

Biochemical conversion of biomass to biofuels

Pretreatment–Detoxification–Hydrolysis–
Fermentation

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Akademisk avhandling

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ABSTRACT

The use of lignocellulosic materials to replace fossil resources for the industrial production of fuels, chemicals, and materials is increasing. The carbohydrate composition of lignocellulose (i.e. cellulose and hemicellulose) is an abundant source of sugars. However, due to the feedstock recalcitrance, rigid and compact structure of plant cell walls, access to polysaccharides is hindered and release of fermentable sugars has become a bottle-neck. Thus, to overcome the recalcitrant barriers, thermochemical pretreatment with an acid catalyst is usually employed for the physical or chemical disruption of plant cell wall. After pretreatment, enzymatic hydrolysis is the preferred option to produce sugars that can be further converted into liquid fuels (e.g. ethanol) via fermentation by microbial biocatalysts.

However, during acid pretreatment, several inhibitory compounds namely furfural, 5-hydroxymethyl furfural, phenols, and aliphatic acids are released from the lignocellulose components. The presence of these compounds can greatly effect both enzymatic hydrolysis and microbial fermentation. For instance, when Avicel cellulose and acid treated spruce wood hydrolysate were mixed, 63% decrease in the enzymatic hydrolysis efficiency was observed compared to when Avicel was hydrolyzed in aqueous citrate buffer. In addition, the acid hydrolysates were essentially non-fermentable. Therefore, the associated problems of lignocellulose conversion can be addressed either by using feedstocks that are less recalcitrant or by developing efficient pretreatment techniques that do not cause formation of inhibitory by-products and simultaneously give high sugar yields.

A variety of lignocellulose materials including woody substrates (spruce, pine, and birch), agricultural residues (sugarcane bagasse and reed canary grass), bark (pine bark), and transgenic aspens were evaluated for their saccharification potential. Apparently, woody substrates were more recalcitrant than the rest of the species and bark was essentially amorphous. However, the saccharification efficiency of these substrates varied based on the pretreatment method used. For instance, untreated reed canary grass was

more recalcitrant than woody materials whereas the acid treated reed canary grass gave a higher sugar yield (64%) than the woody substrates (max 34%). Genetic modification of plants was beneficial, since under similar pretreatment and enzymatic hydrolysis conditions, up to 28% higher sugar production was achieved from the transgenic plants compare to the wild type.

As an alternative to the commonly used acid catalysed pretreatments (prior to enzymatic hydrolysis) lignocellulose materials were treated with four ionic liquid solvents (ILs): two switchable ILs (SILs) -SO₂DBUMEASIL and -CO₂DBUMEASIL, and two other ILs [Amim][HCO₂] and [AMMorp][OAc]. After enzymatic hydrolysis of IL treated substrates, a maximum amount of glucan to glucose conversion of between 75% and 97% and a maximum total sugar yields of between 71% and 94% were obtained. When using acid pretreatment these values varied between 13-77% for glucan to glucose conversion and 26-83% for total sugar yield. For woody substrates, the hemicellulose recovery (max 92%) was higher for the IL treated substrates than compared to acid treated samples. However, in case of reed canary grass and pine bark the hemicellulose recovery (90% and 88%, respectively) was significantly higher for the acid treated substrates than the IL treated samples.

To overcome the inhibitory problems associated with the lignocellulose hydrolysates, three chemical conditioning methods were used 1. detoxification with ferrous sulfate (FeSO₄) and hydrogen peroxide (H₂O₂) 2. application of reducing agents (sulfite, dithionite, or dithiothreitol) and 3. treatment with alkali: Ca(OH)₂, NaOH, and NH₄OH. The concentrations of inhibitory compounds were significantly lower after treatments with FeSO₄ and H₂O₂ or alkali. Using reducing agents did not cause any decrease in the concentration of inhibitors, but detoxification of spruce acid hydrolysates resulted in up to 54% improvement of the hydrolysis efficiency (in terms of sugar release) compared to untreated samples. On the other hand, application of detoxification procedures to the aqueous buffer resulted in up to 39% decrease in hydrolysis efficiency, thus confirming that the positive effect of detoxification was due to the chemical alteration of inhibitory compounds. In addition, the fermentability of detoxified hydrolysates were investigated using the yeast *Saccharomyces cerevisiae*. The detoxified hydrolysates were readily fermented to ethanol yielding a maximum ethanol concentration of 8.3 g/l while the undetoxified hydrolysates were basically non-fermentable.

Keywords: Lignocellulosic materials, Ionic liquids, Pretreatment, Inhibitors, Detoxification, Ferrous sulfate and hydrogen peroxide, reducing agents, alkaline treatments, Hydrolysis, Fermentation, Biofuels.

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