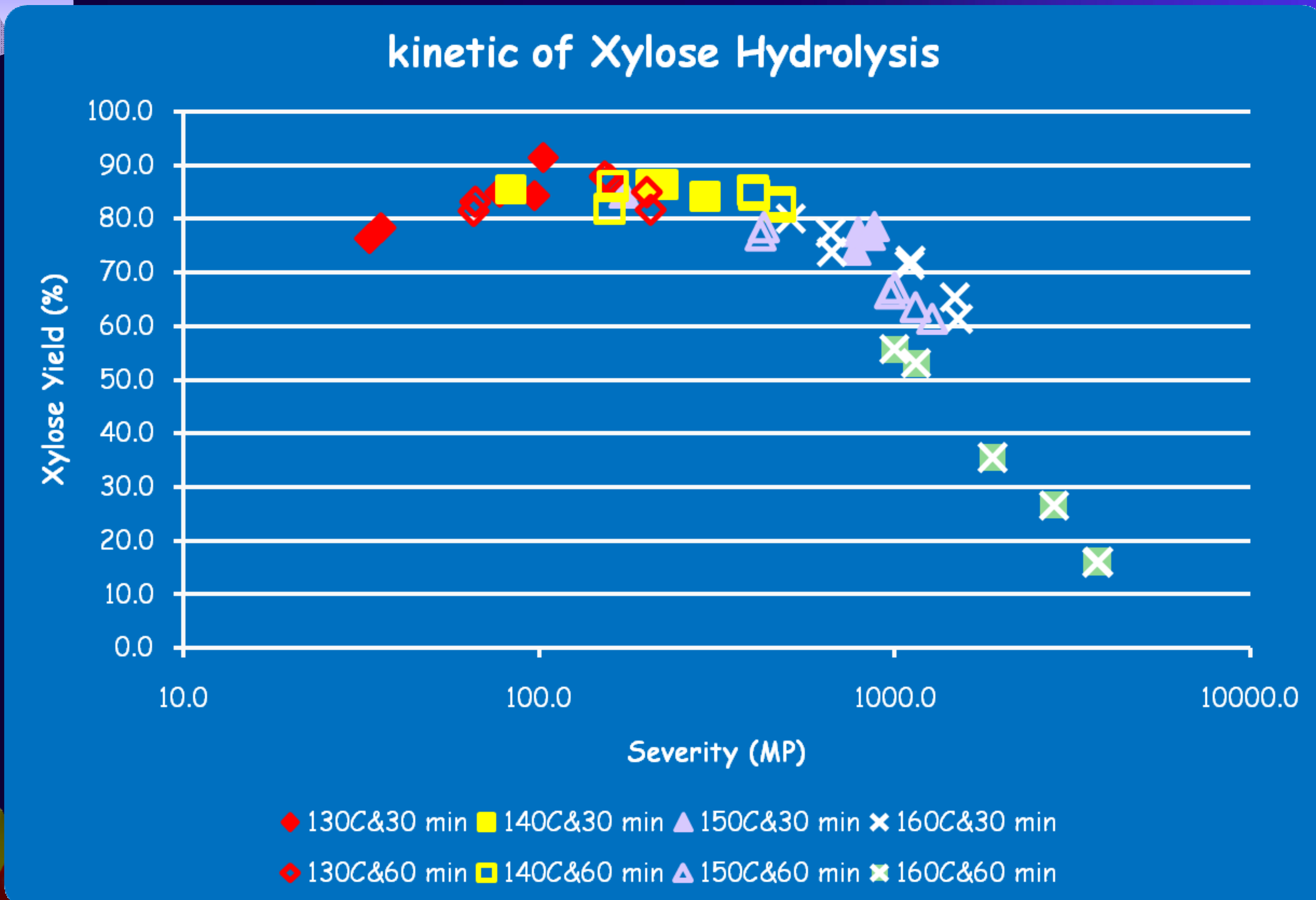


1. Lloyd, T., Wyman, C.E. (2003). Application of a depolymerization model for predicting thermomechanical hydrolysis of hemicellulose. Appl. Biochem. Biotechnol. 105/108, 53-67
2. Tunc, M.S., van Heiningen, A.R.P. (2009). Autohydrolysis of mixed southern hardwoods: effect of P-factor. Nordic Pulp an Paper Journal (accepted for publishing).

Results: Using Mo

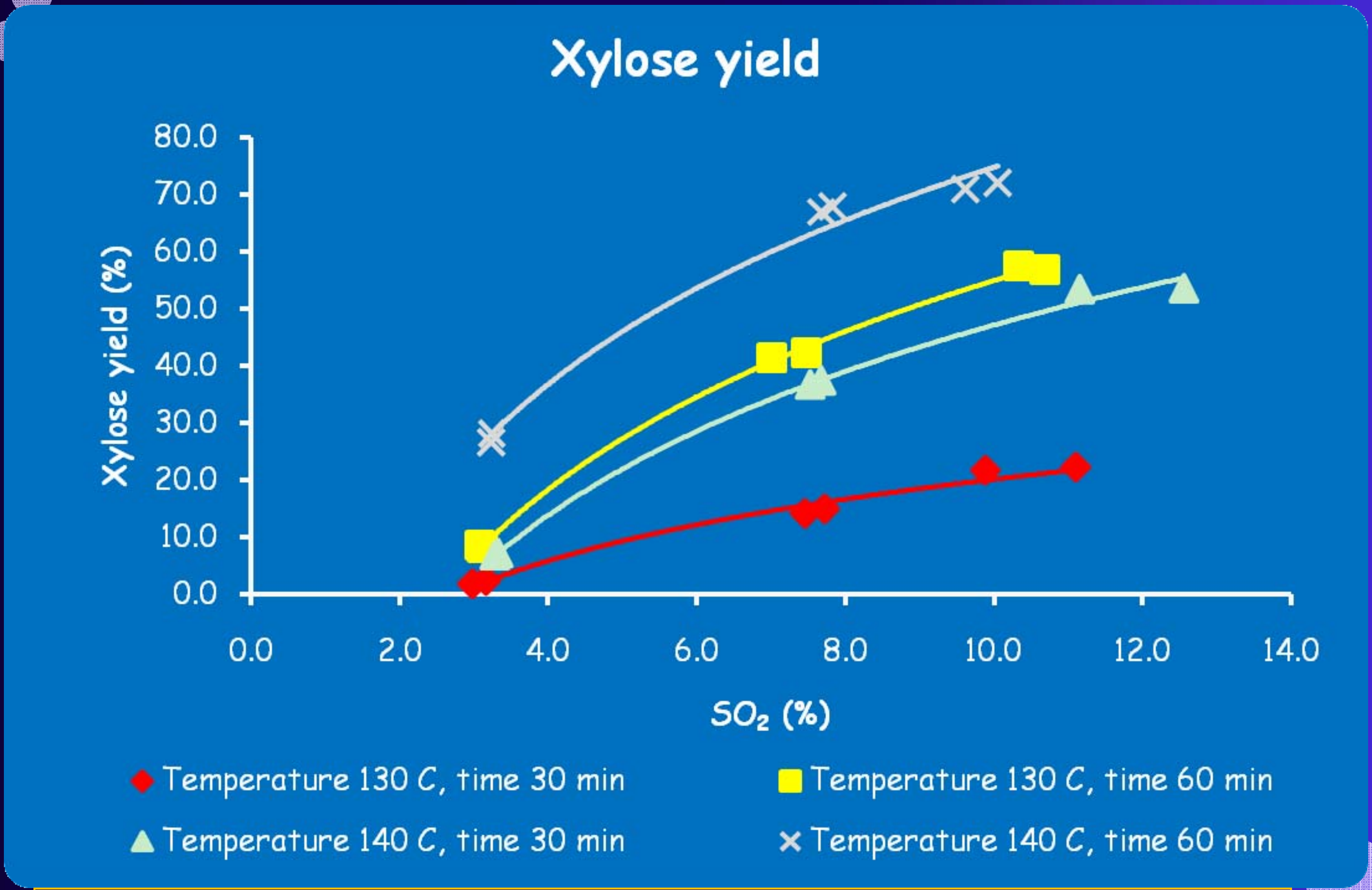


Results: Using MP



Results: Hydrolysis NNE

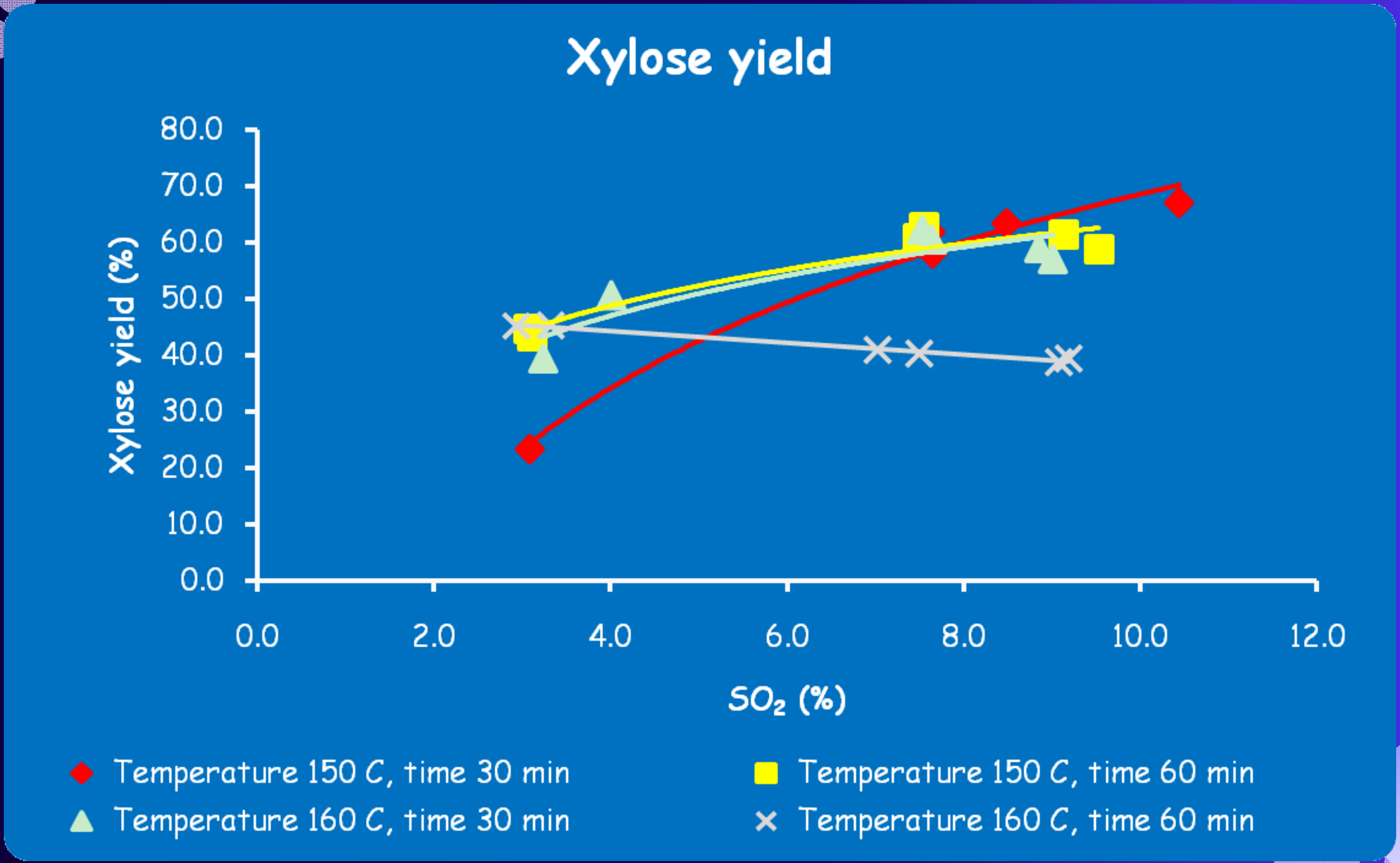
130 & 140 C



Lower xylose yield than in HWE case
Sodium acetate works as a buffer

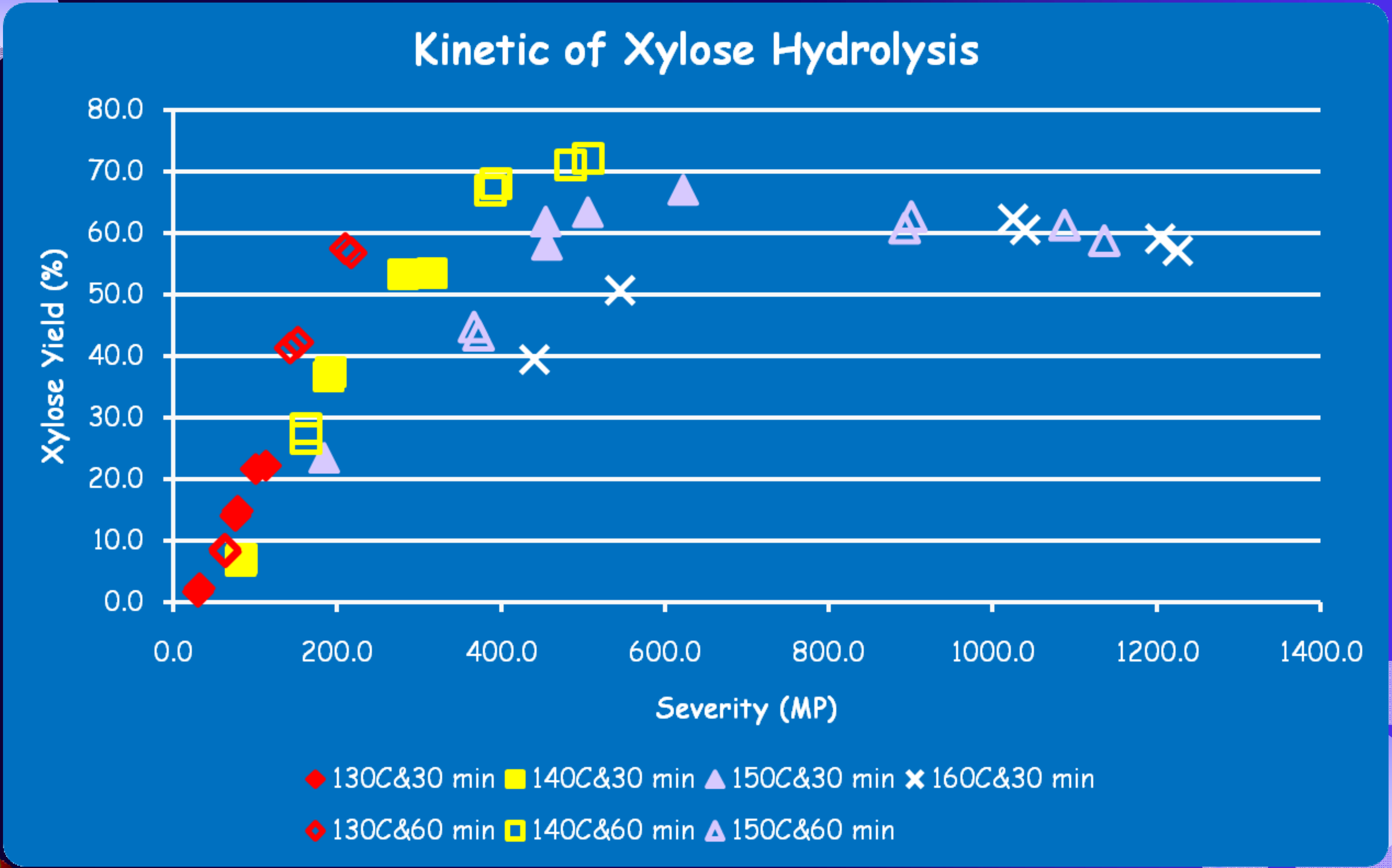
Results: Hydrolysis NNE

150 & 160 C

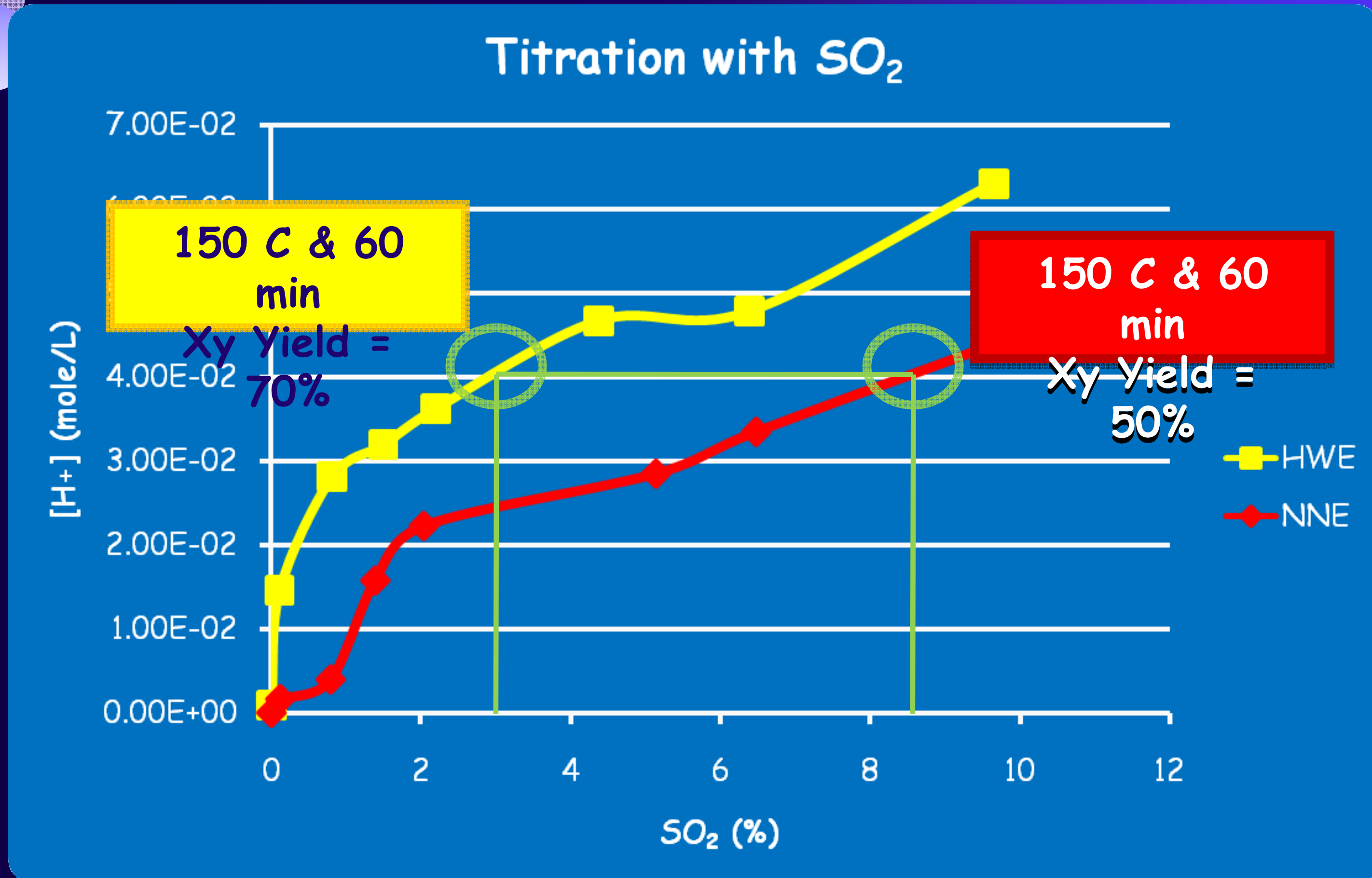


Lower xylose yield than in HWE case
Sodium acetate works as a buffer

Results: Using MP



MP changing with temperature

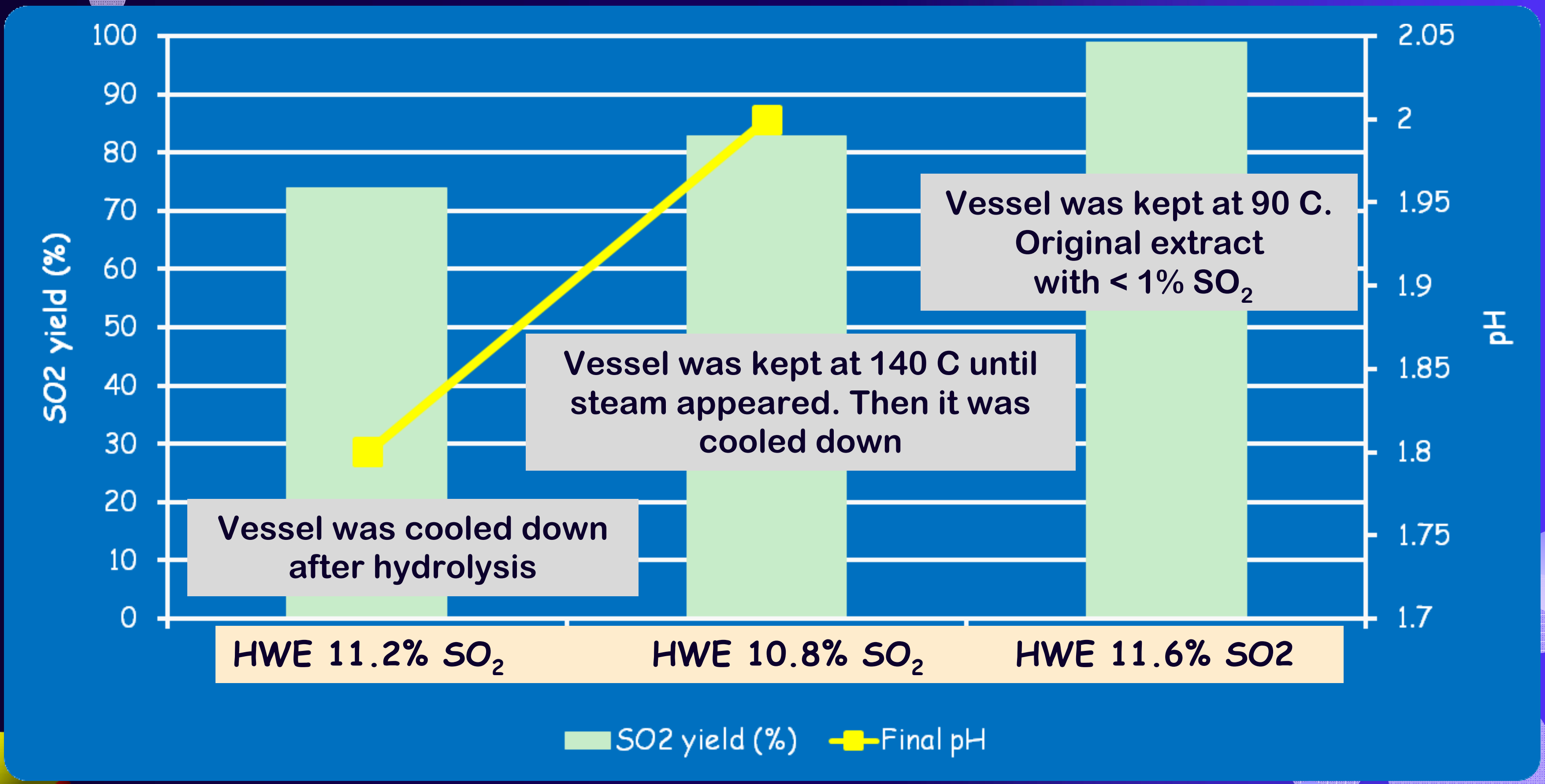


$$CH_3COO^- + H^+ \xrightarrow{T\uparrow} CH_3COOH$$

$$C_5H_9O_5COO^- + H^+ \xrightarrow{T\uparrow} C_5H_9O_5COOH$$

Results

SO_2 recovery after hydrolysis (140C & 30 min)



Preliminary conclusions

- Hemicellulose oligomers can be hydrolyzed using SO_2 as catalyst.
- NNEs need higher SO_2 concentrations than those for HWE in order to get high xylose yields.
- Xylan degradation becomes important for a MP-factor value higher than 800.
- SO_2 is a promising catalyst that may be recovered and recycled in a industrial application.

Current work

- Effect on pressure and protons concentration will be studied during the hydrolysis process.
- Actual Near Neutral Extracts will be tested for the hydrolysis of hemicellulose oligomers.

Acknowledgments

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