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MODIFIED ORGANOSOLV AS A FRACTIONATION PROCESS OF LIGNOCELLULOSIC BIOMASS FOR CO-PRODUCTION OF FUELS AND CHEMICALS

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ABSTRACT: Modified organosolv is a process by which lignocellulosic biomass can be fractionated into its three main constituents, i.e. hemicellulose, cellulose and lignin. In the process, lignocellulosic biomass is brought into contact with an organic solvent-water mixture at elevated temperature and pressure. Thus, lignin is extracted from the biomass and hemicellulose is hydrolysed, while the solid residue (mainly cellulose) is made more accessible for enzymatic hydrolysis in the subsequent process step. The goal is to achieve full fractionation of all biomass fractions, including lignin, in a sufficient quality for production of (bio)chemicals. In this work, the effect of process conditions applied, type of organic solvent and the use of catalysts is explored.

Keywords: biomass pre-treatment, biorefining, lignin.

1 INTRODUCTION

In the biorefinery approach, the aim is to make optimal use of the existing chemical functionalities in biomass by fractionation of the main constituents for further conversion to multiple products [1]. In this work, we present a process for pre-treatment of lignocellulosic biomass for co-production of fermentable sugars (e.g. for bioethanol production) and high quality lignin. Fermentable sugars can be produced from lignocellulose by physical/chemical pre-treatment and subsequent enzymatic hydrolysis of cellulose. The function of the pre-treatment step is to break open the fibrous structure and increase the accessibility of the cellulose polymers for enzymatic hydrolysis [2]. Other aims of the pre-treatment process may include hydrolysis of the hemicellulose fraction and separation of the lignin fraction. Most pre-treatment technologies are optimized for sugar production and produce a residue containing lignin, unhydrolyzed sugar polymers, feedstock minerals and added process chemicals. This type of residue is most suited for thermal conversion for heat and power generation. In addition, the currently developed methods have other disadvantages, such as: waste production due to neutralisation of acids used and the formation of fermentation "inhibitors" such as organic acids, and breakdown products from sugars and the lignin fraction. The goal of this modified organosolv process is to achieve full fractionation of all biomass fractions, including lignin, in a sufficient quality for production of (bio)chemicals.

In the organosolv fractionation process [3,4], biomass is mixed with a mixture of an organic solvent (e.g., ethanol) and water. The resulting slurry is thermochemically treated at typically 160-200 °C. The aims of the process are: (1) hemicellulose hydrolysis to C5 and C6 sugars, (2) improvement of the degradability of the cellulose fraction for subsequent enzymatic hydrolysis, and (3) delignification of the biomass. At the end of the process, a solid and a liquid fraction remain. The solid fraction is enriched in cellulose and the liquid fraction contains sugars from the hemicellulose fraction as well as lignin (including their degradation products). Subsequently, lignin can be separated from the liquid by precipitation upon addition of water.

Previously, we presented the first results of our work on a modified organosolv process using willow wood, ethanol-water mixtures in combination with the use of CO_2 as a catalyst [5]. Experiments presented showed substantial hydrolysis of hemicellulose and low formation of potentially inhibiting degradation products (except acetic acid, which is a structural component of the hemicellulose fraction). Enzymatic hydrolysis tests showed a 4 to 5 fold higher glucose yield from pre-treated willow as compared to untreated wood, which indicates a strongly improved accessibility of the cellulose fraction for the enzymes. In spite of promising preliminary results, the use of CO_2 was found not to improve the process. The effect of the addition of CO_2 on the pH was probably too limited at the process conditions tested (up to 50 bar). Further optimization of the process both with regard to hemicellulose hydrolysis as well as delignification of the biomass was absolutely required to improve the economics of the process.

Therefore, the follow-up research on organosolv has focussed on the influence of process parameters on the process (such as solvent-water ratio) as well as other solvents than ethanol and the use of solid catalysts. In addition, organosolv tests have been performed on other feedstock including poplar and wheat straw.

2 METHODOLOGY

Lab scale experiments were performed in an autoclave reactor (Büchi, 0.5 litre). Most organosolv experiments were performed with willow wood (in addition to wheat straw and poplar). The willow wood was milled to <0.5mm. Subsequently, a suspension of biomass-water-organic solvent was made (typically, 10ml solvent per 1g biomass and an ethanol-water mixture of 60 wt% EtOH and 40 wt% H_2O). In some experiments, a catalyst was added. This suspension was heated to a specific reaction temperature (in the range 160-200°C) while being stirred. The suspension was kept at its set-point during a certain reaction time (typically, 60 min) and subsequently cooled down. After filtration of the resulting slurry, the solid residue was washed with an identical organic solvent-water mixture and dried at

50 °C maximum. From the filtrate and the washing solution, samples were taken for GC analysis (inhibitors) and HPLC analysis (sugars). The HPLC analyses were performed both directly at the filtrate solution (monomeric sugars) as well as after addition of H_2SO_4 for conversion of oligomeric sugars into monomeric sugars. The difference between the two HPLC analyses was used to determine the amount of oligomeric sugars present. Both the fresh biomass and the solid residues remaining after organosolv were analysed for their biochemical composition (i.e., extractives, lignin, and (hemi)cellulose content).

3 RESULTS

3.1 Physical appearance pre-treated material

Figure 1 shows photographs of wheat straw and poplar before and after organosolv. Both materials tend to get a darker colour after organosolv (probably due to recondensation of a part of the lignin that has been released from the lignin-carbohydrate-complex on the biomass). In addition, the structure of particularly the wheat straw after organosolv has dramatically changed compared with the fresh material (from fibres to a 'cardboard' like appearance).

Figure 1: Photographs of fresh (left) and pre-treated (right) biomass. Poplar (top) and wheat straw (bottom).

3.2 (Hemi)cellulose hydrolysis

Organosolv was found to be effective in increasing the enzymatic degradability of biomass (see Figure 2). Furthermore, it was found that hemicellulose hydrolyses substantially during the pre-treatment itself, whereas cellulose is hardly affected during the organosolv process. The hydrolysis of the hemicellulose fraction results in negligible amounts of monomeric sugar, but ends at the stage of soluble oligomeric sugars (based upon HPLC analyses). The organosolv process increases the susceptibility of willow wood to enzymes substantially, both for C5 and C6 sugars. The hydrolysis of the sugar polymers was found to be strongly dependent on temperature. The maximum hydrolysis degrees were 76 and 56% at the process conditions applied for glucose and xylose, respectively.

The hemicellulose hydrolysis can be improved by lowering the ethanol:water ratio (Figure 3). At 28wt% ethanol, the xylan hydrolysis has increased to 80% (of which about 70% during pre-treatment). At very high ethanol:water ratio the hemicellulose hydrolysis is very small as well as the enzymatic degradability of the pre-treated willow.

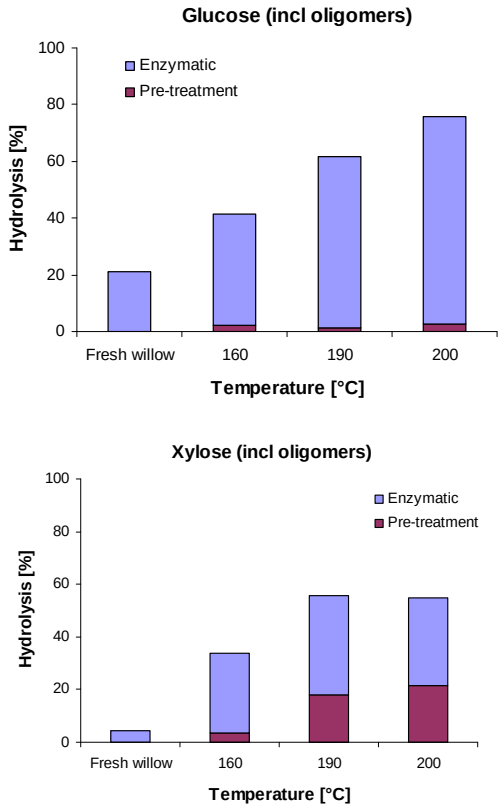

Figure 2: Hydrolysis of (hemi)cellulose during organosolv pre-treatment and further treatment with enzymes (Genencor GC220, 250 mg/g enzyme, 69h). The (cumulative) hydrolysis is shown as a percentage of the theoretical maximum. A selection of experiments performed on willow wood is shown (60 min, ethanol-water ratio: 60:40 wt%).

3.3 Formation of inhibitors

At lower temperature (≤180°C), the organosolv process was found to result in a limited formation of inhibitors. However, at higher temperature, the formation of inhibitors increased considerably. Therefore, the process temperature should preferably be limited (results not shown).

3.4 Delignification

The effect of the process conditions on the delignification of willow wood are given in Figures 4 and 5. Figure 4 shows the influence of reaction temperature on the delignification process. The effect of the ethanol - water ratio is given in Figure 5. Similarly to the (hemi)cellulose hydrolysis, the reaction temperature was found to be a key process variable for the delignification. A maximum decrease of the amount of lignin present in pre-treated willow compared to fresh willow wood by a factor of about 3 was obtained at 200 °C. In addition to

temperature, the ethanol-water ratio is a very important factor. Figure 5 indicates that the optimal ethanol-water ratio for delignification is around 60:40 wt%. Apparently, the lignin fragments that are formed during the thermal breakdown of the lignin polymer are more soluble in a mixture with relatively high ethanol content. This corresponds roughly with the solubility of commercially obtained organosolv lignin as measured in ethanol-water mixtures (see figure 5). This graph shows an optimum around 80wt% ethanol. Particularly at lower ethanol concentration, the solubility of lignin drops dramatically.

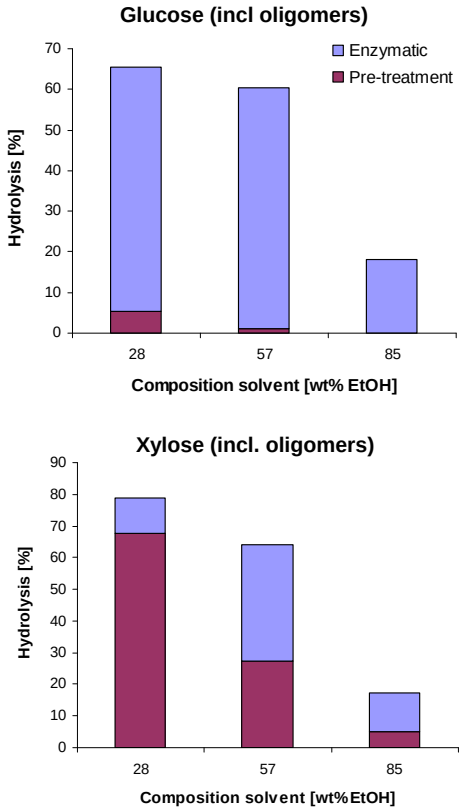

Figure 3: Influence of ethanol:water ratio on the cellulose and hemicellulose hydrolysis. Process conditions: 190 °C, 60 min, biomass: willow wood.

In contrast to delignification, the hydrolysis of hemicellulose was found to proceed more rapidly at a lower ethanol content, as discussed above (which can also be observed from Figure 5, since at low ethanol:water ratios the lignin content of the organosolv product is higher than that of the fresh biomass). In addition to the composition of the solvent, also the temperature has an ambivalent effect on the process (i.e., improved fractionation/pre-treatment vs. increased formation of inhibitors). For 'classical' non-catalysed ethanol-based organosolv, no single set of process conditions was found at which full fractionation of all three biomass constituents in sufficient quality for further conversion was achieved. Therefore, other modifications to the organosolv process were tested, including the application of alternative solvents and catalysts.

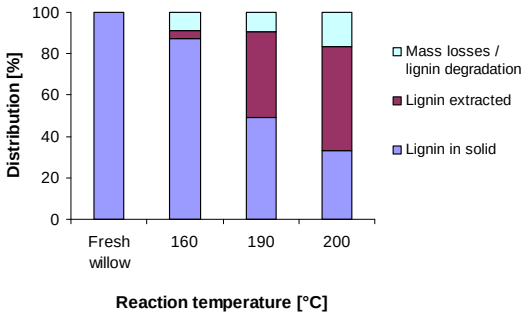

Figure 4: Mass balance for lignin for a selection of experiments performed on willow wood (60 min, ethanol:water 60:40 wt%). Lignin in solid = mass * lignin content solid biomass residue. Lignin extracted = mass * lignin content freeze-dried filtrate.

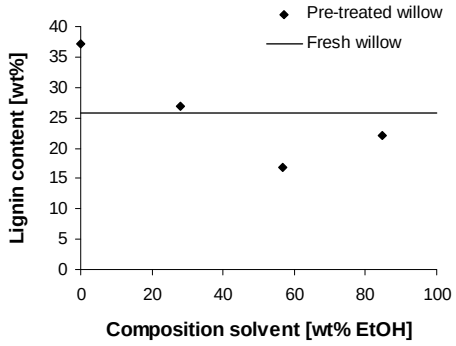

Figure 5: Influence of the ethanol : water ratio on the delignification of willow wood (<0.5 mm, 190 °C, 60 min). Hemicellulose hydrolysis leads to an increase of the lignin content, whereas delignification has a decreasing effect.

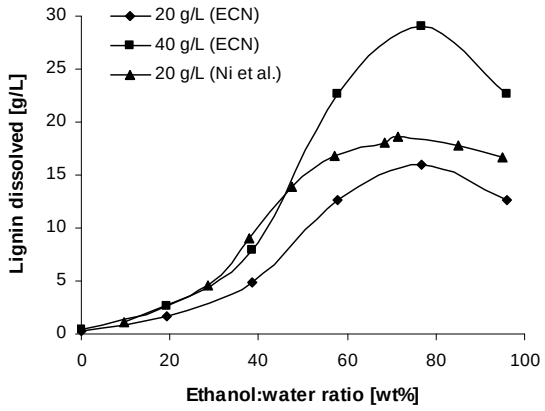

Figure 6: Solubility of organosolv lignin as a function of the composition of the solvent. (Ni et al.): literature data obtained from reference [6]. 20-40 g/L: ratio of solid lignin to ethanol-water used for the solubility tests.

Two alternative approaches to improve the organosolv process are presented in the remaining part of this paper paper: (1) alternative organic solvents, other than ethanol, and (2) the use of catalysts.

3.5 Alternative solvents

For the selection of alternative solvents an extensive literature study has been performed and selection criteria

have been determined. A number of solvents has been selected for first screening experiments including butanol, acetone, dioxane and dioxolane. These solvents are known to be good solvents for lignin. Preliminary results of experiments with these solvents are given in Figures 7 and 8. In Figure 8 (as well as the similar Figures 9 and 10), the amount of solid residue after organosolv is given as fraction of the starting material. In addition, the amount of lignin precipitated is shown. Thus, the mass loss due to organosolv can be observed as well as the part of that mass loss that can be allocated to precipitated lignin.

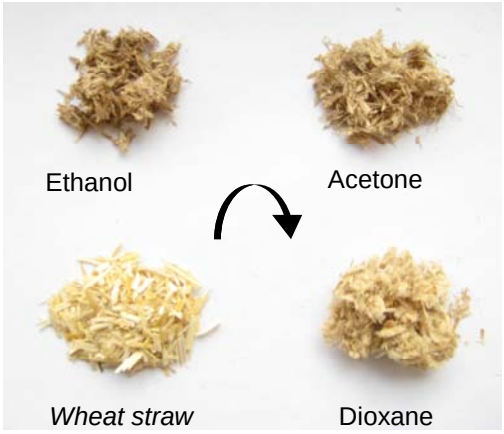

Figure 7: Physical appearance of wheat straw before and after organosolv pre-treatment in various solvents. Pre-treatment conditions: 200 °C, 30 min, solvent:water 60:40wt%.

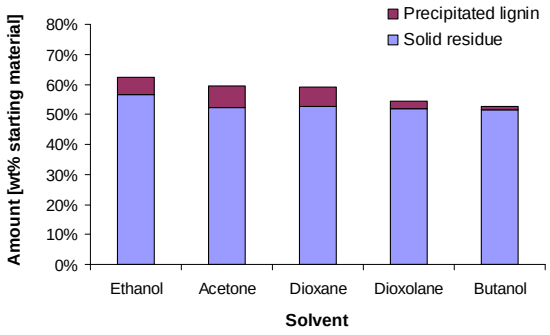

Figure 8: The effect of organic solvent used on the conversion and delignification of wheat straw. Pre-treatment conditions: 200 °C, 30 min, solvent:water 60:40wt%. Lignin: amount of lignin precipitated from filtrate and washing solution. Wheat straw residue: solid residue remaining after organosolv.

Based on these preliminary results, it can be concluded that the solvent used has an influence on the delignification of wheat straw. The colour of the pre-treated material becomes lighter in the following order: ethanol, acetone and dioxane. Although differences are small, this effect is also visible in the measured mass loss during the organosolv experiments and the amount of lignin precipitated (Figure 8). The lignin extracted with the help of dioxolane and butanol could not be adequately separated from the filtrate by precipitation due to improper flocculation and the immiscibility of the solvent with water, respectively. Based upon the total mass loss measured, the influence of the solvent type on the hemicellulose hydrolysis seems limited. In future research, the optimum temperature and organic solvent-water ratios will be studied for acetone and dioxane.

3.6 Catalysts

Another possibility to improve the organosolv process might be the application of a catalyst. In the literature, H_2SO_4 is a well known catalyst for biomass pre-treatment processes [2,7]. Figure 9 shows the effect of the addition of H_2SO_4 at different concentrations. Both the total mass loss (or conversion) and the amount of lignin precipitated was shown to increase substantially upon addition of H_2SO_4. By comparing the mass loss with the composition of fresh willow wood (see Figure 9), it can be concluded that also the hemicellulose hydrolysis increases with the concentration of H_2SO_4 added (as expected). Moreover, at the highest concentration the weight of the remaining willow after pre-treatment implies that the cellulose fraction of the material has been depolymerised (probably by hydrolysis). Since this is not required for this process and a lower catalyst concentration has benefits in terms of costs and formation of inhibitors, a concentration of 0.025 mol/L was chosen for comparison of various catalysts (Figure 10). This figure shows that, of the catalysts tested, H_2SO_4 has the largest effect on the organosolv process with the other acids (HCl and H_3PO_4) following. The concentration of NaOH was probably too low to be effective because of neutralizing reactions with acids formed. $MgCl_2$ is an interesting catalyst known from the literature [7] which does not lower the pH by itself and could thereby lead to a relatively lower inhibitor formation.

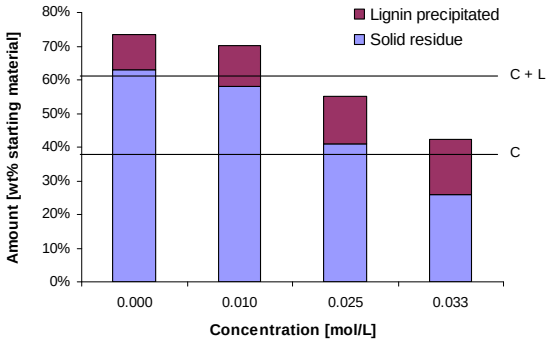

Figure 9: Effect of the addition of H_2SO_4 on organosolv pre-treatment of willow wood. Conditions: 200 °C, 30 min, ethanol:water 60:40 wt%. Lignin: amount of lignin precipitated from filtrate and washing solution. Willow residue: residue remaining after organosolv. C: cellulose content of fresh willow. C+L: cellulose + lignin content of fresh willow.

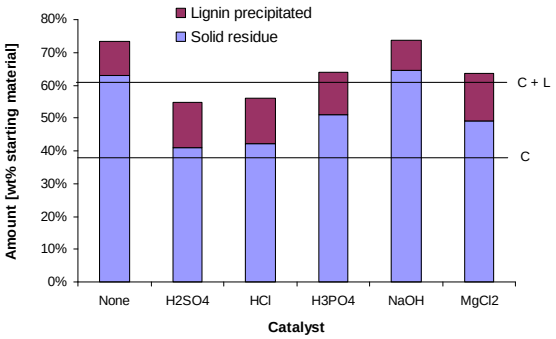

Figure 10: The effect on catalysts on organosolv pre-treatment of willow wood. Catalyst concentration: 0.025 mol/L. See also Figure 9.

The addition of H_2SO_4 seems an effective way to achieve simultaneous hemicellulose hydrolysis and delignification. At optimal conditions about 2/3 of the lignin present in willow is separated from the biomass by extraction and subsequent precipitation from the filtrate. This lignin was shown to have a good purity (low amounts of sugars present) and have a narrow molecular weight distribution compared to other types of lignin (results not shown), which both could facilitate the use of lignin for the production of chemicals.

4 CONCLUSIONS

Based upon the results obtained so far, the following conclusions can be drawn:

- 'Classical' non-catalysed ethanol-based organosolv is capable of delignifying lignocellulosic biomass, hydrolysing its hemicellulose and increasing its enzymatic degradability substantially. However, the optimum process conditions (i.e., water:ethanol ratio applied and temperature) required for these tasks differ.
- Modification of the organosolv process by addition of catalysts or using alternative organic solvents seems an interesting approach. By both means it was shown that the delignification can be enhanced. Addition of acids as catalysts also resulted in increased hemicellulose hydrolysis.

The effect of the addition of catalysts on e.g. the formation of inhibitors and process costs is subject of further research. In addition, the combination of catalysts with different organic solvent and process conditions will be studied.

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