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ORGANOSOLV PRETREATMENT AS A MAJOR STEP OF LIGNOCELLULOSIC BIOMASS REFINING

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ABSTRACT

Five solvents (ethanol, methanol, diethylene glycol, acetone, butanol) were evaluated for organosolv pretreatment of wheat straw. The biorefinery process was catalyzed by H₂SO₄ at 160 °C for 20 min. Maximum cellulose concentration was 72% w/w using acetone while delignification was 59% w/w and 95% w/w of xylan hydrolyzed to xylose.

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 (1). 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% (2).

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 (3). Thus, organosolv pretreatment is necessary to render the carbohydrate fraction to acid, enzymatic and microbial action (4).

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. Fig. 1 depicts a possible lignocellulosic biorefinery scheme (5-6).

From structure study to pulping and currently to energy usage organosolv fractionation has a long history. The earliest study applying organic solvents to treat lignocellulosic material was back in 1893, when Klason (7-8) used ethanol and hydrochloric acid to separate wood into its components to study the structure of lignin and carbohydrates. Nowadays organosolv pretreatment has been used for lignin and other potentially valuable co-products (e.g. acetone, butanol, biogas) production (9-14).

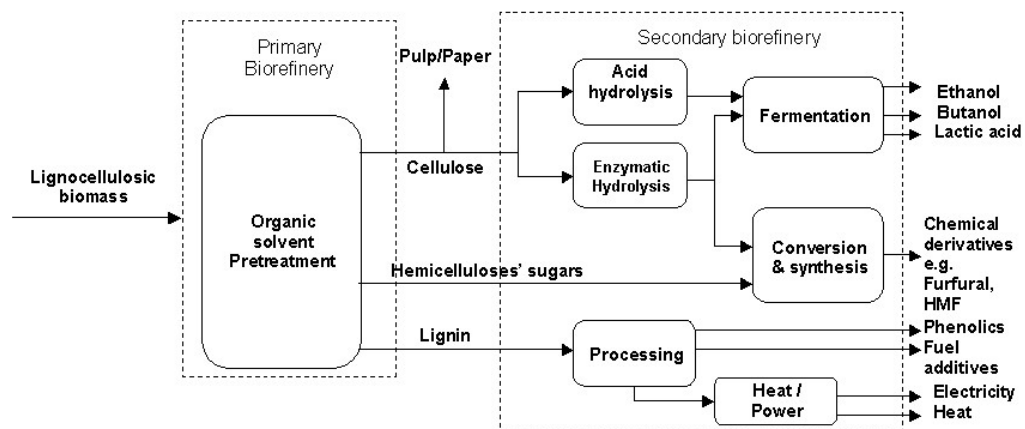


Fig.1: Organosolv-based lignocellulosic biorefinery

Treatment with organic solvents involves the use of an organic liquid and water, with or without addition of a catalyst agent (acid or base). This mixture partially hydrolyzes lignin bonds and lignin–carbohydrate bonds, resulting in a solid residue composed mainly by cellulose and some hemicellulose. Organosolv pretreatment efficiently removes lignin from lignocellulosic materials but most of the hemicellulose sugars are also solubilized by this process.

As catalysts, organic or inorganic acids, bases, and so on have been tested for lignocellulosic biomasses (15). Sulfuric acid, a strong mineral acid, is one of the most-used reagents for the pretreatment process due to its strong reactivity and high efficiency (16). Although ethanol seems to be the most popular organic solvent over the years (17-20) other solvents like methanol (21), acetone (22) formic acid (23-26), acetic acid have been also studied (27-30).

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.

MATERIALS AND METHODS

2.1 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. The composition of the raw material was as follows (expressed in % w/w on a dry weight basis): 33.7% cellulose, hemicelluloses

24.1% (xylan 18.9 %, arabinose 2.7% and acetic groups 2.5%), 17% Klason lignin (acid insoluble) and 14.4% others.

2.2 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 H₂SO₄, 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.

2.3. Analytical techniques

The Saeman et al. (1945) technique was used for the quantitative saccharification of the original lignocellulosic material as well as the autohydrolysis solid residues. The filtrates from the quantitative saccharification, as well as those from the autoclave (before and after the secondary hydrolysis, i.e. post-hydrolysis with 0.9 N H₂SO₄ at 100 °C for 4.5 h), were analyzed for their content of glucose and xylose enzymatically (Megazyme D-Glucose HK Assay kit K-GLUHK-220A and D-xylose Assay kit K-xylose). Glucose and xylose were produced via quantitative saccharification of the solid residue in each one of the experiments. Cellulose was estimated as glucan, and hemicelluloses were estimated as xylan. Finally, the acid-insoluble lignin (Klason lignin) was determined according to the Tappi T222 om-88 method.

RESULTS AND DISCUSSION

Due to the different molecular structure of the examined organic solvents the temperature and pressure profiles are presented in Fig. 2. As shown in Fig.2b the maximum pretreatments' pressures varie among the different organic solvents between 4.9 (Diethylene glycol) and 13.6 bar (Acetone). More specifically, were: 12.2 bar for Methanol, 11.2 bar for Ethanol and 8.6 bar for Butanol acid catalysed organosolv pretreatment.

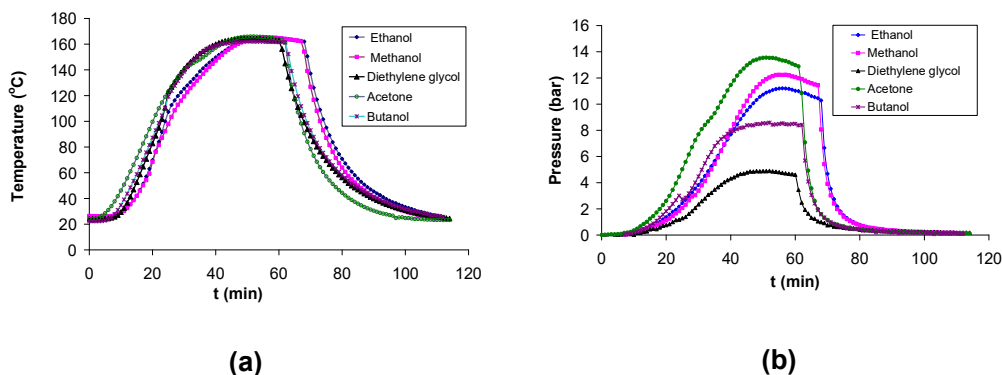


Fig.2: Organosolv pretreatment's (a) temperature and (b) pressure profile vs. time. Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1.

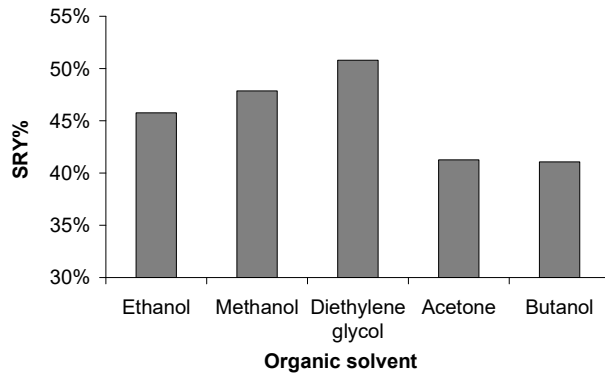


Fig.3: Effect of organic solvent on Solid Residue Yield. Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1.

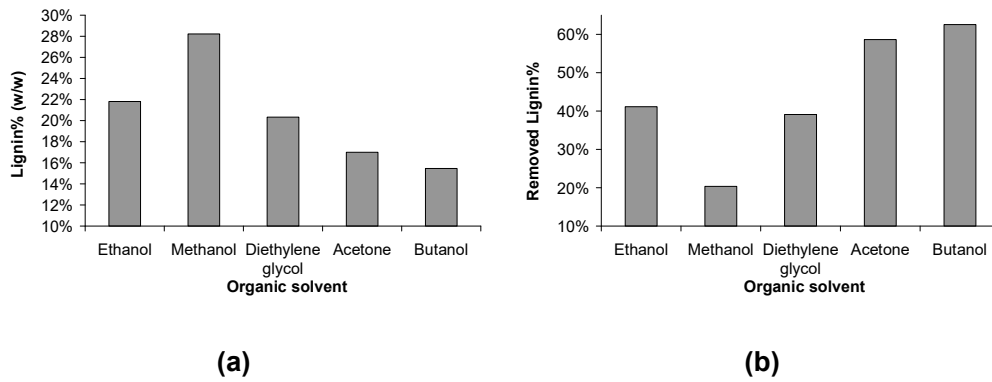


Fig.4: Effect of organic solvent on (a) lignin composition and (b) removed lignin percentage. Sulfuric acid 0.045N; 160°C; 20 min; liquid: solid ratio = 20:1.

The highest percentage (50.8%) of Solid residue yield (SRY) was achieved, as shown in Fig.3, using diethylene glycol as organic solvent. Regarding lignin removal (Fig.4) methanol use appears to have the poorest results just 20.4% while butanol has the best 62.6%. When examined the correlation between removed lignin % and SRY % (Fig.5) a simple linear regression fits the data. It must be noted that diethylene glycol was not included in the graph due to its disproportionately high delignification compared to SRY %. Diethylene glycol acid pretreatment combines high delignification percentage with low cellulose removal (Fig.6). All five solvents show low cellulose removal (See Fig. 6b).

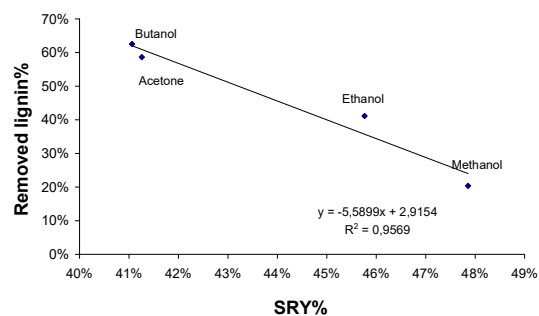


Fig.5: Removed lignin vs. Solid Residue Yield. Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1.

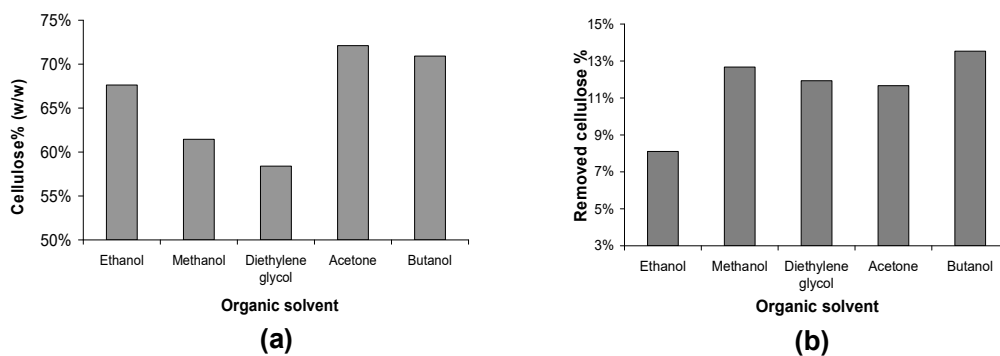


Fig.6: Effect of organic solvent on (a) cellulose composition and (b) removed cellulose percentage. Sulfuric acid 0.045N; 160°C; 20 min; liquid: solid ratio = 20:1.

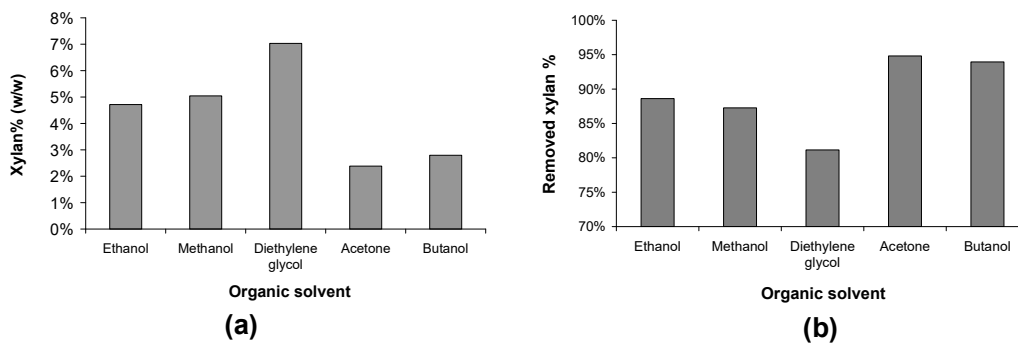


Fig.7: Effect of organic solvent on (a) xylan composition and (b) removed xylan percentage. H₂SO₄ 0.045N; 160°C; 20 min; liquid: solid ratio = 20:1.

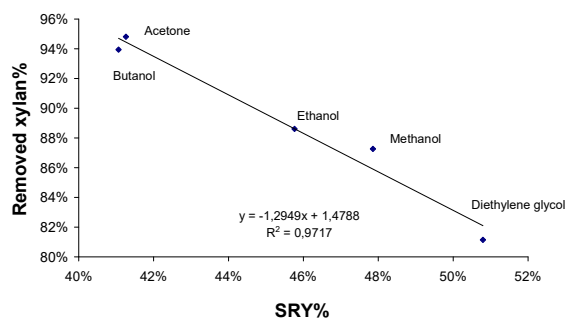


Fig.8: Removed xylan vs. Solid Residue Yield. Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1.

In Fig. 7 acetone and butanol stand out among the other organic solvents due to their high xylan removal percentages 94.81% and 93.94% respectively. The correlation between removed xylan % and SRY% was also examined (Fig.8). In this case the linear regression gave also good results ($R^2=0.97$) without exception. Unlike low glucose concentration before and after post hydrolysis, xylose concentration appears to be promising. As shown in Fig. 9 xylan of the initial straw in the case of acetone was hydrolyzed to 88% w/w xylose (expressed as % w/w on initial xylan).

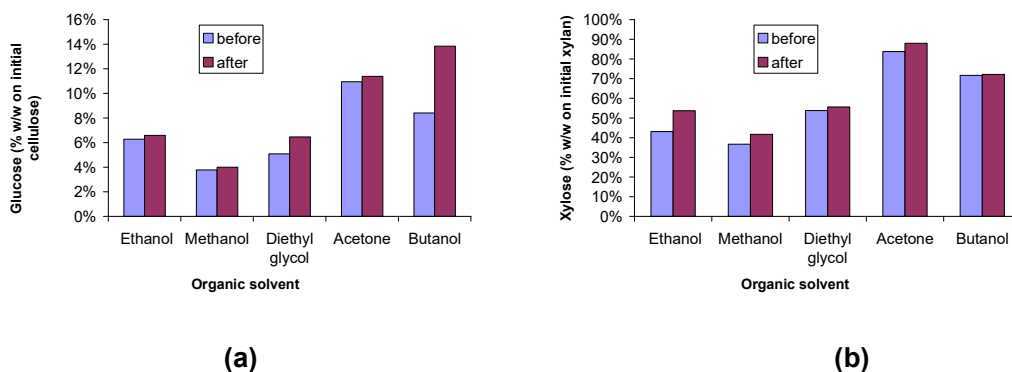


Fig.9: Effect of organic solvent on (a) glucose and (b) xylose concentration, before and after post-hydrolysis. Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1.

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., 63% 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.

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