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Paper-ID	24651
Paper title	A Molecular Dynamic Protocol to Study Deconstruction of Crystalline Cellulose Systems at High Temperatures
Presentation format	Poster
Date of submission	21.01.2017 00:26 Uhr
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Content

Bioethanol is the most widely used biofuel in the world transportation segment and has long been used as an alternative fuel especially after the Second World War and during the 1970s with the oil crisis [1]. In the production of second generation bioethanol an industrial problem is the decreasing of crystallinity of cellulose obtained from pulp, which is one of more important factors that governs enzymatic hydrolysis rate [2]. The better conditions for transforming crystalline cellulose into amorphous cellulose by thermal treatment including water or gaseous molecules can be obtained by using molecular dynamic (MD) simulations [3]. MD simulation is a well-adapted technique to investigate thermophysical properties connected with thermal motion such as heat capacity (C_p), glass transition temperature (T_g), isotropic thermal expansion ($\propto_p$), and isothermal compressibility (β_T). In turn, these properties are strongly related with industrial processability of cellulose and effective use of energy and operation of processing plants based on biomass, which depend on structure of crystalline phases into the solid matrix, as well as of molecular mass. Even for crystalline cellulose, very limited information about thermodynamic properties of cellulose and lignin, the major components of the stem part of biomass, is available [4]. In this study, amorphous structures from native crystalline cellulose I (Iα, Iβ) are obtained at high temperatures using a new molecular dynamic protocol with CHARMM36 (C36) force field. The crystallinity characterization of these structures was carried out using simulation techniques as X-ray diffraction, IR spectroscopy, radial distribution function, and order parameters. The MD simulations provided thermophysical properties, such as C_p, T_g, $\propto_p$, and β_T, for amorphous cellulose of different molecular masses, which were in fair agreement with published data taking into account crystallinity index. These results allowed concluding that C36 is a suitable force field to study deconstruction of crystalline cellulose systems at high temperatures.

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Paper-ID	62336
Paper title	Effect of a previous extraction step on the steam explosion pretreatment of olive mill leaves
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Date of submission	30.01.2017 23:13 Uhr
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Content

Olive leaves and thin branches that are generated during the olive harvesting have to be separated from olives in the olive mills before the oil extraction process. This residual food-processing material is named in this work as olive mill leaves (OML). Due to its lignocellulosic composition, this residue can be of interest to obtain bioethanol and other high added-value compounds.

The release of sugars from OML requires a pretreatment step in order to break down the fibrous structure, thereby reducing barriers to subsequent enzymatic hydrolysis. In this study, steam explosion (SE) is the proposed pretreatment because its potential has been demonstrated in previous work to obtain sugars and antioxidants compounds from olive leaves [1]. SE has also been applied to many others raw materials such as olive pruning biomass, sugarcane bagasse, corn stalks and rice husks.

In addition, a previous stage of water extraction has been carried out in order to evaluate how it affects the subsequent pretreatment and the enzymatic hydrolysis. OML contains a high extractive content (> 40%). Removal of these extractives could facilitate subsequent pretreatment by avoiding undesired reactions of the extracts with the lignin present in the raw material. The extraction step was carried out in an autoclave at 130 ºC for 60 min with a 15 % solid/liquid ratio. Subsequently, the extracted OML was pretreated in a batch pilot unit, equipped with a 4 L reaction vessel. The experiments were performed with 200 g of dry sample at 180 ºC for 10 min. The resulting water insoluble solid was enzymatically hydrolyzed by a commercial cellulose complex. Besides, fermentability test were performed with both liquid fractions obtained from the extraction and SE steps. The total phenolic compounds and antioxidant activity of these liquids were also evaluated.

The results showed that more than 60% of the OML extractives were removed in the extraction step. Further SE pretreatment and enzymatic hydrolysis led to the solubilization of 75% of the structural glucose present in the raw material, representing an increase of almost 20% compared to the direct SE pretreatment without previous extraction. The recovery of antioxidant compounds from the liquid extract could also favor the viability of the process under a biorefinery approach.

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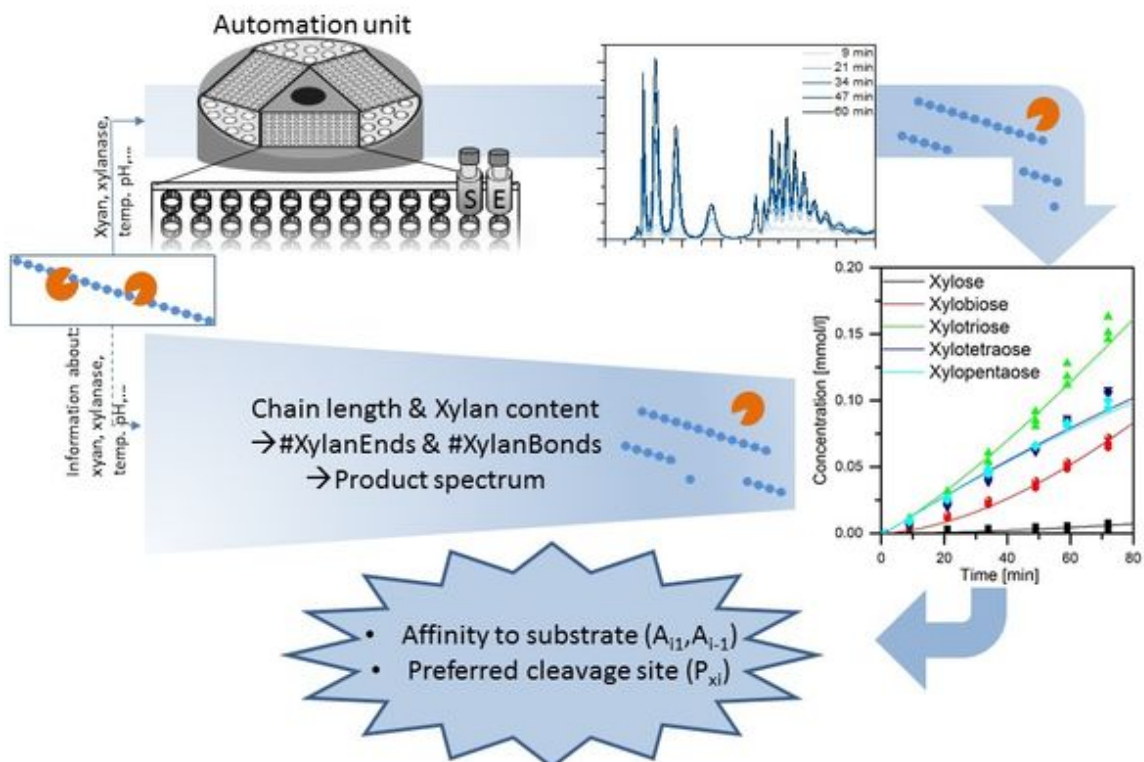| Paper-ID	28296
Paper title	MECHANISTICAL MODELLING OF XYLAN HYDROLYSIS USING AUTOMATED DATA COLLECTION VIA HIGH PERFORMANCE ANION EXCHANGE CHROMATOGRAPHY
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Date of submission	25.01.2017 15:58 Uhr
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Content

The depletion of fossil carbon sources motivates the replacement of fossil raw materials by renewable lignocellulosic biomasses. An economically feasible process requires the complete hydrolysis of lignocellulose and therefore, knowledge of the activity of cellulases and additional enzymes. Of these additional enzymes, xylanases are prominent since they degrade the main hemicellulose component, xylan. Xylanases produce the fermentable sugar xylose and increase the accessibility of cellulose, and thereby, the glucose yield. This study aimed at building a modular mechanistic model for xylanase activities, which provides parameters characterizing the enzyme's product spectrum and affinity to certain substrates.

The necessary dataset for the development of the model was generated for a endoxylanases from Aspergillus niger, Bacillus stearothermophilus and B. subtilis on soluble xylan (0.2-2 g/L) diluted in a 100 mM sodium acetate (pH 3.5-5.5) or citrate buffer (pH 6-6.5). The reaction was automated in 1.5 ml vials at 40°C by the autosampler of an ion chromatography (HPAEC-PAD) (Fig. 1). The developed method detects the products xylose to xylopentaose with a limit of detection ranging from 0.22 to 0.39 mg/L. The developed model calculates the number of xylan chains depending on the initial xylan concentration and chain length (Fig.1). From this information, the number of existing bonds is counted and the reaction rate is calculated using the parameters k_1, k_{-1} and k_2. The predicted product spectrum depends on the current chain length as well as on enzyme-dependent parameters (P_{Xi}). Furthermore, the rate of enzyme binding and release to short xylan oligomers (chain lengths from i=1 to 5) can also be adapted by parameters (A_{i1}, A_{i-1}), thus implementing product inhibition. The resulting mathematical model was fitted to data collected by an automated online chromatography method.

Modular mechanistic models for single enzyme activities are the basis for integrated mechanistic models for biomass degradation, which will be able to predict optimal enzyme cocktails for specific biomasses. A coupled system of such modular models might enable biorefinery operators to vary seasonally available substrate streams efficiently at low enzyme costs and optimal yield.

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Content

Different Colombian agro-industrial wastes, like coffee silverskin (CS), oil palm empty fruit bunch (OPB) and sugarcane bagasse (SB), were selected for the xylose content, availability and amount of waste generated in the region, for the production of xylooligosaccharides (XOs) (see Figure 1). XOs production was performed by enzymatic hydrolysis of xylan, which was obtained by autohydrolysis from these agro-industrial wastes. Different temperatures (160 to 200°C) and reaction times (15 to 100 min) were used for autohydrolysis[1]. The hemicellulose-rich solution (autohydrolysate) was subjected to further enzymatic hydrolysis with 10-80 U/mL of commercial endo-(1,4)-β-xylanases (EC 3.2.1.8) at different temperatures (40 to 50°C) and pH (4.5 to 6.5)[2], to evaluate the influence on the degree of polymerization, composition and yield of XOs obtained. Ultrafiltration membrane was evaluated to purify the XOs obtained, varying the molecular weight cut-off of membrane (1 to 10 kDa) and transmembrane pressure (2 to 8 bar) on XOs characteristics[3].

Figure 1. Composition of selected lignocellulosic materials from Colombian agroindustry.

Keywords: Xylooligosaccharides, agro-industrial wastes, autohydrolysis, enzymatic hydrolysis, ultrafiltration.

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Figure 1. Composition of selected lignocellulosic materials from Colombian agroindustry.
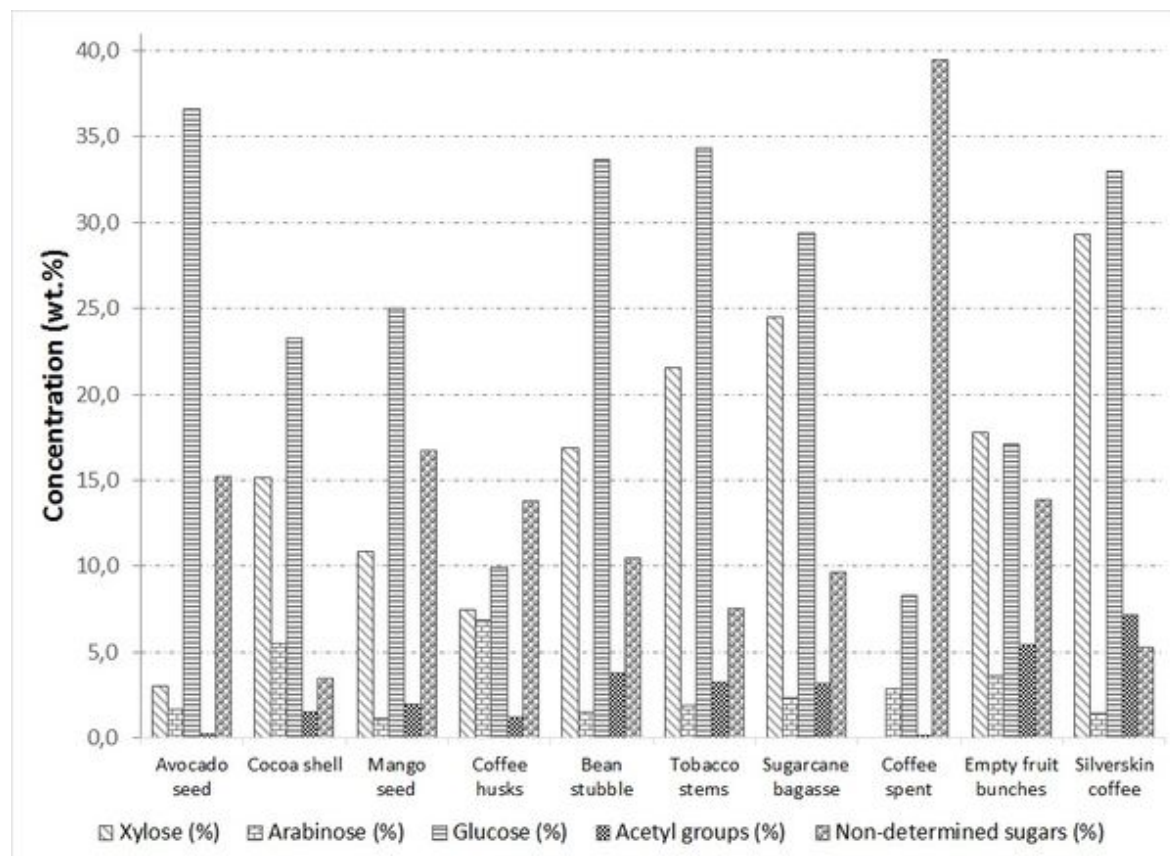
Paper-ID	59866
Paper title	Rapid microwave-irradiated catalytic conversion of non-edible lignocellulose (Sunn hemp fibres) to cellulosic biofuels
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Content

Identifying non-food energy crops that can rapidly produce cellulosic fuels is an undeniable tool for fighting climate change – the biggest threat to our planet today. In this work, we identify a new non-edible lignocellulosic fuel source – fibres of Sunn hemp (Crotalaria juncea), a shrubby, herbaceous, fast-growing sub-tropical annual legume with 19 MJ of energy/kg dry biomass [1] and a global production of 130,000 MT/year across Bangladesh, Brazil, India, Pakistan, Russia, Sri Lanka, USA, Uganda, etc. Here, we show that the lignocellulosic fibres Sunn hemp are composed of 75.6% cellulose, 10.05% hemicellulose, 10.32% lignin, 3.6% moisture, and 0.43% ash, with 80.17% crystallinity and a degree of polymerization of 600-700, and can be converted to biofuel precursors such as glucose, 5-hydroxymethyl furfural (HMF), levulinic acid and formic acid [2] in less than 50 minutes. The key to such rapid rupture of its glycosidic bonds lies in a microwave-based ionic liquid-mediated alkali metal-catalyzed reaction process. The ionic liquid, transition metal catalyst, cellulose and water form a supra-molecular complex that attracts electrons away from the glycosidic oxygen and develops a large dipole moment, as shown by our molecular dynamics simulation. The alternating polarity of the microwave radiation engender frequent dipole rotation that results in bond stretching, intermolecular collisions, heat generation and activation energy reduction, rupturing the glycosidic bonds via autocatalytic pathways and hydrolysing the cellulose to produce dissipative structures. Only 46 minutes of optimized reactions at 160-200°C and 5 bar pressure with water addition of 5% to 90% (wt% of ionic liquid)result in up to 78.7%, 26.8%, 44.9% and 10.8% yields of biofuel precursors such as glucose, HMF, levulinic and formic acids, respectively [3]. The glucose is then either microbially fermented to bioethanol or dehydrated to HMF for producing gasoline. HMF is further rehydrated to produce levulinic and formic acids, which can be converted to fuels such as C_8-C_{20} alkenes.Bioethanol yield is 75.6% after 15 hours of fermentation of the glucose separated from the ionic liquid using the yeast Saccharomyces cerevisae, and the ionic liquid is recycled for cost-effective cellulosic biofuel production.

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Paper-ID	34881
Paper title	Selection of membranes for lignocellulosic biomass hydrolysis integrated with separation of products
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Content

Due to the increased energy requirements and limited supply of fossil fuels the quest for renewable and environmentally friendly energy resources is still unresolved problem. For this reason during last decades many efforts to biochemical conversion of lignocellulosic biomass into alternative liquid fuels suitable for transportation have been made. An enzymatic hydrolysis of lignocellulosic stock into fermentable sugars is recognized as the crucial stage of the second generation biofuels production. Due to the complex chemical structure of the raw material, the step of hydrolysis requires the application of different hydrolases with synergistic activities. Products of hydrolysis of lignocellulose molecules are inhibitors of enzymes used in the reaction, therefore the separation of them from reaction mixture can increase total yield of the whole process.

The enzymatic bioconversion of lignocellulosic biomass integrated with membrane-based separation, has been investigated and discussed. An application of appropriate membranes provided selective removing of hydrolysates in the permeate stream. The possibility of adsorption of enzymatic proteins on the surface of membranes is recognized as the negative effect associated with the usage of membrane, which finally leads to the loss of enzymes activities.

The feasibility of various asymmetric ultrafiltration membranes to retain enzymes in the reaction mixture and as well as separation of the inhibitors has been examined. Influence of both, the membrane material and cut-off as well, on enzymatic proteins concentration in the retentate has been investigated. Enzyme adsorption on the surface of membranes has been taken into considerations. The aim of the study was an investigation and selection of suitable membranes for hydrolysis of corn cob wastes pre-treated in alkaline conditions. Cellic CTec2, as commercially available preparation containing cocktail of cellulolytic enzymes was used as catalyst. Experiments were carried out in small-scale membrane bioreactors (with a total volume of 200 mL). The influence of membrane fouling on pressure drop, as well as on permeate flux was evaluated. Different values of the transmembrane pressures were tested and its impact on the rate of hydrolysis was recognized. The concentration of the hydrolysis products in permeate and retentate streams were measured by HPLC technique. The enzyme concentration in the streams were spectrophotometrically determined. Based on the results it was concluded, that integration of two independent processes: enzymatic hydrolysis and membrane separation of products, significantly increased the total yield of enzymatic degradation of lignocellulosic raw materials.

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Content

Lignin must be considered as the most important renewable source for aromatic chemicals. However, until now, the production of cellulose has been the main target of wood transformation. This fact has implied the sacrifice of the other main components of wooden biomass (hemicellulose and lignin). This unsustainable approach must be corrected to take into consideration the successful implementation of bio-refineries, with proposed high value added applications for all the lignocellulosic components. For the particular case of lignin, this transition requires the development of new separation processes.

The viability of ionic liquids (ILs) to dissolve, separate and recover the main lignocellulosic components has been analyzed. The dissolution of lignin has been mainly investigated using imidazolium-based ILs; but alternative options, such as ILs based on phosphonium, can exhibit certain advantages during the following lignin processing. Nevertheless, the high price of commercially available ILs impedes their industrial-scale implementation.

Membrane separation systems allow drastic process improvements thanks to low energy consumption, waste generation and capital investment. Supported ionic liquids membranes (SILMs) basically consist of a porous support whose pores have been impregnated with an IL. SILMs can be a promising option to separate and purify lignin. The extraction from the feed phase to the stripping phase in an only stage allows the compaction of the system, without requirements of high energy demand (no heating or pressure to be applied). The reduced amount of IL required for SILMs minimizes the economic drawback that characterizes the use of such expensive chemicals.

The main objective of this work is the investigation of SILMs for lignin extraction from aqueous solution in order to advance in its purification. Several ILs based on imidazolium ([BMIM]MeSO$_4$, [EMIM]EtSO$_4$ and [EMIM]Ac) and phosphonium (Cyphos 101 and 108) were supported in hydrophobic PVDF and PTFE membranes with 0.45 µm pores [1-3]. The transport of lignin from the feed compartment to the stripping one was measured and compared with those of other components (for example, monosaccharides such as glucose or xylose) to determine the selectivity of each membrane and its stability.

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