2015

ORGANOSOLV PRETREATMENT AS A MAJOR STEP OF LIGNOCELLULOSIC BIOMASS REFINING

Dimitrios Sidiras
University Piraeus

Ioanna Salapa
University Piraeus

Biorefinery I: Chemicals and Materials From Thermo-Chemical Biomass Conversion and Related Processes. September 27-October 2, 2015
Chania (Crete), Greece

ORGANOSOLV PRETREATMENT AS A MAJOR STEP OF LIGNOCELLULOSIC BIOMASS REFINING

Dimitrios Sidiras and Ioanna Salapa

Lab. Simulation of Industrial Processes, Dep. Industrial Management and Technology, Sch. Maritime and Industry, Univ. Piraeus,

80 Karaoli & Dimitriou, GR 18534 Piraeus, Greece

Phone Number +302104142360, e-mail sidiras@unipi.gr

Introduction

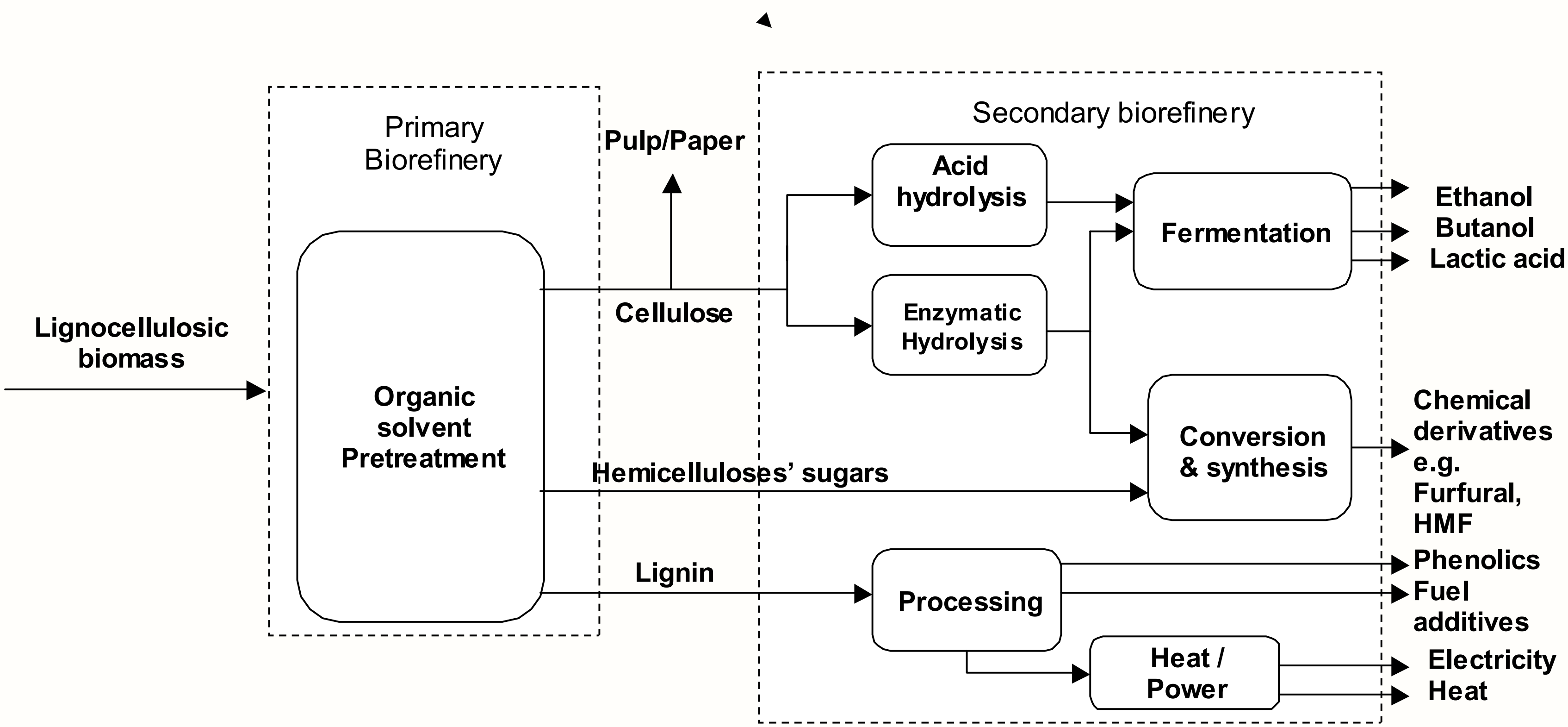
- The conversion of biomass within biorefineries is seen as a potential alternative to current reliance on non-renewable resources.
- The transition from a traditional ‘‘oil-refinery’’ to a ‘‘bio-refinery’’, based on renewable lignocellulosic biomass, is crucial if we are to move to a more environmentally 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 (CH_3CH_2OH), Methanol (CH_3OH), Diethylene glycol ($C_4H_{10}O_3$), Acetone (C_3H_6O) and Butanol (C_4H_9OH) 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

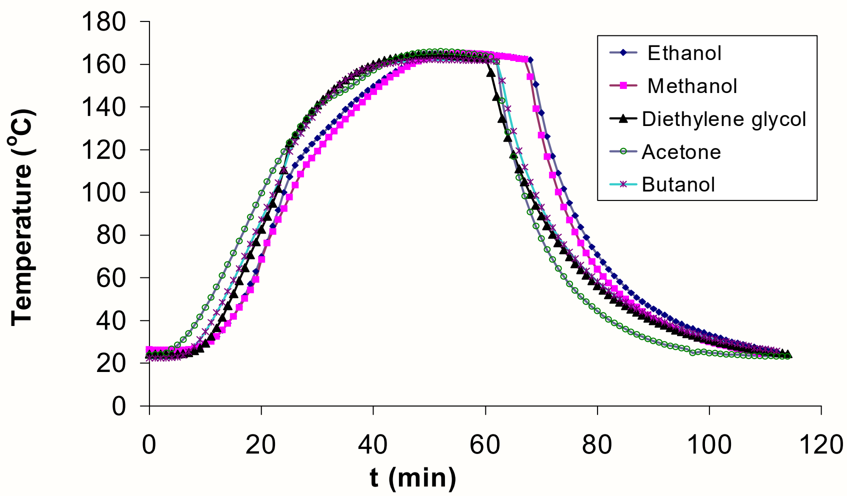
Component	% w/w
Cellulose	33.7
Hemicelluloses	24.1
• Xylose	18.9
• Arabinose	2.7
• Acetyl groups	2.5
Klason lignin (acid insoluble)	17.0
Ash	4.7
Extractives	6.2
Other components	14.4

Experimental equipment and procedures

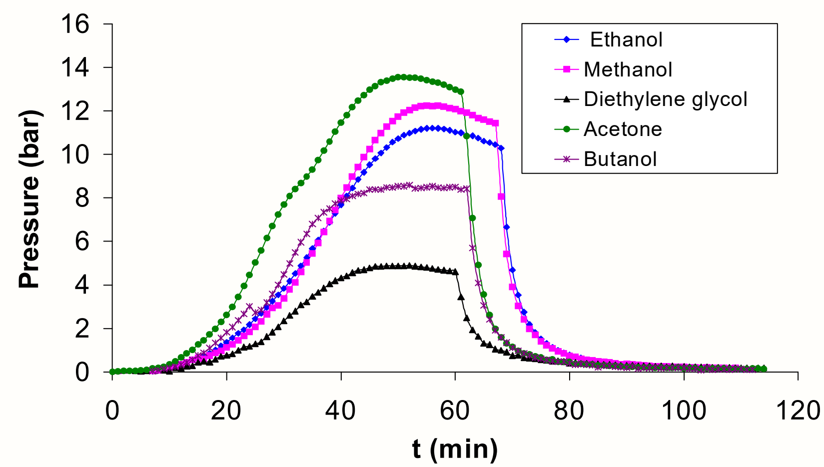
- A 3.75-L batch reactor PARR 4843 was used for the organosolv fractionation.
- Reaction ending temperature was 160 ºC whereas the reaction time was 20 min (not including the preheating time).
- The reaction was catalyzed by H_2SO_4, 0.045 N, in a 50% v/v aqueous/organic solvent solution; the liquid/solid 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).



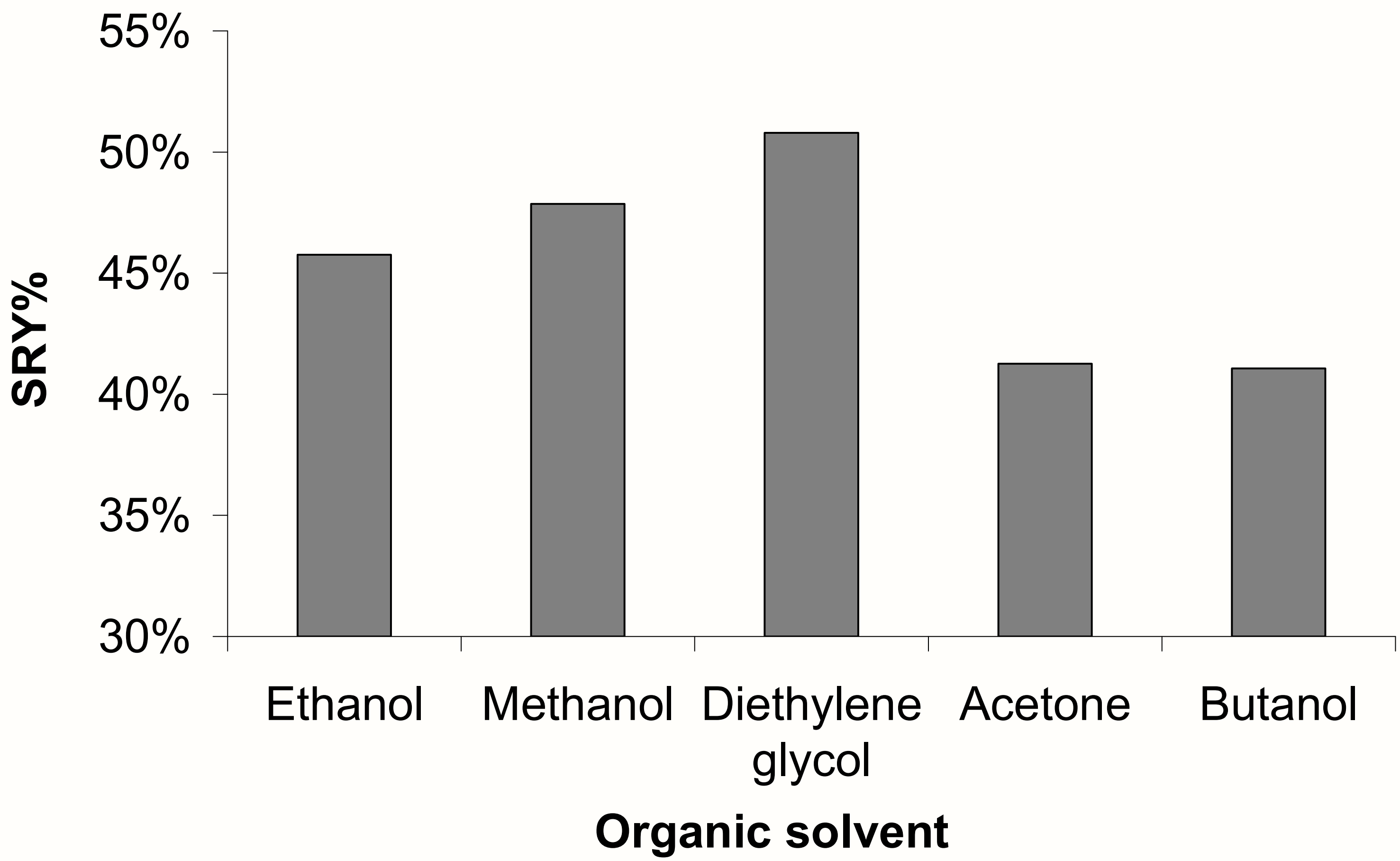
(a)



(b)

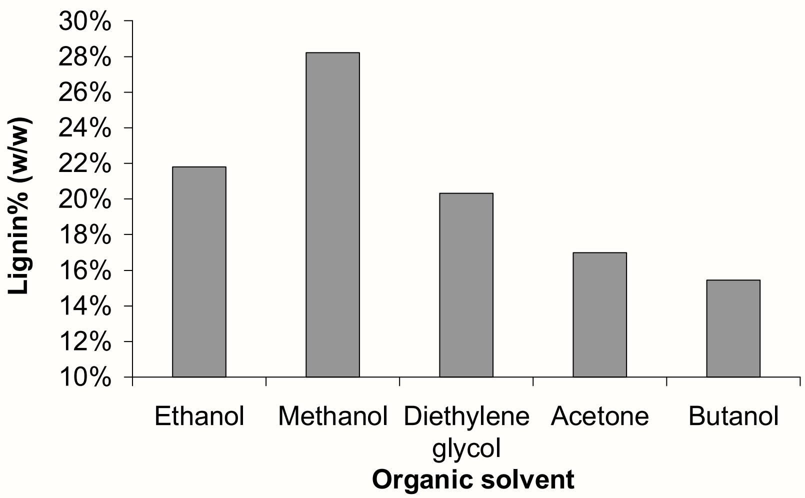
Effect of organic solvent on Solid Residue Yield.

Sulfuric acid 0.045N; temperature 160^{o}C; time 20 min; liquid: solid ratio = 20:1.

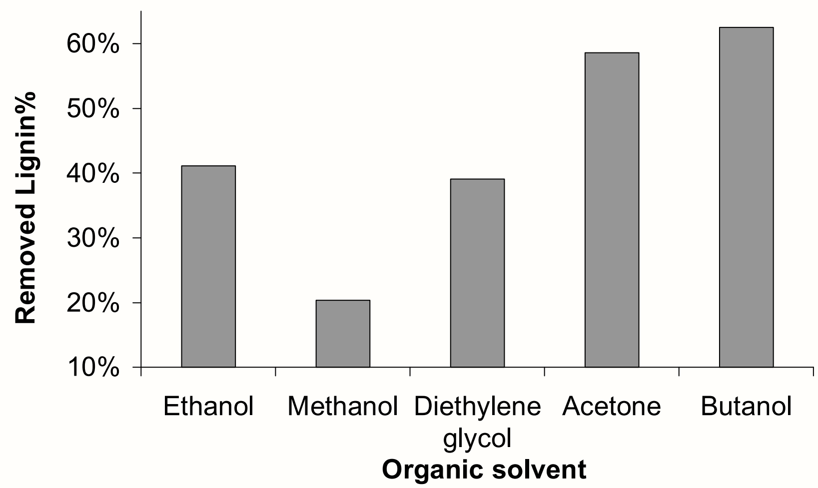


Effect of organic solvent on (a) lignin composition and (b) removed lignin percentage

(Sulfuric acid 0.045N; temperature 160^{o}C; time 20 min; liquid: solid ratio = 20:1)



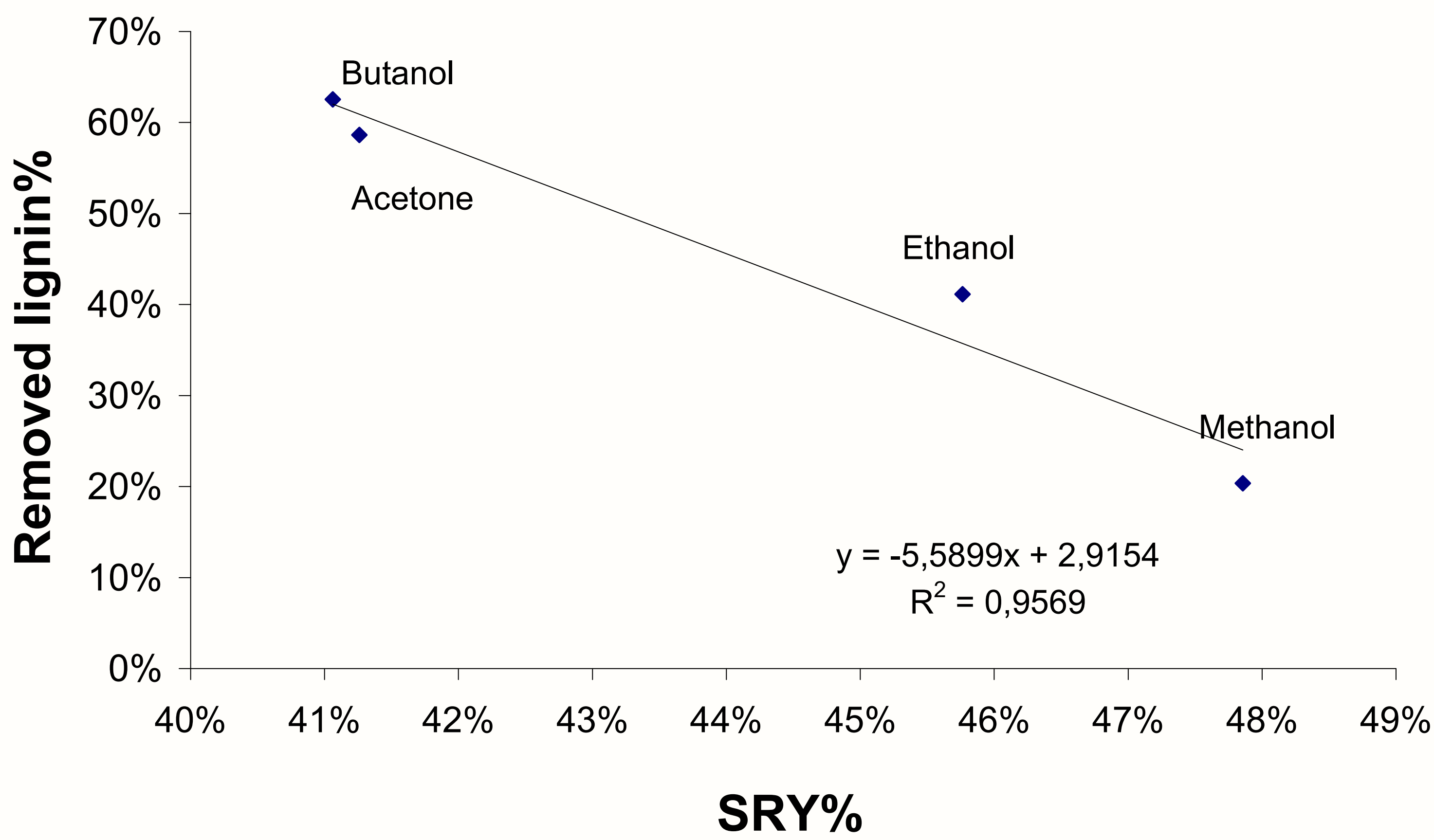
(a)



(b)

Removed lignin vs. Solid Residue Yield

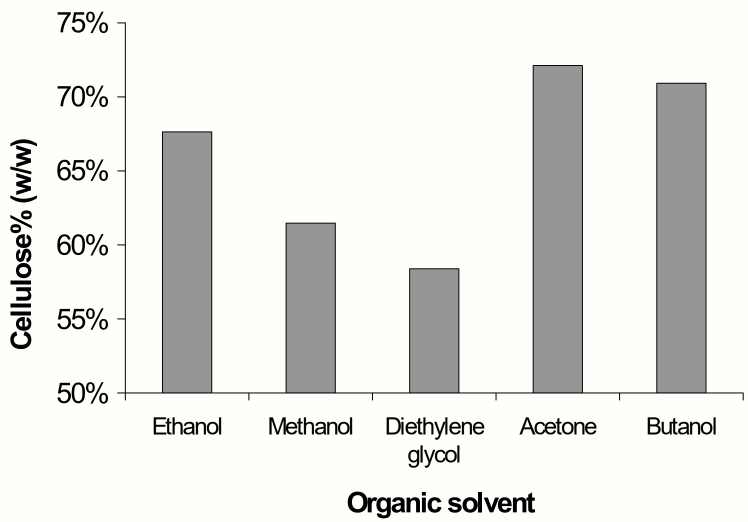
(Sulfuric acid 0.045N; temperature 160^{o}C; time 20 min; liquid: solid ratio = 20:1)



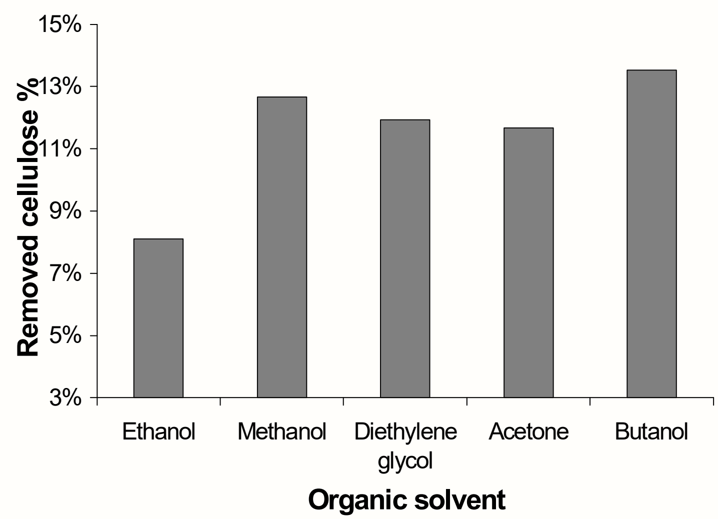
Effect of organic solvent on (a) cellulose composition and (b) removed cellulose percentage

(Sulfuric acid 0.045N; temperature 160^{o}C; time 20 min;

liquid: solid ratio = 20:1)



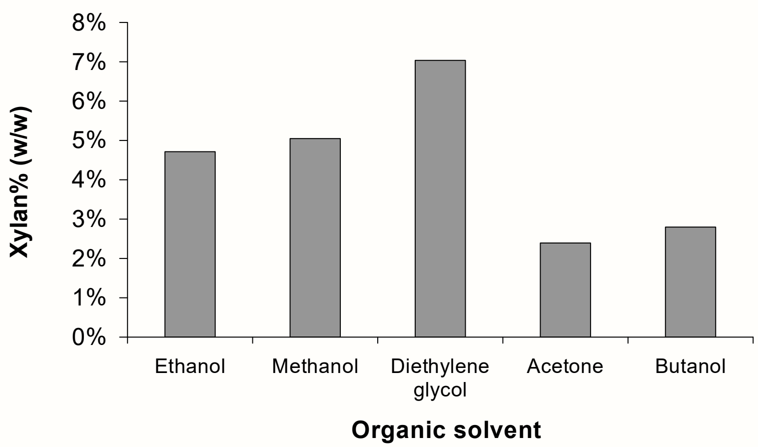
(a)



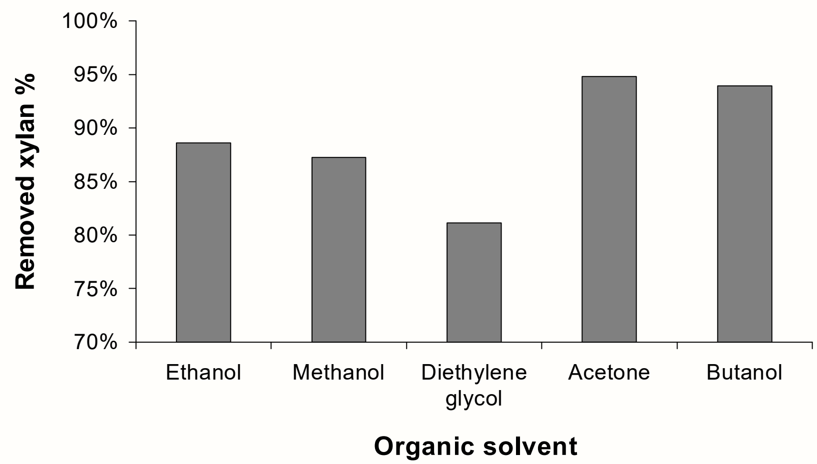
(b)

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)

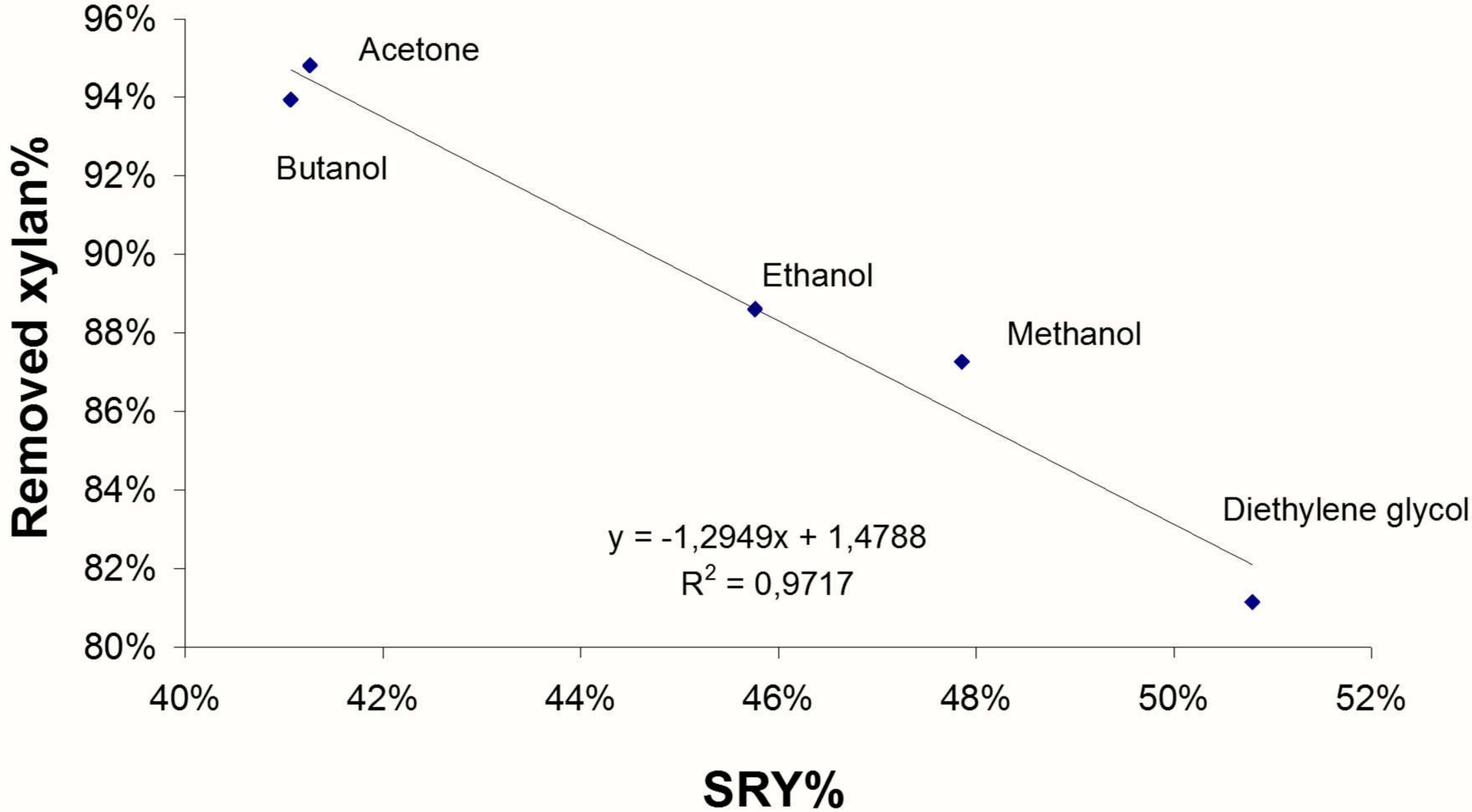


(b)

Removed xylan vs. Solid Residue Yield

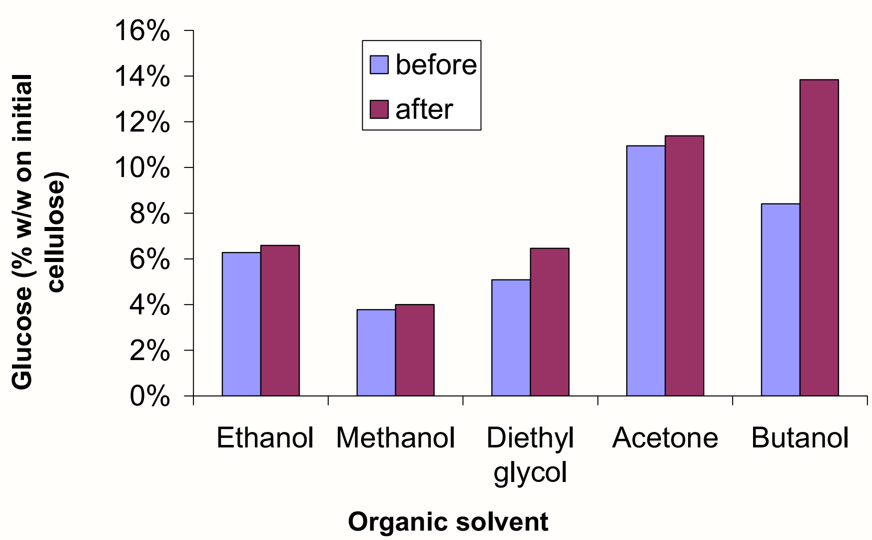
(Sulfuric acid 0.045N; temperature 160°C; time 20 min;

liquid: solid ratio = 20:1)

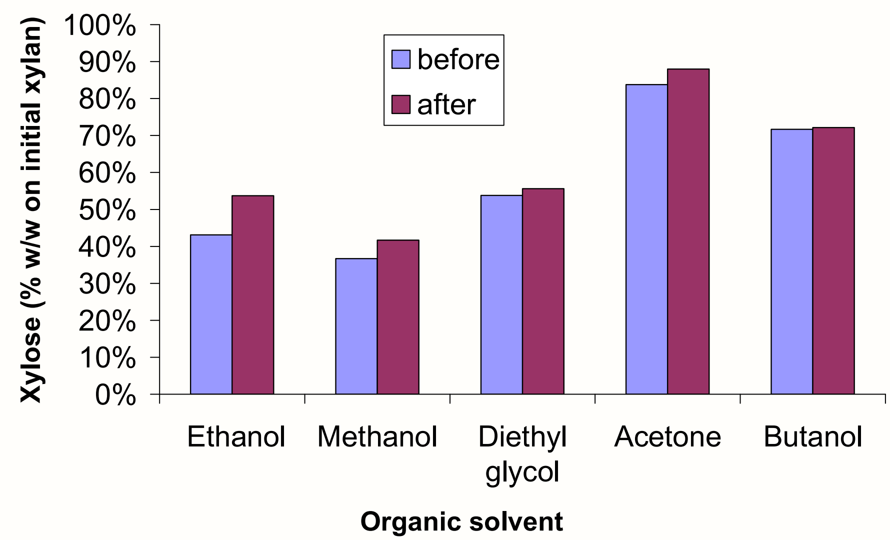


Effect of organic solvent on (a) glucose and (b) xylose concentration, before and after post-hydrolysis

(Sulfuric acid 0.045N; temperature 160^{o}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 ºC, 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).