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ORGANOSOLV PRETREATMENT AS A MAJOR STEP OF LIGNOCELLULOSIC BIOMASS REFINING

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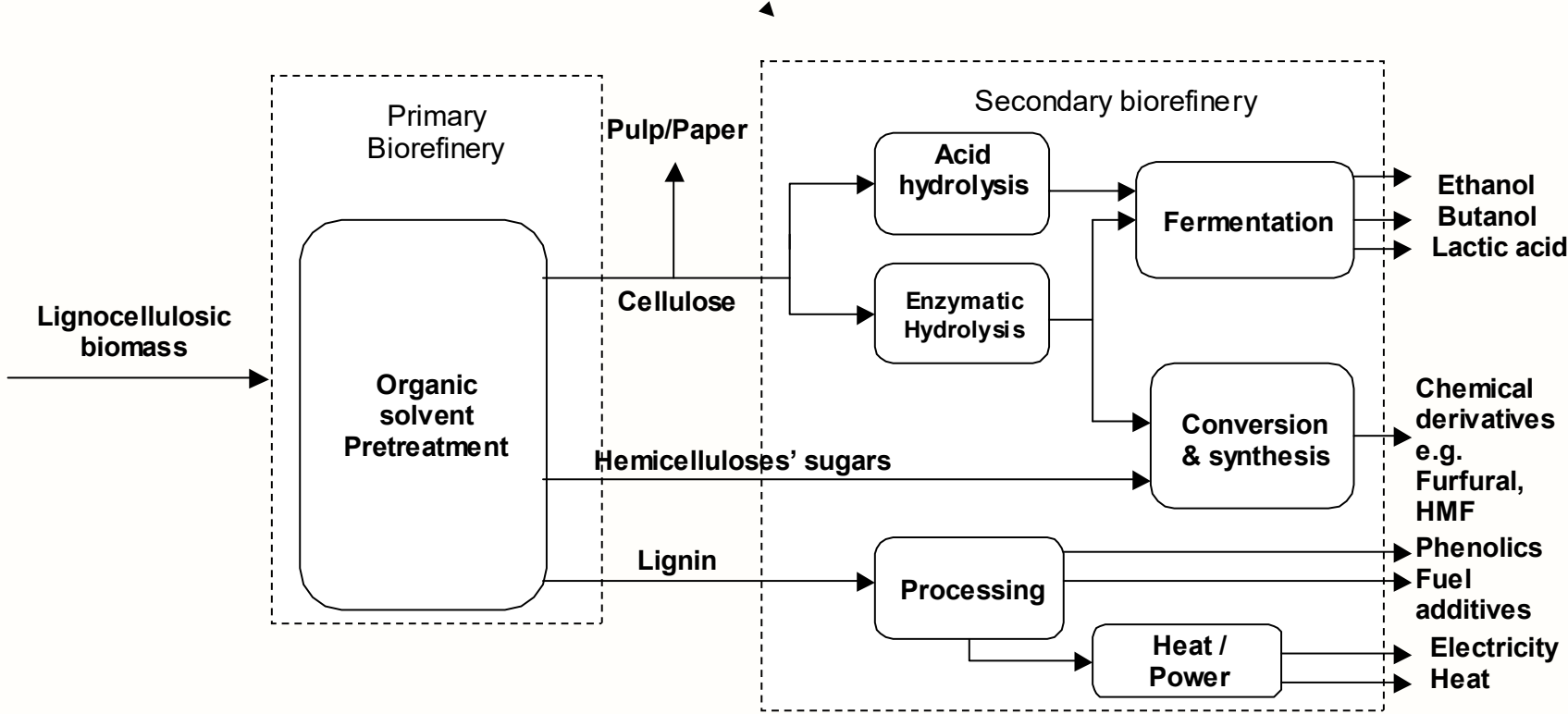
Introduction

- The conversion of biomass within biorefineries is seen as a potential alternative to current reliance on non-renewable resources.
- The transition from a traditional “oil-refinery” to a “bio-refinery”, based on renewable lignocellulosic biomass, is crucial if we are to move to a more environmentally friendly economy.
- Lignocellulosic biomass receives more attention because it does not compete as a food resource, and it can reduce carbon dioxide in the atmosphere by up to 75–100%.

- The key components of lignocellulosic biomass, i.e., cellulose, hemicelluloses and lignin, are closely associated with each other at the plant cell level.
- This close association, together with the partly crystalline nature of cellulose, reduces cellulose reactivity towards acid and enzymatic hydrolysis in native biomass.
- Thus, organosolv pretreatment is necessary to render the carbohydrate fraction to acid, enzymatic and microbial action.

- Biorefining is the sustainable processing of biomass into a spectrum of marketable products (food and feed, materials, and chemicals) and energy (fuels, power, and heat).
- In biorefinery appropriate fractionation of the complex lignocellulose material, into its constituents, is of most importance.

Lignocellulosic biorefinery scheme



- This study focused on the organosolv pretreatment process of wheat straw which facilitates hydrolysis and fermentation processes.
- Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), Methanol (CH_3OH), Diethylene glycol ($\text{C}_4\text{H}_{10}\text{O}_3$), Acetone ($\text{C}_3\text{H}_6\text{O}$) and Butanol ($\text{C}_4\text{H}_9\text{OH}$) were evaluated as solvents.
- Sulfuric acid was the pretreatments' catalyst.
- The effect of the five organic solvents on pretreatment results was analyzed.

Experimental

Raw material

- The wheat straw used was obtained from Kapareli Village of Thebes, Greece, as a suitable source for full-scale industrial applications.
- The moisture content of the material when received was 9% w/w; after screening, the fraction with particle sizes between 10 and 20 mm was isolated.

Composition of wheat straw

Component	% w/w
Cellulose	33.7
Hemicelluloses	24.1
• Xylose	18.9
• Arabinose	2.7
• Acetyl groups	2.5
Klason lignin (acid insoluble)	17.0
Ash	4.7
Extractives	6.2
Other components	14.4

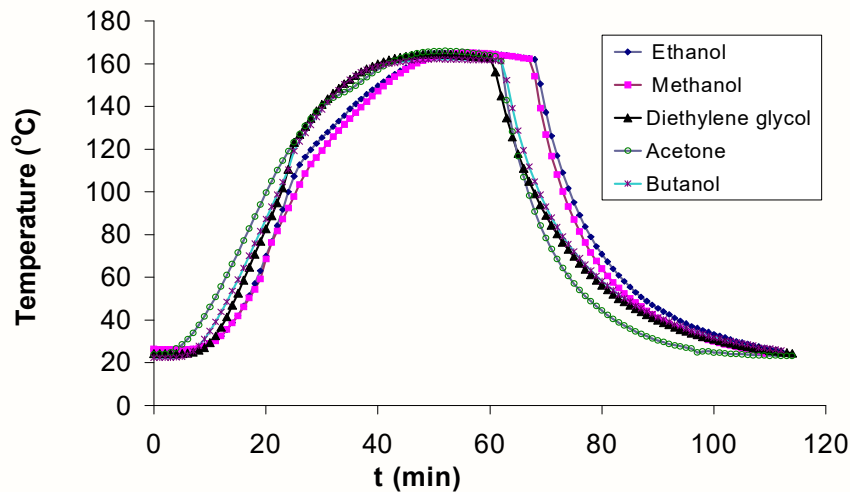


Experimental equipment and procedures

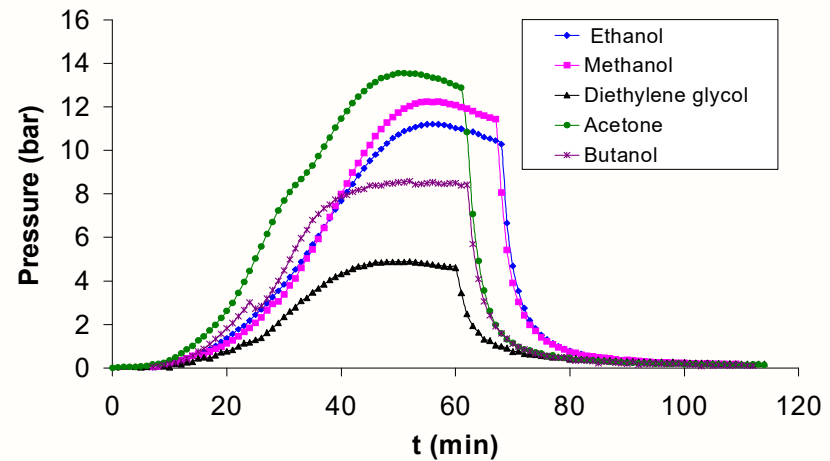
- A 3.75-L batch reactor PARR 4843 was used for the organosolv fractionation.
- Reaction ending temperature was 160 °C whereas the reaction time was 20 min (not including the preheating time).
- The reaction was catalyzed by H_2SO_4 , 0.045 N, in a 50% v/v aqueous/organic solvent solution; the liquid/solid ratio was 20/1.
- The organic solvents used were: ethanol, methanol, diethylene glycol, acetone and butanol.

Organosolv pretreatment's (a) temperature and (b) pressure profile vs. time

(Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1).



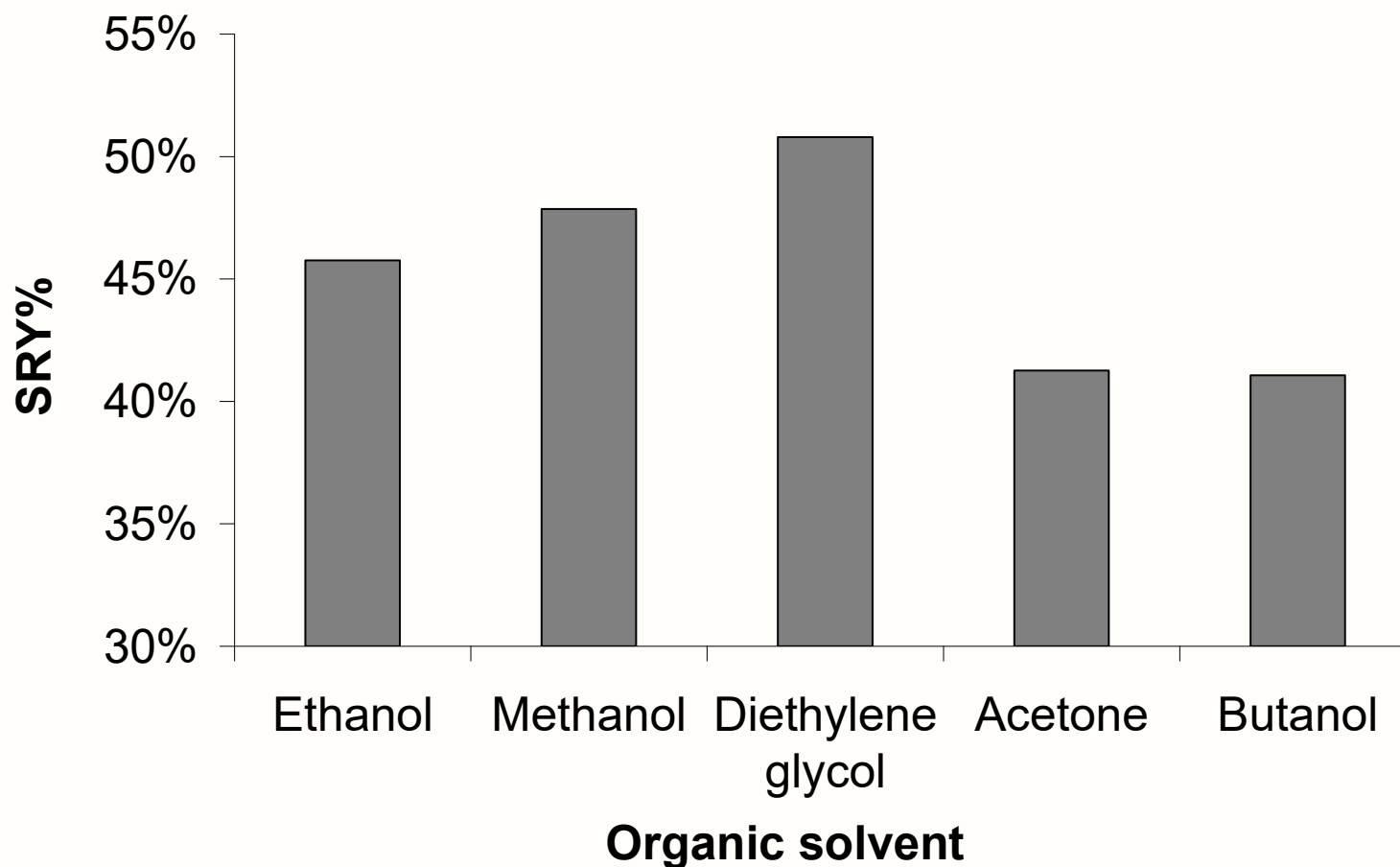
(a)



(b)

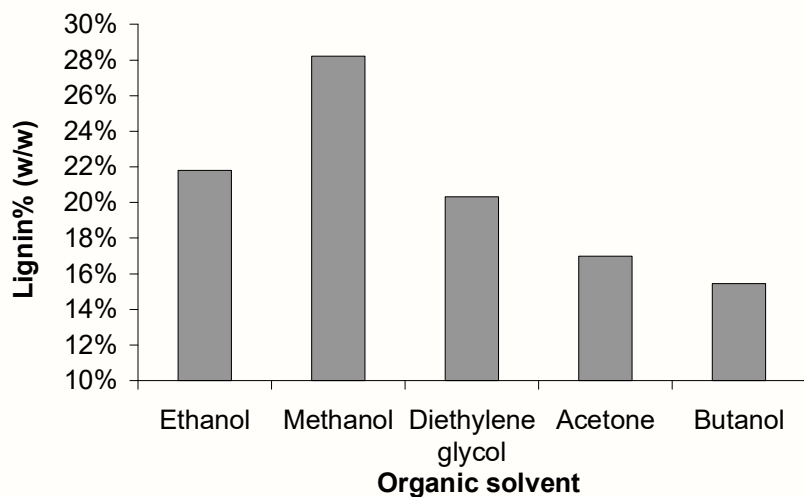
Effect of organic solvent on Solid Residue Yield.

Sulfuric acid 0.045N; temperature 160°C; time 20 min;
liquid: solid ratio = 20:1.

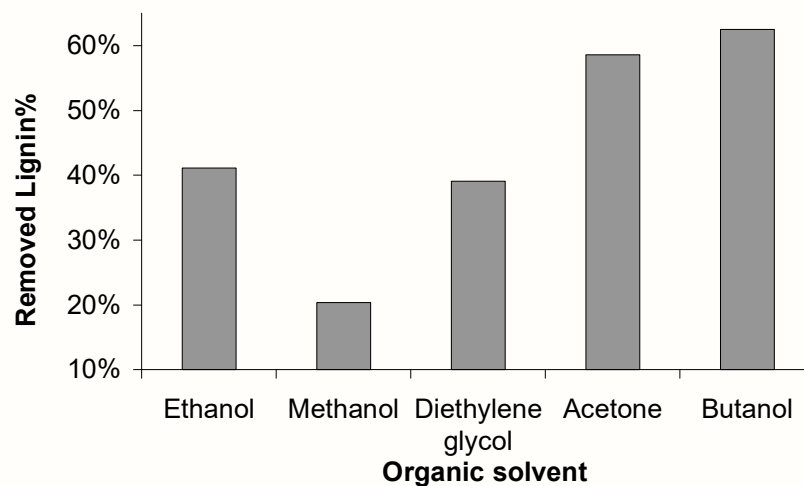


Effect of organic solvent on (a) lignin composition and (b) removed lignin percentage

(Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1)



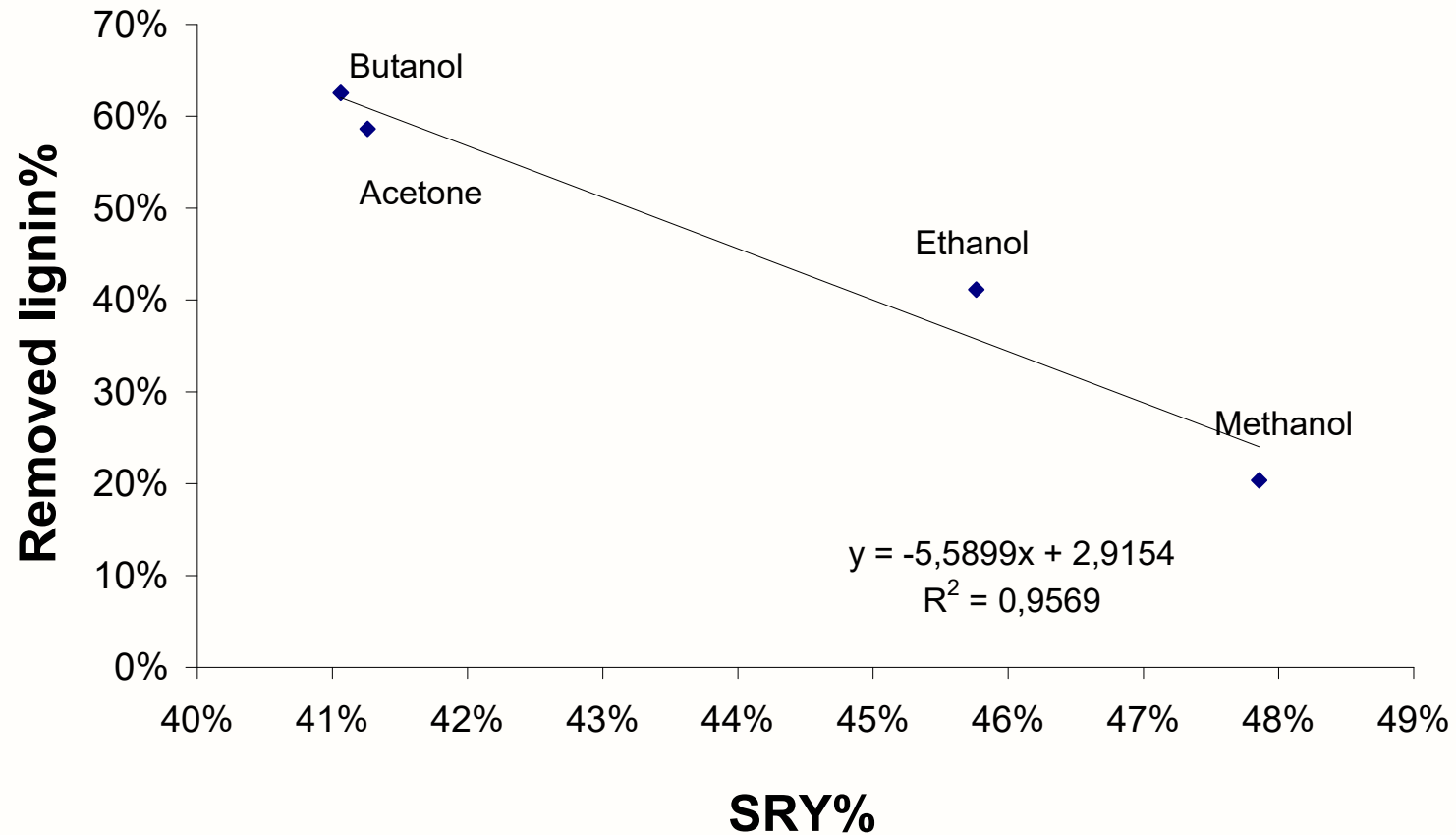
(a)



(b)

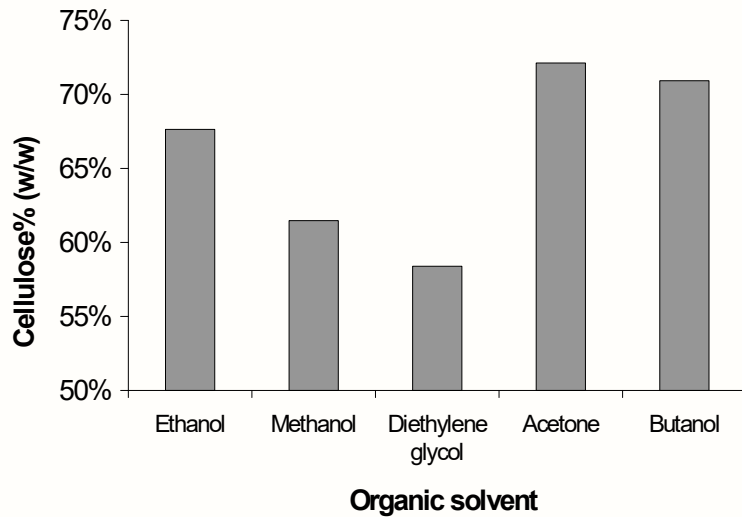
Removed lignin vs. Solid Residue Yield

(Sulfuric acid 0.045N; temperature 160°C; time 20 min;
liquid: solid ratio = 20:1)

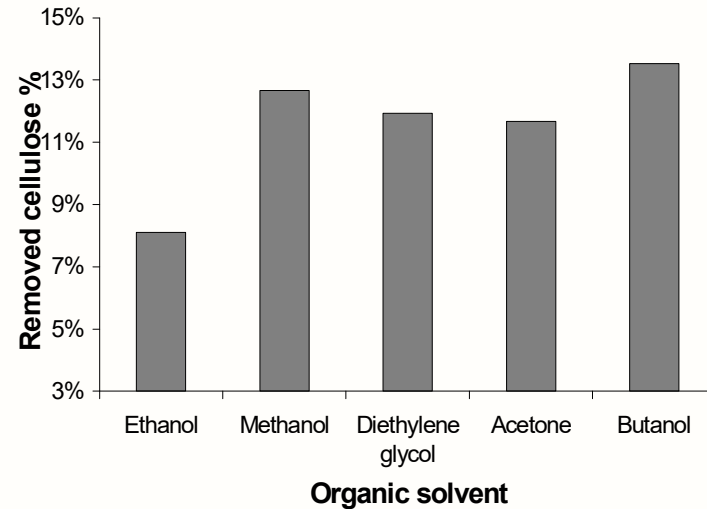


Effect of organic solvent on (a) cellulose composition and (b) removed cellulose percentage

(Sulfuric acid 0.045N; temperature 160°C; time 20 min;
liquid: solid ratio = 20:1)



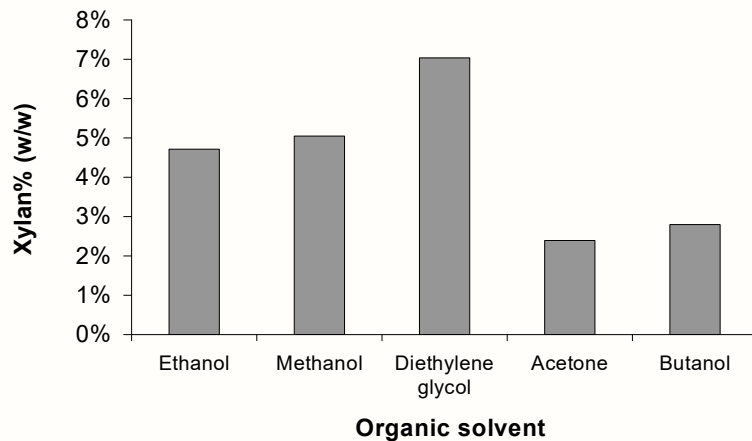
(a)



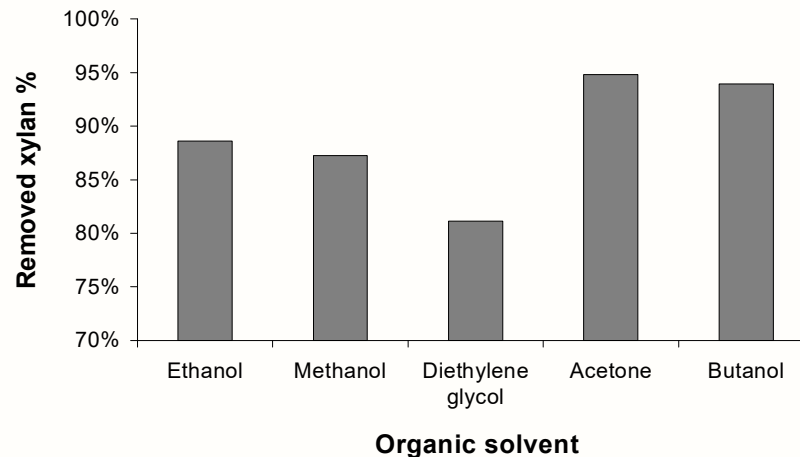
(b)

Effect of organic solvent on (a) xylan composition and (b) removed xylan percentage

(Sulfuric acid 0.045N; temperature 160°C; time 20 min;
liquid: solid ratio = 20:1)



(a)

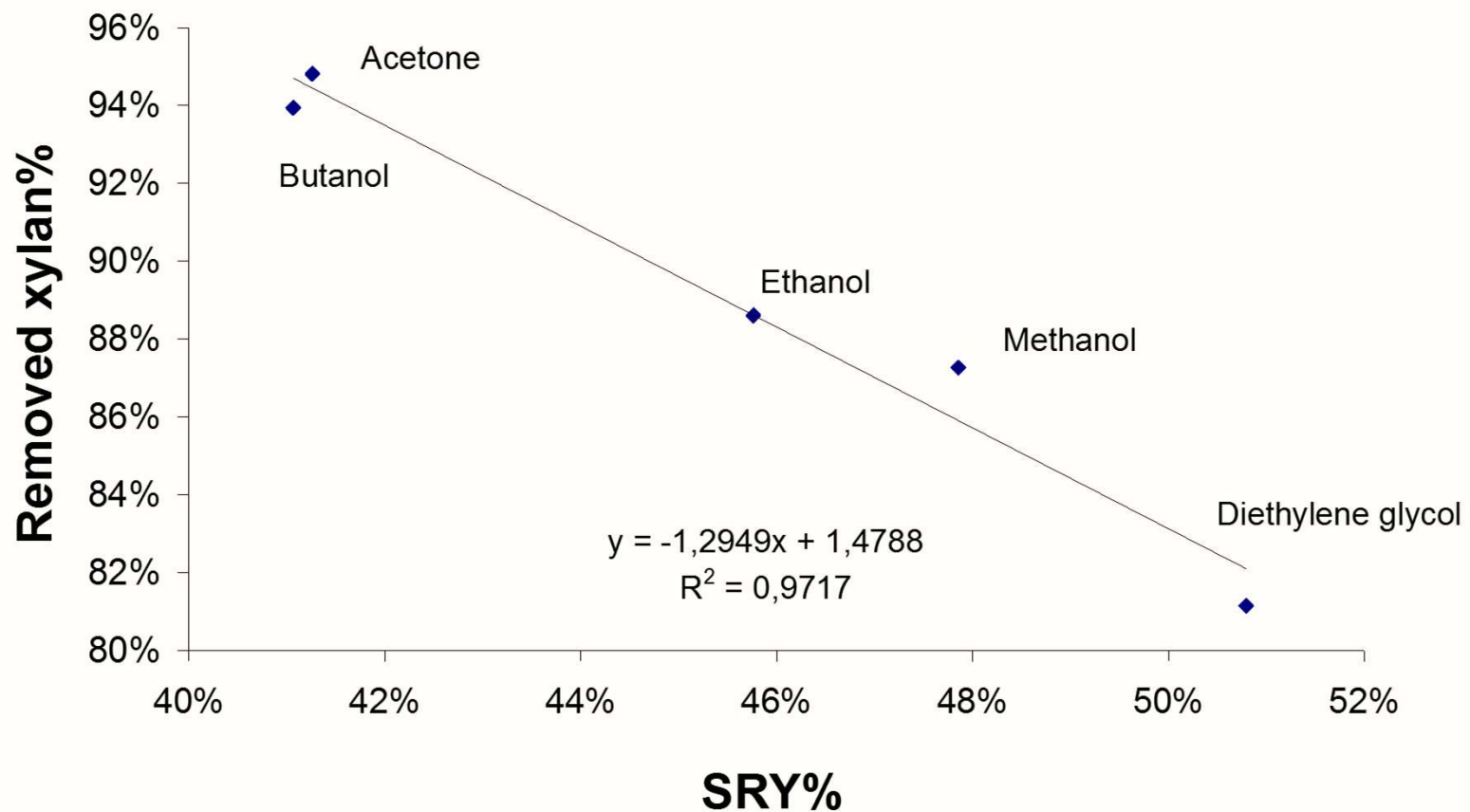


(b)

Removed xylan vs. Solid Residue Yield

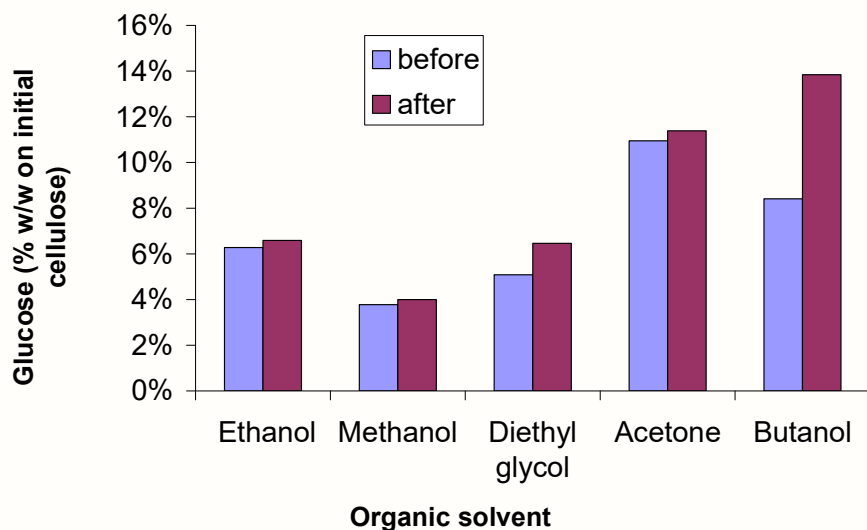
(Sulfuric acid 0.045N; temperature 160°C; time 20 min;

liquid: solid ratio = 20:1)

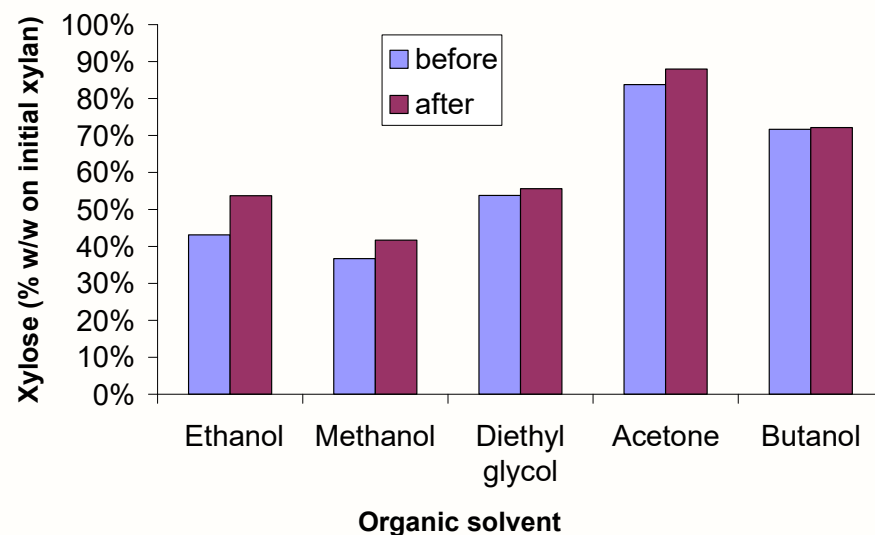


Effect of organic solvent on (a) glucose and (b) xylose concentration, before and after post-hydrolysis

(Sulfuric acid 0.045N; temperature 160°C; time 20 min;
liquid: solid ratio = 20:1)



(a)



(b)

Conclusions

- Within the Biorefinery concept, from the five solvents (ethanol, methanol, diethylene glycol, acetone, butanol) examined herein as regards organosolv pretreatment (sulfuric acid 0.045 N, 160 °C, 20 min) of wheat straw, butanol gave the highest delignification effect, i.e., 60% lignin removal.
- Maximum cellulose concentration was 72% w/w (on pretreatment's solid residue) using acetone while delignification was 59% and 95% of xylan of the initial straw was hydrolyzed to 88% w/w xylose (expressed on initial xylan).