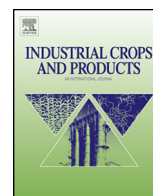




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Pretreatment optimization from rapeseed straw and lignin characterization

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ABSTRACT

The objective of this work are (1) to optimize the operating conditions of chemical pretreatments (organosolv, soda), (2) to present a comprehensive and comparative assessment for delignification of rapeseed straw to make the cellulose more accessible to hydrolysis and (3) to characterize for the first time the rapeseed straw lignin. Evaluation criteria for optimization of the pretreatment conditions were based on high lignin yield in the hydrolysate and high sugars recovery from the solid residues obtained after filtration of whole pretreated materials for further valorization into eco-sourced polymers. Several experiments have been conducted according to a central rotatable design in which reaction temperature, holding time and NaOH concentration were varied and different aspects have been observed. The optimized results showed a sugar recovery yield of 59% and lignin removal of 31% at soda conditions 4.4 h, 89 °C and 0.4 M NaOH compared to 63% sugars recovery and 43% lignin removal with Organosolv pretreatment at conditions of 78 min, 162 °C and 1.6% H₂SO₄. Cellulolytic enzyme lignin, soda and organosolv lignins extracted from rapeseed straw were subjected to structural analysis by FTIR, ¹³C NMR and HSQC. The rapeseed lignin is mainly composed of S and G basic units with S/G = 1.64. The lignin produced with the organosolv process appears to be primarily unaltered and potentially suitable for future applications.

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1. Introduction

Lignocellulosic waste materials from agriculture, agro-industrial processing and forestry are an attractive source of biomolecules converted into renewable energy and biomaterials.

Rapeseed crop (*Brassica napus*) traditionally associated to animal feed and vegetable oil received considerable interest in recent years due to their abundance and use in biodiesel production. According to FAO (FAO, 2013), over 75 million tons of rapeseed were harvested worldwide in 2013, France is among the top 5 producers with cultivated area. and rapeseed straw recovered after seed harvesting represent the most abundant and lowest-cost waste in France.

As a lignocellulosic biomass, rapeseed straw is composed of three main polymers which are cellulose, hemicelluloses, and lignin (Kang et al., 2012a). Cellulose and hemicelluloses can be hydrolyzed

to fermentable sugars by enzymes but the presence of lignin impedes enzymatic action.

Lignin is a complex cross-linked polymer composed of phenylpropanoid units. Its structural characteristic depends on the botanic origin and on the applied extraction processes. Decision on suitability of these lignin fractions for future applications require prior studies on their composition and properties (Ragauskas et al., 2014). In addition, recent studies have suggested that an understanding of the structure of lignin is essential to identify the fundamental properties that contribute to its recalcitrance and to the efficient conversion of biomass to biofuels (Foston et al., 2015). Structural characterization of lignin from herbaceous crop has been already described but data regarding rapeseed lignin is rather poor.

Additionally to being a physical barrier, the harmful effects of lignin include: (i) non-specific adsorption of hydrolytic enzymes to “sticky” lignin; (ii) interference with, and non-productive binding of cellulolytic enzymes to lignin-carbohydrates complexes; and (iii) toxicity of lignin derivatives to microorganisms.

Traditional chemical pulping processes depend on their ability to progressively break down and modify the lignin macromolecule

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until the resulting molecular fragments become small enough to dissolve in the pulping liquor.

Among all the pretreatment technologies already described to enhance the cellulose and hemicelluloses enzyme digestibility, alkali and ethanol organosolv treatments seem to be very efficient especially starting from an annual crops because these treatments allow an efficient removal of lignin from these feedstocks and constitute an alternative method for producing chemical or semi chemical pulps from non-wood lignocellulosic materials (Kang et al., 2012b; Park et al., 2010; Zhang et al., 2016).

Besides, organosolv pretreatment despite its cost provides a clean separation of the 3 main biomass components. A good recovery and valorization of those fractions (including organosolv lignin) might promote the organosolv pretreatment to biorefining lignocellulosic feedstock in the future. The responsible reaction, which very likely occurs in organosolv pulping, is believed to be the solvolytic splitting of α -ether linkages (El Hage et al., 2009; McDonough, 1992).

The advantage of employing ethanol as extraction alcohol is its low boiling point, ease of recovery by simple distillation with concomitant low energy requirement. It is also fully miscible with water and more cost-effective than other solvents. Ethanol losses during this step may be readily replenished from next biorefinery step like the fermentation of the dissolved sugars.

The main effect of sodium hydroxide pretreatment on lignocellulosic biomass is the disruption of the ester bonds cross-linking lignin and xylan, thus increasing the porosity of biomass (Silverstein et al., 2007; Tarkov and Feist, 1969). In addition, dilute NaOH treatment of biomass causes swelling, leading to an increase in the internal surface area, a decrease in crystallinity, separation of structural linkages between lignin and carbohydrates, and disruption of the lignin structure (Castro et al., 2011).

There is a growing interest in applying Soda pretreatment for non woody material such as straw and soda pretreatment of rapeseed straw has been already reported by Kang et al. (2012a,b) but with a special focus on enzymatic hydrolysis yields. On the other hand, until now, pretreatment of rapeseed straw with ethanol-organosolv has not been attempted. Therefore, this work was conducted to investigate the possibility of enhancing lignin removal by application of pretreatments either sodium hydroxide or ethanol-organosolv and to determine optimal conditions of pretreatment with rapeseed straw comparing both treatments impacts on recovered lignin.

In this paper, soda and ethanol organosolv pretreatments were investigated and optimized for the pretreatment of rapeseed straw using response surface methodology (RSM) to delineate the effects of five level-three factors and their reciprocal interactions. The rapeseed straw lignin was for the first time subjected to a comprehensive structural characterization: the structure of the isolated lignin fractions obtained with both processes was investigated by spectroscopic methods and cellulolytic enzyme lignin was also extracted from rapeseed straw and characterized by liquid ^{13}C NMR for comparison.

The effects of process parameters on the yields and distributions of cellulose, hemicellulose, and lignin in the fractions generated during the pretreatment were examined, and the process mass balance of the resulting substrate were investigated.

2. Materials and methods

2.1. Biological material

The rapeseed straws were provided by the company SEGAGRI (Sezanne, France). The air-dried rapeseed residues were stored at

room temperature until use. The dry matter content of provided straws is 83% (w/w).

The enzyme preparation (Novozyme 188) was supplied by Sigma-Aldrich (Steinheim, Germany).

2.2. Chemicals

Anhydrous sodium acetate (99%) was purchased from FlukaSigma-Aldrich (Steinheim, Germany), sodium hydroxide, pyridine, chloroform trichloromethane, dioxane, sulfuric acid (72%) from Fisher Scientific (Illkirch, France).

2.3. Lignin extraction

2.3.1. CEL extraction: cellulosic enzymatic lignin

CEL (cellulolytic enzyme lignin) extraction is a recovering technique of pure lignin based on the effect of enzymes to attack the cellulose and hemicelluloses. Preparation of cellulolytic enzyme lignin from rapeseed straw was carried out according to Chang et al. (1975). The milled biomass (10 g) was suspended in acetate buffer (100 mL, pH 4.8) and 1 mL of cellulolytic enzyme solution (50 IU/mL) was added and incubated for 48 h at 50 °C. The reaction system was centrifuged, the supernatant was removed, and the residue was again suspended in acetate buffer (50 mL, pH 4.8) and treated with enzyme (1 mL) for an additional 24 h at 50 °C. The residue was again collected by centrifugation, washed with distilled water (200 mL), centrifuged and freeze dried. The freeze dried residue was treated with 210 mL of pyridine/HOAc/water (9:1:4, v/v) and extracted twice with HCCl_3 . The lignin solution in HCCl_3 was condensed under vacuum and dropped into ethyl ether. The precipitated lignin (CEL) was collected after drying.

2.3.2. Organosolv: acid extraction

Pretreatment was performed in a laboratory scale Parr cylindrical reactor with a total volume of 1 L. The reactor was heated at a rate of $\approx 5^\circ\text{C min}^{-1}$. The liquid to solid ratio was fixed at 10. The solvent was composed of H_2O : EtOH/35:65 v/v with sulfuric acid as catalyst (see Table 1). When the desired temperature (150–210 °C) inside the reactor was reached, the treatment time was started to be counted. After the target treatment time was reached, the reactor was cooled and the wet material was filtrated by vacuum pump, obtaining a solid phase and a liquid phase. The solid phase was washed thoroughly with water, weighed and analyzed for carbohydrate content. Liquid phase was analyzed for sugar, acetic acid, furfural and HMF content.

2.3.3. Soda: alkaline extraction

Soda extraction was carried out in a 250 mL glass beaker. 20 g of rapeseed hulls were used for experiments. The liquid to solid ratio was fixed at 10. The solvent was composed of water and various proportions of NaOH (see Table 2). The soda extraction was carried out at different temperatures (56–97 °C) under agitation (750 rpm). After extraction, the mixture was filtered. The solid residue (pulp) was washed with 1 L distilled water. The pulp was then dried at 60 °C for weight determination and characterization. The liquid (black liquor) was collected and stored at 4 °C until analysis.

2.3.4. Central composite design

A central composite design was employed to reduce the total number of experiments needed to determine the best combination of parameters for optimization of the process. The statistical software “jmp”, version 10 was used for the central composite design and to analyze the experimental data obtained. The conditions for each experiment are shown in Supplementary material, SP1.

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