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Research paper

Efficiency of acetic acid and formic acid as a catalyst in catalytical and mechanocatalytical pretreatment of barley straw

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ABSTRACT

In this study, the potential of organic acids (formic acid, acetic acid) in a catalytical and mechanocatalytic conversion of lignocellulosic barley straw to valuable sugars is explored using sulfuric acid as a reference. Acid-catalyzed hydrolysis has been carried out with acid-impregnated samples as well as unmodified barley straw. In the mechanocatalytical approach, pretreatment consists of impregnation with the acid catalyst and mechanical treatment by ball milling following chemical hydrolysis. Straw samples and residues were analyzed by Fourier transform infrared spectrometry (FT-IR) whereas hydrolysate analysis was based on total reducing sugar (TRS) determination following the DNS method and capillary electrophoresis (CE) analysis. The results indicated that acetic acid and formic acid are rather mild acids yielding low TRS levels compared to the reference acid. Mechanocatalytical pretreatment slightly increased TRS yields, but not significantly. Strikingly, sulfuric acid showed an efficient conversion efficiency yielding almost 45% of TRS. Furthermore, this study provided evidence for the acetylation of straw components when acetic acid was used as catalyst. Alkali hydrolysis induced the de-esterification, but revealed no significant increase of TRS yields.

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1. Introduction

Strengthening the commitment of renewable energy sources is one of the major bioeconomy challenges in order to safeguard a sufficient supply of energy and to reduce greenhouse gas emissions. The European Commission states the binding target in the EU's Renewable Energy Directive (2009/28/EC) that 20% of final energy consumption should be derived from renewable sources as well as a minimum of 10% of transportation fuels, both by 2020 [1]. Moreover the targets for 2030 include at least a 27% share of renewable energy consumption, a 30% improvement in energy efficiency as well as a 40% cut in greenhouse gas emissions compared to the levels in 1990 [2]. Biomass is a strong growing stock of natural raw material source which has high potential for contribution in the sustainable production of energy, biofuels and biochemicals. Generation of bioenergy from renewable resources lowers CO_2 emissions and decreases the dependence on energy imports and fossil materials whose reservoirs are about to run out.

Biomass can be efficiently recycled by catalytic conversion to carbohydrates which can in turn be converted to biofuels such as ethanol and butanol, e.g. by gasification (Fischer-Tropsch process) or fermentation [3]. These days, bioethanol production derives predominantly from the turnover of food supply chain products such as corn, beet and cane sugar. This is clearly not sustainable and conflicts with food and feed production security. Biomass does not interfere with food production. In this study, barley straw is explored for its potential as a raw material for catalytic and mechanocatalytic conversion to valuable sugars. Barley straw, as a second generation biomass, belongs to the lignocellulosic resources group whereas starch and sugar-based raw materials represent first generation biomass.

Currently, less commercial technological applications for biofuel production exist which requires the establishment of innovative techniques. The present research aims at the determination of the efficiency of acetic acid and formic acid as a catalyst in catalytic and mechanocatalytic fractionation of lignocellulosic barley straw to valuable carbohydrates. The mechanocatalytic approach, schematically illustrated in Fig. 1, is carried out under solvent-free

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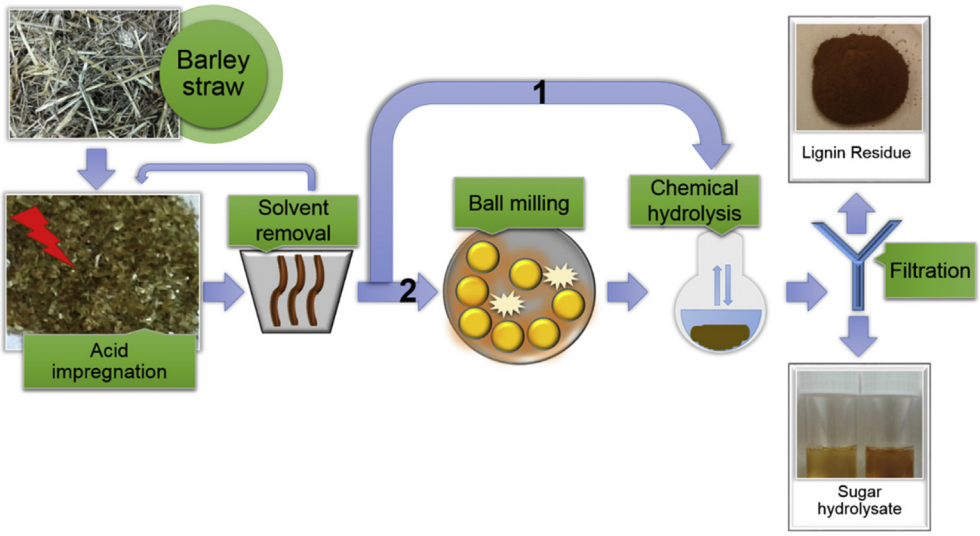

Fig. 1. Scheme of the fractionation of lignocellulosic barley straw excluding (1) and including (2) mechanical treatment using a ball mill.

conditions by the combination of chemical catalysis and mechanical assisted processing. The conversion of lignocellulosic barley straw into sugars is a two-step process which includes the impregnation of the material with an acid catalyst in the first step and mechanical treatment driven by milling in the second leading to the disruption of the lignocellulosic matrix [4]. Resulting oligosaccharides from the conversion reaction are hydrolyzed yielding monosaccharides [3]. These mechanocatalytically obtained sugars constitute the basic product for the formation of biofuels with high conversion efficiency.

2. Material and methods

2.1. Raw materials

Barley straw examined in the present study was provided from a local Finnish farmer. The straw was dried and grinded to a particle size of 0.5 mm using a Retsch SM100 Comfort cutting mill. Other chemicals included: Formic acid (98–100%, Merck), acetic acid (99–100%, J.T.Baker), sulfuric acid (95%, VWR), sodium hydroxide pellets (Merck), ammonium hydroxide (25%, J.T. Baker).

2.2. Mechanocatalytical pretreatment

The acid catalyst (2 mmol per gram straw) was dissolved in 150 mL diethyl ether. 10 g of barley straw sample was added to the acid solution and kept for 30 min shaking at room temperature (Stuart orbital incubator S1500, 170 rpm). The solvent was removed using a vacuum rotary evaporator (Heidolph Laborota 4010 digital, 40 °C). Dry acid-impregnated straw (2.4 g) was applied to a stainless steel container (45 mL, 16 milling balls each 2.93 g and 1 cm in diameter) and grinded in a ball mill (Fritsch premium line Pulverisette 7) at 800 rpm. The grinding time was set at 1 h including 12 cycles of 5 min grinding and a break time of 10 min in order to avoid overheating and burning of the sample. The temperature was controlled manually after every run (TM-903 LT Lutron).

2.3. Acid-catalyzed hydrolysis

Acid hydrolysis was carried out without any further addition of acid catalyst with the pretreated barley straw. Pretreated straw samples of 5 wt% in distilled water were hydrolyzed for 1 h either by shaking at room temperature (RT) or by heating in an oil bath at 100 °C. The hydrolysis causes the formation of a precipitate which is separated from the sugar solution by filtration. Additionally, direct hydrolysis of the non-impregnated straw has been performed by adding the acid catalyst directly to the 5 wt% suspension without prior impregnation and mechanical pretreatment.

2.4. Alkali hydrolysis

Alkali hydrolysis was carried out with either 1 M sodium hydroxide (2 mL) or 25% ammonium hydroxide in a 5 wt% sample suspension with a total volume of 10 mL. The samples were hydrolyzed for 1 h either by shaking at room temperature or by heating in an oil bath at 100 °C. Additionally, direct hydrolysis of unmodified straw has been performed by adding the base catalyst directly to the 5 wt% suspension without prior impregnation and mechanical pretreatment.

2.5. Analytical methods

2.5.1. Determination of acid loading by titration

Acid loading of the impregnate was determined by titration. 1 g of straw impregnate was suspended in 40 mL of distilled water and titrated with 0.01 M and 0.1 M NaOH for organic acid-impregnated and sulfuric acid-impregnated straw, respectively.

2.5.2. Elemental and structural analysis

The total carbon content (TC) of the dry straw sample was determined by elemental analysis with a Perkin Elmer CHNS analyzer. Structural analysis of the raw materials were carried out by Fourier transform infrared spectrometry (FT-IR) which provided detailed information on the chemical bonds in the molecules.

2.5.3. Barley straw composition analysis

The composition fractionation process was carried out following a modified method from Chen et al. and Sun et al. [5,6]. Ethanol extraction according to Chen et al. was performed by suspending barley straw, 10 g, in ethanol 100 mL (in a volume ratio of 60%), adding sodium hydroxide in a weight ratio of 0.5% and then heating at 100 °C for 2 h. The residue, consisting of holocellulose, was separated from the supernatant by vacuum filtration, washed with distilled water until the filtrate was neutral and then air-dried.

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