

New method for lignocellulosic biomass polysaccharides conversion in butanol, an efficient route for the production of butyl glycosides from wheat straw or poplar wood

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Abstract Wheat straw and poplar wood are abundant biomass which are increasingly considered as a feedstock for the production of fuels, energy and chemicals. Based on our work on optimized concentrated acid saccharification of wheat straw polysaccharides, we developed a method for the conversion of cellulose and hemicelluloses of wheat straw and poplar wood in *n*-butanol. Hemicelluloses and cellulose have been efficiently converted into butyl-pentosides and butyl-glucosides respectively by a one-pot decrystallization-glycosylation procedure. This process differs from published results as it is highly productive and it does not use ionic liquids for cellulose solubilisation which renders the glycosides recovery complicated, or require the use of costly acid catalyst or drastic temperature and pressure conditions. The butyl-glycosides are obtained in high yields and can be used as raw materials for the production of long tailed glycosides that are molecules of market value in the fields of detergents and cosmetics. The recovery of the sulfuric acid has also been studied and a method is proposed displaying the economic potential of the overall method and opening a new

avenue for the use of wheat straw and poplar wood polysaccharides as raw materials in the surfactant industry.

Keywords Wheat straw · Poplar wood · Decrystallization · Transglycosylation · Glucosides · Pentosides

Introduction

One of the promising option in the context of alternative renewable energy is biomass because of its abundance. Hemicelluloses and cellulose are two major components of biomass and are currently regarded as promising alternative raw materials in the field of chemistry and biofuels (Klass 1998). Wheat straw and poplar wood represents valuable sources of hemicelluloses, cellulose and lignin. In a context where interest is constantly growing for integrated lignocellulosic biorefineries, there is a need for a more efficient use of hemicelluloses and cellulose and for an improvement of the added value of such concept (Kamm et al. 2006). The chemical industry and especially the surfactant manufacturers are also looking for new feedstock and lignocellulosic polysaccharides represent a renewable source of raw material (Martel et al. 2010). Among the main options for the direct production of alkyl glycosides from lignocellulosic biomass, several works have been

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using glycosylation reaction (Bouxin et al. 2010; Marinkovic and Estrine 2010, Marinkovic et al. 2012; Ochs et al. 2011; Seguin et al. 2012). These methods are efficient for the conversion of hemicelluloses into value added alkyl-pentosides surfactants (Papadopoulou et al. 2011; Renault et al. 2012) but the cellulose part remains unconverted thus proposing an incomplete valorisation of the lignocellulosic polysaccharides. Other strategies for the conversion of cellulose into alkyl glucosides have been published but they require drastic conditions or the use of ionic liquids and costly catalysts, long reaction times or several steps till the surfactant recovery, thus rendering these processes difficult to implement at an industrial scale (Deng et al. 2010; Villandier and Corma 2010; Ignatyev et al. 2010). Based on our recent work on concentrated acid saccharification of cellulose and hemicelluloses from wheat straw (Hausser et al. 2011), we attempted to apply the optimised decrystallisation procedure in a glycosylation process of wheat straw and poplar wood polysaccharides. The present work thus describes a new method to directly convert cellulose and hemicelluloses from these two biomass materials into butyl glycosides. The butyl glycosides represent raw materials for the longer tailed glycosides production (Eskuchen and Nitsche 1997) or can be directly used in the formulation of detergents (Ochs et al. 2011). The surfactant industry being a bulk oriented market (Martel et al. 2010), it represents a good vector for the wide use of lignocellulosic biomass and a good potential for the partial substitution of fossil based chemicals in daily used goods such as detergents and cosmetics.

Material and method

Raw material

The chopped wheat straw (up to 2 mm particle size) was supplied by local farmers from Champagne

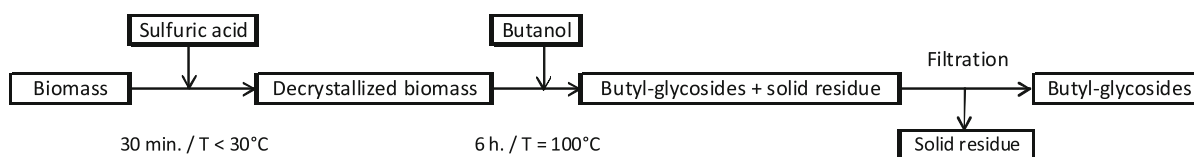
Ardennes region (FRANCE). The dry matter content of the wheat straw was 89 wt%. The carbohydrate content was determined according to NREL (National Renewable Energy Laboratory) analytical methods (Sluiter et al. 2007). The composition is given in wt% based on dry material: glucan 39 %, pentosan 29 % (24 % of xylan, 5 % of araban). The poplar wood chips (up to 2 mm particle size) was supplied by Wageningen University (NL) during the EU Biosynthesis project. The carbohydrate content was determined as for wheat straw: glucan 42 %, xylan 15 %. Sulfuric acid (96 %) and *n*-butanol (99 %) have been purchased from Acros Chemicals and were used as received without further treatment.

Decrystallisation-glycosylation procedure

In a 250-mL round bottom flask, equipped with a magnetic stirring apparatus and a refluxing condenser, 15 g of sulfuric acid was added and then 10 g of biomass. The mixture was slowly stirred for about 30 min maintaining the temperature below 30 °C with an ice bath. Then, 75 g of *n*-butanol were added to yield a slurry that is heated for 6 h at 100 °C. At the end of the glycosylation, the remaining biomass residue is then filtered-off over a cellulose filter (Scheme 1). Butyl-glucosides and pentosides (xylosides and arabinosides) productions are monitored by gas chromatography (GC) as described in precedent work (Bouxin et al. 2010). Yields of each glycoside were expressed based on available concentrations of each carbohydrate in wheat straw and poplar wood chips. The glycosides yields indicated are the mean values obtained from 2 repeat trials. Following this protocol, we established a minimum accuracy of the results of 97 % (Seguin et al. 2012).

Glycosylation procedure without decrystallization

In a 250-mL round bottom flask, equipped with a magnetic stirring apparatus and a refluxing condenser,



Scheme. 1 Simplified flow-sheet of the decrystallisation-glycosylation procedure

75 g of *n*-butanol, 15 g of sulfuric acid and then 10 g of biomass were added. The mixture is heated for 6 h at 100 °C. At the end of the glycosylation, the remaining biomass residue is then filtered-off over a cellulose filter. Butyl-glucosides and pentosides (xylosides and arabinosides) productions are monitored by GC analysis.

Decrystallisation-hydrolysis procedure

In a 250-mL round bottom flask, equipped with a magnetic stirring apparatus and a refluxing condenser, 15 g of sulfuric acid was added and then 10 g of biomass. The mixture was slowly stirred for about 30 min maintaining the temperature below 30 °C with an ice bath. Then, 75 g of water were added to yield a slurry that is refluxed for 6 h. Glucose and pentoses (xylose and arabinose) productions are monitored by high performance liquid chromatography (HPLC) as described in precedent work (Hausser et al. 2011).

Recovery of sulfuric acid by solvent extraction

The sulfuric acid is recovered after the decrystallisation of biomass by solvent extraction with butanol. In a 250-mL round bottom flask, equipped with a magnetic stirring apparatus and a refluxing condenser, 15 g of sulfuric acid was added and then 10 g of biomass. The mixture was slowly stirred for about 30 min maintaining the temperature below 30 °C with an ice bath. Then, 75 g of *n*-butanol were added to yield a slurry that is stirred for 30 min at 25 °C and then the pretreated solid biomass is filtered over a sintered-glass filter and washed with 75 g of *n*-butanol. The recovered solid biomass is then used in a glycosylation procedure as described precedently without any further addition of sulfuric acid. The recovered butanol phase containing sulfuric acid from decrystallisation is extracted three times with 150 g of water. The water phases containing extracted sulfuric acid are collected and concentrated till a 65 % dry matter is obtained. The sulfuric acid concentration of the thus recovered solution is determined by NaOH titration. Yield of the recovered sulfuric acid is based on the sulfuric acid introduced in the decrystallisation procedure.

Results and discussion

Effect of the decrystallisation on the butyl-glucosides production

A preliminary trial has been carried out by applying the decrystallizing conditions of our precedent work (Hausser et al. 2011). The decrystallization process uses a 80 wt% sulfuric acid solution during 30 min (prior the butanol glycosylation step at 100 °C for 1 h). The time of glycosylation was first limited to 1 h due to possible degradation of glycosides at such high concentration of acid (Marinkovic and Estrine 2010). The results are shown in Table 1 (Entries 1 and 2) for wheat straw and poplar wood. Comparative trials were carried out without the decrystallisation step (Entries 3 and 4, Table 1). The yields of butyl-glucosides (64 and 79 % for wheat straw and poplar wood respectively) were encouraging and noteworthy clearly displayed the positive impact of the decrystallisation procedure on the glycosylation reaction as without the pretreatment step the cellulose from wheat straw or poplar wood were not efficiently converted. The higher yields of butyl-glucosides observed for poplar wood is probably due to the lower hemicelluloses concentration of this material compared to wheat straw. The role of decrystallisation seems to be beneficial to a lower extent for the glycosylation of hemicelluloses. Indeed, for both studied biomass, the yields of butyl-pentosides were higher for glycosylation reactions carried out with a decrystallisation step. The high yields of butyl-pentosides for wheat straw were of the same

Table 1 Yields of butyl-glucosides obtained from wheat straw and poplar wood with and without decrystallisation

Entry	Biomass	Butyl-pentosides yield (%)	Butyl-glucosides yield (%)
1	Wheat straw	92	64
2	Poplar wood	58	79
3*	Wheat straw	75	7
4*	Poplar wood	33	0

Conditions: Glycosylation of wheat straw or poplar wood chips (10 g) after decrystallisation into a 80 wt% sulfuric acid solution (15 g) for 30 min maintaining the temperature below 30 °C with an ice bath. 75 g of *n*-butanol are then added to yield a slurry that is refluxed for 1 h. Yields of butyl-glucosides and pentosides are expressed as percent of carbohydrates available in original feedstock

* Run done without decrystallisation

Table 2 Yields of carbohydrates obtained from wheat straw and poplar wood after decrystallisation and hydrolysis

Entry	Biomass	L-arabinose yield (%)	D-xylose yield (%)	D-glucose yield (%)
1	Wheat straw	100	100	80
2	Poplar wood	–	78	86

Conditions: Transglycosylation of wheat straw or poplar wood chips (10 g) after decrystallisation into a 80 wt% sulfuric acid solution (15 g) for 30 min maintaining the temperature below 30 °C with an ice bath. 75 g of water are then added to yield a slurry that is refluxed for 6 h. Yields of carbohydrates are expressed as percent of carbohydrates available in original feedstock

* Run done without decrystallisation

magnitude than those described in precedent work although a higher quantity of sulfuric acid was used (Marinkovic and Estrine 2010). Decrystallisation-hydrolysis procedures were carried out in order to compare glycosylation and hydrolysis of the decrystallised biomasses (Table 2). Higher yields were reached for carbohydrates than for butyl-glycosides although they were obtained in longer time. As the decrystallisation procedures did not differ, the higher yields of glucose and pentoses achieved were probably due to a better stability of carbohydrates monomers during the hydrolysis step. Butyl-glycosides are quickly produced but their stability in the butanol phase require to carefully limit the reaction time to avoid their degradation.

The effect of time on the glycosylation procedure of wheat straw after decrystallisation was studied with the aim to improve butyl-glycosides yields (Fig. 1).

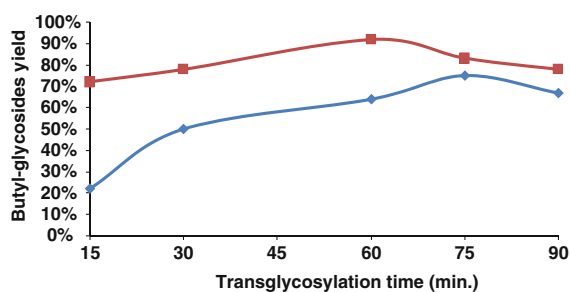


Fig. 1 Glycosylation of wheat straw after decrystallization into a 80 wt% sulfuric acid solution for 30 min maintaining the temperature below 30 °C with an ice bath. 75 g of *n*-butanol are then added to yield a slurry that is heated to 100 °C for 2 h. Butyl-glycosides yield (blue line) and Butyl-pentosides yield (red line) are expressed based on carbohydrates available in original feedstock

The results displayed the need to carefully select the time to optimize yields of butyl-glycosides. The pentoses are known to be more reactive than glucose in glycosylation reaction (Martel et al. 2010) and thus it is not surprising to observed a peak of butyl-pentosides yield 15 min before the one of butyl-glycosides.

The solid residue collected by filtration at the end of the glycosylation step displayed similarities with lignin (Seguin et al. 2012). The same similarities were observed for the final residue from poplar (see Electronic supplementary material for infra-red spectra).

Recovery of sulfuric acid by solvent extraction

The interest in hydrolysis of lignocelluloses using concentrated acids has been recently renewed due to the development of effective acid recovery solutions (Hausser et al. 2011; Moe et al. 2012). In order to preserve the potential industrial interest of the decrystallisation-glycosylation method, we investigated the possibility to recover the sulfuric acid charge used during the first step of the process. As the sulfuric acid is also playing the role of glycosylation catalyst, its complete recovery is not necessary (Marinkovic and Estrine 2010). Solvent extraction of the sulfuric acid is a widely applied techniques in the steel and electroplating industries (Archana and Sahu 2009) but in the present study the solvent needs to be compatible with the glycosylation reaction. The extraction of sulfuric acid was carried out with *n*-butanol as it is the raw material in the glycosylation step. Although the sulfuric acid solubility in this solvent is high, it is important to maintain the temperature below 30 °C not to let esterification reactions begin. Thus, in a typical decrystallisation procedure carried out on wheat straw (10 g of wheat straw and 15 g of 80 wt% sulfuric acid), the addition of 75 g *n*-butanol is followed by 30 min of stirring at 25 °C. The pretreated wheat straw is then filtered over a sintered-glass filter and washed with 75 g of *n*-butanol. The recovered butanol phase is extracted three times with 150 g of water. The water phases are collected and concentrated till a 65 % dry matter is obtained. The sulfuric acid concentration is then determined by NaOH titration. Yield of the recovered sulfuric acid based on the sulfuric acid introduced in the decrystallisation procedure is 90 wt%.

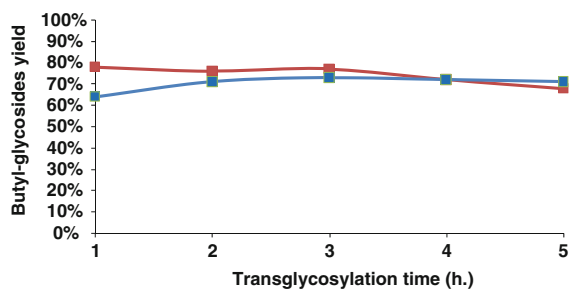


Fig. 2 Glycosylation of wheat straw after decrystallisation into a 80 wt% sulfuric acid solution for 30 min maintaining the temperature below 30 °C with an ice bath and solvent extraction of sulfuric acid with 75 g of *n*-butanol. The solid pretreated wheat straw is then filtered over a sintered glass filter and washed with another 75 g of *n*-butanol. Then the solid wheat straw is added into the reaction glass vessel and 75 g of *n*-butanol are then added to yield a slurry that is heated to 100 °C for 5 h. Butyl-glucosides yield (blue line) and Butyl-pentosides yield (red line) are expressed based on carbohydrates available in original feedstock

The solid wheat straw is used in a glycosylation reaction (Fig. 2). Although the concentration of sulfuric acid is significantly reduced during the glycosylation step, butyl-pentosides are still produced very quickly. Their maximal yield is however reduced (78 % in Fig. 2 vs. 92 % in Fig. 1). Analysis of the recovered sulfuric acid solution did not allowed to determine whether this yield is due to hemicelluloses losses during the sulfuric acid recovery procedure. Interestingly, butyl-glucosides yield was maximal at 3 h and near the yield observed without the acid recovery (73 vs. 75 % in 1.25 h, Fig. 1). The main impact of the sulfuric acid concentration reduction is the enlargement of the “high yield window” as butyl-glucosides became more stable in the new conditions as a yield of 71 % is maintained at 5 h of reaction.

The butyl-glycosides can be recovered after butanol excess distillation (Bouxin et al.) and used as such in detergent formulation or as raw material in the production longer tail glycosides (Eskuchen and Nitsche 1997).

Conclusions

The production of butyl-pentosides and glucosides mixtures from wheat straw or poplar wood have been efficiently carried out by decrystallization-glycosylation procedure. The decrystallisation step revealed

necessary to obtain high yield of butyl-glucosides meaning a high conversion of cellulose. By carefully selecting the reaction time, it is possible to reach butyl-pentosides yield up to 92 % and butyl-glucosides up to 78 %. To our knowledge, this method is the first one directly applied on lignocellulosic biomass and allowing such high yields of butyl-glycosides without using any ionic liquid or high temperature and pressure conditions. The solvent extraction of sulfuric acid by *n*-butanol prior the glycosylation step revealed efficient. Good yield of butyl-glycosides were obtained with an improvement of the butyl-glycosides stability during the glycosylation. The high rate of sulfuric acid recovery confirms the potential industrial interest of this method. The final residues recovered by filtration after the glycosylation were similar to organosolv lignin. Our coming efforts are now going to focus on upgrading and recycling of the sulphuric acid solutions. The butyl glycosides represent raw materials for the longer tailed glycosides production or can be directly used in the formulation of detergents. The surfactant industry being a bulk oriented market, it represent a good vector for the wide use of lignocellulosic biomass and a good potential for the partial substitution of fossil based chemicals in daily used goods such as detergents and cosmetics.

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