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Paper-ID 46676

Paper title A green biorefinery method for hardwood valorization based on reactions catalyzed by acids and enzymes

Presentation format Poster

Date of submission 30.01.2017 13:17 Uhr

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Content

The current demand for chemicals, fuels and advanced materials is supplied by products manufactured from fossil resources, which pose a number of problems derived from sustainability, mainly related to the declining reserves and environmental impact (particularly, the emissions of CO₂).

A sustainable development of the chemical industry requires to switch from fossil resources to renewable raw materials, and the processing of these later by green technologies enabling their integrated benefit.

Lignocellulosic materials are the most important renewable source of organic carbon in earth, and can be fractionated into their major components (according to the biorefinery concept), and further converted in an array of chemicals, fuels or materials. When the fraction to be processed is rich in polysaccharides and/or oligosaccharides made up of hexoses, the platform chemicals levulinic acid (LA) and hydroxymethylfurfural (HMF) can be obtained by coupling hydrolysis and dehydration reactions. Usually, when using fractions derived from cellulose or glucomannan, the yields in LA and/or HMF achievable in practice are far below the stoichiometric ones, due to the effects of side reactions leading to the consumption of substrates and/or HMF (leading, for example, to the formation of humins). The results are better when fructose (and not glucose or mannose) are employed as substrates for manufacturing HMF and/or LA, since the kinetic mechanism is simpler (no sugar isomerization stage is needed), suggesting the idea that overall improvements could be obtained by implementing a glucose isomerization stage before dehydration.

This work deals with a biorefinery scheme for levulinic acid manufacture based on consecutive stages of fractionation, enzymatic hydrolysis of the resulting solid to produce glucose, enzymatic isomerization of glucose into fructose, and acidic processing of the resulting solutions. Following this strategy, hardwood samples were subjected to aqueous pretreatments under different conditions for hemicellulose solubilization and for improving the susceptibility of the cellulose-rich solid to enzymatic hydrolysis. Hemicellulose-free, cellulose-enriched solids resulting from aqueous wood fractionation performed under selected conditions were treated with alkaline solutions, and hydrolyzed to yield glucose solutions. These later were treated with immobilized glucose-isomerase for obtaining fructose-containing solutions, which were subjected to dehydration-rehydration for levulinic acid production.

Paper-ID 49691
Paper title Bio-butanol production from agricultural waste hydrolysates using *Clostridium saccharobutylicum*
Presentation format Poster
Date of submission 30.01.2017 15:25 Uhr
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Content

Most of soybean seed coats and sugarcane bagasse produced in Thailand each year are sold as a low value product for animal feed. The components of these were complex carbohydrates [1]. In recent years, attention has been focused on the utilization of these wastes to create higher value products. Butanol, a product of acetone butanol ethanol (ABE) fermentation, is an excellent feedstock chemical in the plastics, food and fuel industries [2]. It is produced by fermentation using the anaerobic bacterial *Clostridium* strains [3]. The aim of this study was to demonstrate the feasibility of using soybean seed coats and sugarcane bagasse as carbon source for bio-butanol fermentation. In these studies, acetone butanol ethanol (ABE) was produced from both waste hydrolyzate in batch cultures using *Clostridium saccharobutylicum* ATCC BAA 117. Thermal pretreatment for lignocellulosic biomass was investigated. The acid used to hydrolyze pretreated soybean seed coats and sugarcane bagasse to fermentable sugars was optimized. Hydrolysis parameters (acid concentration, solid to liquid ratios, and reaction time) was investigated with respect to reducing sugar and inhibitor yields [4]. In control fermentation 48.3 g L⁻¹ glucose (initial sugar 60.0 g L⁻¹) was used to produce 21.04 g L⁻¹ ABE with a productivity and yield of 0.31 g L⁻¹ h⁻¹ and 0.41, respectively. Fermentation of both untreated hydrolyzate exhibited no cell growth and no ABE production. Inhibitors present in untreated hydrolyzate were removed by overliming with Ca (OH)². After detoxification, the culture was able to produce 23.22 and 20.74 g L⁻¹ ABE from soybean and sugarcane bagasse hydrolyzate. The results demonstrate that *Clostridium saccharobutylicum* ATCC BAA 117 has good capacity to convert biomass derived sugars from these wastes to solvents efficiently.

Reference

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Paper-ID	52676
Paper title	Catalysis meets non-thermal separation for the production of (alkyl)phenols and hydrocarbons from pyrolysis oil
Presentation format	Oral presentation
Date of submission	30.01.2017 17:02 Uhr
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Content

To ensure high profitability in the petroleum industry, it is crucial to maximize the revenue obtained from both fuels and petrochemicals. Relying on just 3.4 wt% of the crude oil feedstock, such chemicals amount to approximately the same monetary value as the fuel output, which consumes 70.6 wt% of the crude oil [1]. The same strategy should be applied to the valorisation of lignocellulosic biomass, in order to realize the full economic potential of the biorefinery, and to lower CO₂ emissions from transportation. To produce high-quality chemicals from biomass, separation/fractionation is normally an energy-consuming first step due to the complex native structure of lignocellulosic biomass, i.e., an framework containing cellulose (a regular, linear polymer of repeated glucopyranose units), hemicellulose (a polymer of pentose and hexose sugars, partly functionalized) and lignin (a water-insoluble polymer of oxygenated aromatic monomer units). One well-established procedure is separation of the holocellulose and lignin fractions, followed by depolymerization and dehydration to develop furan-derived chemicals. Nevertheless for application at large scale the cost of this pre-separation is excessive, therefore a strategy based on whole biomass is preferable.

Herein, a simple and kinetically-controlled MoC_x/C-catalyzed hydrodeoxygenation strategy is described, to separate high-value alkylphenols and hydrocarbons from thermal pyrolysis bio-oil. The overall process is efficient, demanding only low pressures of hydrogen gas (5 bar). The resultant products – phenol and alkylphenols – may be easily separated from the product mixture, serving as important potential feedstocks for industry. The strategy requires no prior fractionation of the lignocellulosic biomass, no further synthetic steps, and no input of additional (e.g. petrochemical) platform molecules, as shown in figure 1.

Initially, an investigation using model compounds indicates that MoC_x/C is a promising catalyst for targeted HDO, selectively retaining the desired Ar–OH substituents. Applying this procedure to pyrolysis bio-oil, the primary products – phenol/4-alkylphenols and hydrocarbons – are easily separable from each other by short-path column chromatography. Instead of the pre-separation of lignin and holocellulose, the low-cost non-thermal separation of the product mixture can easily be undertaken in our system to afford the desired alkylphenols from lignin, serving as an important potential feedstock for industry. The integrated procedure could offer significant economic benefits relative to a simple biomass-to-fuel strategy, on account both of the decreased hydrogen consumption and the high value of the (alkyl)phenol products. The extent of this contribution to profitability is hard to assess without a more detailed process layout, but the result of this development represents an attractive approach for generating value-added products from LC biomass.



Paper-ID 54166
Paper title Dilute acid hydrolysis of cellulose assisted by microwave: how chlorine plays an important role
Presentation format Poster
Date of submission 30.01.2017 17:42 Uhr
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Content

Direct combustion remains as the main exploitation route for lignocellulosic materials. However, the different fractions of biomass have a great potential for the production of a wide range of chemical products. Biomass' main component, cellulose, is considered as the main abundant polymeric raw material on Earth.

Different approaches have been suggested for cellulose hydrolysis, among them the most widespread is enzymatic treatment [1]. Nevertheless, high enzyme cost, strict control of temperature and pH are the current disadvantages which increase the expenses of the final product [2]. Due to its energy efficiency, low reaction times and scalability, microwave technology is a good candidate for replacing enzymatic hydrolysis.

Recently, cellulose hydrolysis assisted by microwave has gained more attention. Most of these studies are carried out in aqueous phase, and the parameters which are analyzed are microwave power, irradiation time, catalyst nature, catalyst concentration and cellulose loadings. However, not so many studies concerning the influence of electrolytes present in this aqueous media. Chlorine has been reported to breakdown the hydrogen bond network of cellulose and speeding up cellulose conversion into monomers [3].

In this study, we show how small concentrations of chlorine enhance cellulose hydrolysis, even at short reactions times. As a result, the addition of an inexpensive salt such NaCl, reduces the processing times leading to a more sustainable processes. The comparison with other inorganics salts leads us to elucidate the differences between the diverse effects that may be responsible for such improvements. We suggest that destabilization of the hydrogen bond network of cellulose, increasing ionic conduction of the solution or stabilization of intermediate products might facilitate cellulose hydrolysis. We also observed that electrolytes have also an influence on the further degradation of glucose, leading to formation of levulinic acid and formic acid.

Consequently we purpose that just by adding small concentrations of inorganic salts, the processing times can be reduced, the selectivity towards certain products can be tuned and more energy efficient processes can be achieved.

References

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Paper-ID 66566
Paper title Optimisation of Orange Peel Waste Batch Saccharification: Enzyme Cocktails and Solid/Liquid Ratio
Presentation format Poster
Date of submission 31.01.2017 15:43 Uhr
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Content

Introduction

Residues from the industrial processing of oranges (OPW) summed up to 20 MM tonnes in 2015. This residue is characterised by a sponge structure and a high humidity [1], and it is a source of essential oils, phenolics and carbohydrates. However, very active enzyme cocktails and adequate processing are essential for economical feasibility, increasing glucose and other C6 and C5 monosaccharides at the lowest possible amount of cellulases and auxiliary enzymes, the lowest input of energy and the highest ratio of dry solid to liquid. In this work, these variables are studied.

Experimental

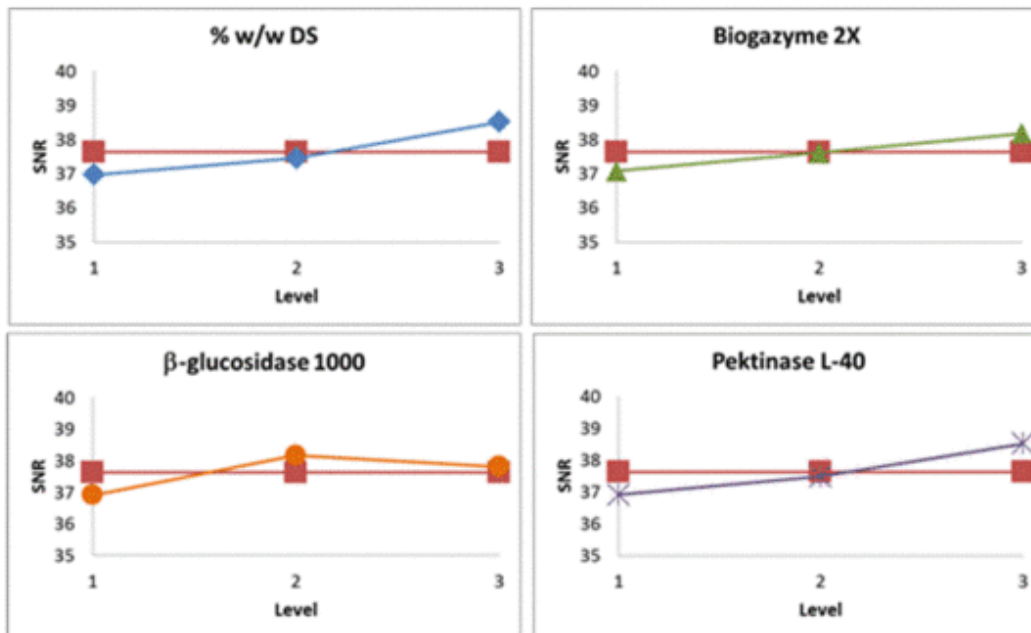
Orange peel wastes (OPW) were pretreated by wet blade milling (final $d_p \leq 2$ mm) followed by partial infrared drying till 66 % humidity. Afterwards, the application of Taguchi experimental design to 4 factors/variables (solid/liquid ratio, amount of cellulases, amount of beta-glucosidases and hemicellulases and amount of pectinase), with 3 levels per factor resulted in 9 duplicated runs (L9 matrix) and 2 confirmation runs with the best conditions for maxima total and saccharification yields, and maxima values for glucose, fructose and total carbohydrates. All runs were carried out in magnetically shaken cylindrical tubes with dry solid to liquid ratio changing from 7 to 12.5 % at low enzymatic activities, withdrawing samples from 0 to 150 hours. The liquid fraction was analysed by HPLC, using a H⁺ Rezex column as stationary phase and a 0.005 M sulphuric acid aqueous solution as eluent.

Results

Taking into account the results from the L9 Taguchi matrix runs for the yields, it is convenient to use maxima dry solid to liquid ratio, pectinase quantity (23.6 PG UI/g dry solid), and amount of glucanases (12 FPU/g dry solid), and medium amounts of beta-glucosidases and the auxiliary hemicellulases that are mixed with them (0.024 CBU/g dry solid). This was confirmed by the final runs, with a total yield of 98.1 % and a saccharification yield of 97.8 %, working with 12.5 % dry solid to liquid ratio and 0.63 mg total enzymatic protein per gram dry solid (Figure 1).

Literature

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Enzyme cocktail	Cellulases	β-glucosidase + hemicellulases	Pektinases	Y_T (%)	Y_S (%)	
B/bglu/PL40	28.44 FPU/g DS	2.44 β-glu UI/g DS	147 pec UI/ g DS	98.1	97.8	
Run	Enzyme cost (€)	glucose (g/L)	fructose (g/L)	glu+fru (kg/10 L)	fru (glu+fru)	Enzyme cost (€/kg glu +fru)
B/bglu/PL40	0.3059	44.42	35.12	0.7954	0.44	0.38

Figure 1. Taguchi L9x2 tendencies and results of optimum experiments concerning enzymes and their activities, enzyme cost estimation per kilogram glucose+fructose, glucose and fructose final concentrations, and total and saccharification yields to glucose.

Paper-ID 63106
Paper title Pine bark biorefinery: A source of valuable chemicals
Presentation format Oral presentation
Date of submission 30.01.2017 23:40 Uhr
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Content

Tree bark represents the first line of defense against severe weather and pathogens, among others, as it contains a wide range of secondary metabolites with defined biological functions, which could potentially benefit human beings. In this sense, the bark of *Pinus radiata* has been extensively studied.

In the Technological Development Unit (UDT) of the Universidad de Concepción, Chile, we have been working for more than a decade on the development of a technology for the extraction of tannins from pine bark and their use as not only as antioxidants but also as a component of adhesive resins for wood. We have developed various formulations to date, including various types of crosslinkers, which have been used at laboratory, pilot and industrial level and the first commercial extraction plant is under construction.

In this study, we propose a broader use of the raw material, extracting in the first stage components of medium polarity and low molecular weight, mainly monomeric polyphenols, such as catechin, taxifolin, quercetin and piceatannol, using ethyl acetate as a solvent. The second stage considers the extraction of condensed tannins, using concentrated methanol that allows to minimize the extraction of unwanted carbohydrates. The yield of the first stage varies between 6 and 8% based on the dry bark and the second between 15 and 20%, depending on the age of the tree, the time elapsed since debarking and the granulometry of the material, among many other factors.

In this way, we propose a biorefinery based on pine bark, a massive raw material with high availability in Chile, whose commercial value does not exceed 25 US \$ / t in dry basis.

Paper-ID 46551
Paper title Production of 5-hydroxymethylfurfural from cellulosic substrates in catalyzed ionic liquids
Presentation format Poster
Date of submission 30.01.2017 13:00 Uhr
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Content

5-hydroxymethylfurfural (HMF) is an important value-added chemical with a bright future in the scope of the sustainable development, since it can be obtained from renewable sources (typically, hexose-containing polysaccharides in vegetal biomass) through efficient processes based on green technologies.

Most reported studies on HMF manufacture deal with reaction in aqueous media catalyzed with acids. As an alternative approach, recent studies have proposed the conversion of the cellulosic fraction of selected biomass types in reaction media made up of ionic liquids, looking for sustainable and green technologies leading to improved yields operating under milder operational conditions.

Implementing this approach requires the previous fractionation of the raw material, in order to accomplish (at least) the separation of hemicelluloses (which would be degraded in the subsequent reactions leading to HMF formation). An autohydrolysis stage is suitable for this purpose, as it enables an extensive and selective solubilization of hemicelluloses while leaving both lignin and cellulose in solid phase. On the other hand, the autohydrolysis reaction also causes chemical and physicochemical alterations of the solid phase, decreasing both the degree of polymerization and the crystallinity structure of the cellulosic fraction, in a way that its reactivity is improved.

This work provides an experimental assessment on the production of 5-hydroxymethylfurfural in catalyzed ionic liquid from pure cellulose (employed as a reference substrate) and hemicellulose-free wood samples (obtained as the solid phases from wood autohydrolysis treatments performed under conditions leading to the optimal generation of hemicellulosic saccharides).

In experiments, the selected substrates were treated in media containing the ionic liquid 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and catalytic species (CrCl₃ or CrCl₃-LiCl mixtures). The effects of selected influential variables (temperature, reaction time, type and concentration of catalyst, presence/absence of externally added water) on the conversion of substrates and HMF generation was assessed.

The experimental results enabled the identification of operational conditions leading to high yields in HMF. The maximum molar conversion of cellulose into HMF reached values near 50% (concentration, 30.6 g HMF /L) operating at 140 °C for 120 minutes or at 160 °C for 45 min in the presence of CrCl₃ (at a charge of 0.5 g/100 g [bmim]Cl). Addition of water or LiCl to the reaction media resulted in molar conversions in the range 47-48%. The experiments performed with hemicellulose-free wood instead of cellulose led to closely related conversions.