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Extraction of hemicelluloses from wood in a pulp biorefinery, and subsequent fermentation into ethanol

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ABSTRACT

This study deals with the production of ethanol and paper pulp in a kraft pulp mill. The use of an acid hydrolysis or a two-step treatment composed of an autohydrolysis followed by a secondary acid hydrolysis was studied. Acid hydrolysis allowed the extraction of higher quantities of sugars but led also to higher degradations of these sugars into inhibitors of fermentation. The direct fermentation of a hydrolysate resulting from an acid hydrolysis gave excellent yields after 24 h. However, the fermentation of hydrolysates after their concentration proved to be impossible. The study of the impact of the inhibitors on the fermentations showed that organic acids, and more specifically formic acid and acetic acid were greatly involved in the inhibition.

1. Introduction

Decreasing the consumption of crude oil derivatives has become one of the main world issues nowadays. As the major part of oil is turned into transport fuels, the development of biofuels is encouraged [1]. The only green substitute for gasoline potentially available in large quantities today is ethanol, given that this is the second bioproduct consumed in the world after paper pulp [2]. Unfortunately, first generation ethanol is produced from crops, which can have harmful repercussions on the prices of food resources. It is therefore important to develop the production of second generation ethanol, which consists in using lignocellulosic biomass as raw material, such as bagasse, straw or wood. Among all the possibilities existing to produce it [3–7], this paper deals with the co-production of hemicellullosic ethanol and cellulose in a kraft pulp mill.

The kraft process enables the production of more than 75% of the virgin paper pulp produced in the world. Wood is mainly composed of cellulose (40–45%), lignin (25–30%), hemicelluloses (20–30%) and extractives (1–5%) [8]. The process consists in solubilizing lignin during a treatment with alkaline liquor composed of sodium hydroxide and sodium sulfide during 2–3 h at 160–170 °C [9]. Then, the resulting cellulose is principally used to produce paper. The extracted lignin is burnt in a boiler to produce energy. The quantity of energy produced by the process is usually higher than the needs of the factory.

Most of the hemicelluloses are lost during the kraft process, especially when softwood is used as raw material. Indeed, softwood hemicelluloses are mainly composed of galactoglucomannans (GGM), a branched polymer composed of three monomer units: mannose, galactose and glucose. Some of their hydroxyl groups are substituted by acetyl groups [10]. This polymer is solubilized during the kraft cooking because of alkaline peeling, and is consequently burnt with the lignin, which is not profitable, given that the calorific value of carbohydrates is twice lower than the calorific value of the lignin [11]. GGM are made of hexoses which could find a better valorization, and one option could be to turn them into ethanol [12]. The developed process would consist in the hydrolysis and extraction of the GGM prior to the kraft process and their subsequent fermentation (Fig. 1).

Several treatments can be used to extract hemicelluloses: in hot water (autohydrolysis) [13–17], in acidic medium [18,19], in alkaline medium [20,21] or in near neutral medium [22–26]. Enzymes can also be used [27,28]. Autohydrolysis and acid hydrolysis allow higher rates of sugar extraction. During the autohydrolysis, acetic acid, coming from the deacetylation of hemicelluloses, catalyzes the hydrolysis of GGM. The efficiency of the treatment can be improved by the addition of a mineral acid to perform an acid hydrolysis. Nevertheless, the severity of the treatment has to be limited to avoid damaging the cellulose, which could then reduce the properties of the pulp [18,29,30]. In acidic medium, hexoses and pentoses can be subjected to dehydratation reactions, leading to the formation of 5-hydroxymethylfurfural (HMF) and furfural

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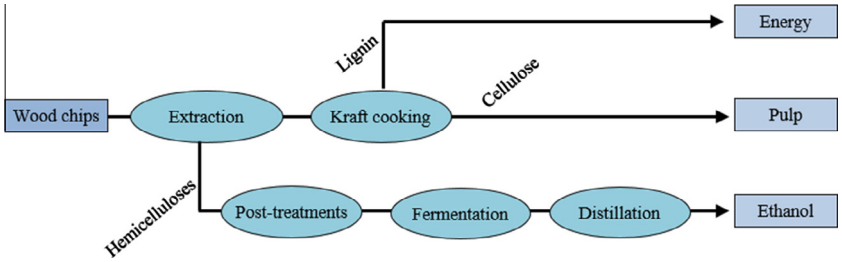

Fig. 1. Flow sheet of a kraft pulp mill producing pulp and ethanol.

respectively. HMF can further be degraded into levulinic acid and formic acid, and furfural into formic acid [31,32]. Furthermore, some phenolic compounds coming from lignin and extractives are also present in the hydrolysates [33,34]. Unfortunately, HMF, furfural, acetic acid, levulinic acid, formic acid and phenolic compounds are known to be potential inhibitors of the fermentation [35–40]. The limitation of the concentrations of such inhibitors is necessary to obtain a profitable process. Alternatively, a post-treatment of detoxification can be added, such as overliming treatment [41–43], ions exchange resins [44,45], evaporation [46], activated charcoals [47] or enzymatic detoxification [41,45].

A secondary hydrolysis or a step of concentration can also be implemented before the fermentation. A secondary hydrolysis can be applied to increase the rate in monomers, given that only monosaccharides can be fermented. It could be performed with an acid or with enzymes. A step of sugar concentration might also be necessary to have a profitable distillation after fermentation. The higher the concentration in ethanol, the lower the demand in energy for the distillation. A concentration of 5% (w/w) is the minimum admitted, meaning that at least 10% (w/w) of fermentable sugars are required prior to the fermentation [21].

The fermentation of extracted sugars can be performed by a large variety of wild or genetically modified microorganisms [48–54]. Among them *Saccharomyces cerevisiae* was selected for this study. This yeast is known to have good fermentation yields [55], to be robust and quite tolerant to inhibitors [7,12].

In this study, the possibility to extract hemicelluloses and ferment them without detoxification step was evaluated. Two extraction steps were compared: an acid hydrolysis and a two-step treatment composed of an autohydrolysis followed by a secondary acid hydrolysis. The resulting hydrolysates were fermented directly, or concentrated prior to the fermentation. Furthermore, the impacts of different inhibitors on the fermentations were studied.

2. Material and methods

2.1. Raw material and hydrolysis treatments

Wood chips used in this study were a mixture of different softwood species containing sylvester pine (35%), black pine (24%), alep pine (18%), douglas fir (16%) and spruce (7%). The average composition is given in Table 1. The amount of GGM in dry wood was 16%, calculated according to the method developed by Janson [56]. The molar ratio mannose:glucose:galactose was set at 2.8:1:0.2, which are typical values for the wood used [8].

The extractions were performed in an autoclave immersed in an oil bath. Each extraction was performed twice on 200 g of dry woodchips. The temperature of acid hydrolysis was raised during 90 min to reach 160 °C and maintained for 120 min. The liquor to wood ratio (L/W ratio) was 4. Sulfuric acid was added to the liquor to obtain a concentration of 2.5 g/L (1 g for 100 g of wood). The temperature of the autohydrolysis was raised during 30 min to reach 170 °C and maintained for 65 min. The L/W ratio was also 4. A secondary hydrolysis was performed on the hydrolysate resulting of the autohydrolysis, after it has been separated from wood chips. The conditions were optimized to reach a complete depolymerization and to limit the degradation of monosaccharides [57]. The time of the hydrolysis was 30 min at 140 °C. Sulfuric acid was added to obtain a concentration of 5 g/L.

Table 1
Composition of the wood chips used in the study.

Chemical component	Amount (% by wt.)	Chemical component	Amount (% by wt.)
Arabinan	2.0 ± 0.2	Acetyl groups	1.3 ± 0.01
Galactan	2.1 ± 0.0	Klason lignin	27.9 ± 0.5
Glucan	40.0 ± 0.5	Acid soluble lignin	0.35 ± 0.02
Xylan	4.90 ± 0.6	Acetone extractives	2.5 ± 0.5
Mannan	10.1 ± 0.2	Others*	8.9

* "others" include ashes, acetyl and uronic groups. Calculated as the difference to get 100% content.

Part of the hydrolysates obtained was concentrated by evaporation, using a rotary evaporator. The round-bottom flask containing the hydrolysate was immersed in a bath at 70 °C. The extraction was performed at a pressure of 35 kPa. The hydrolysate was concentrated until it contained about 60 g/L of hexoses.

2.2. Fermentations

Fermentations were carried out in 100 mL flasks in which 30 mL of solution to be fermented were introduced with 5 mL of a nutrient solution composed of $(NH_4)_2SO_4$ at 5 g/L and $MgSO_4$ $7H_2O$ at 1 g/L. The pH was then adjusted to 4.5 with sodium hydroxide or sulfuric acid before adding 0.4 g of dry *S. cerevisiae* yeasts and closing the flasks. Samples were taken initially and after 4, 24, and 48 h. All fermentations were done in duplicate. The hydrolysates obtained after the two-step treatment and the acid hydrolysis were fermented.

Moreover, synthetic media were also fermented to evaluate the impact of the inhibitors. These synthetic media contained arabinose, galactose, glucose, xylose and mannose, and the inhibitor tested added individually: acetic acid, formic acid, levulinic acid, lignin derivatives and acetone extractives (Table 2). Lignosulfonates were used as lignin derivatives. Furthermore, the three main inhibitors: acetic acid, HMF and furfural, were tested simultaneously in four different synthetic solutions (Table 3). One solution was used to simulate a non-concentrated hydrolysate (fermentations #1 and #2) and another one to simulate concentrated hydrolysates (fermentations #3 and #4).

The sugars and inhibitors concentrations used were typical of the concentrations found in the hydrolysates before and after the step of evaporation.