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# Steam refining as an alternative to steam explosion

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ABSTRACT

In steam pretreatment the defibration is usually achieved by an explosion at the end of the treatment, but can also be carried out in a subsequent refiner step.

A steam explosion and a steam refining unit were compared by using the same raw material and pretreatment conditions, i.e. temperature and time. Smaller particle size was needed for the steam explosion unit to obtain homogenous slurries without considerable amounts of solid chips. A higher amount of volatiles could be condensed from the vapour phase after steam refining. The results from enzymatic hydrolysis showed no significant differences. It could be shown that, beside the chemical changes in the cell wall, the decrease of the particle size is the decisive factor to enhance the enzymatic accessibility while the explosion effect is not required.



## 1. Introduction

Severe steaming is considered as a promising pretreatment method to enhance the accessibility of lignocellulosic material for enzymatic hydrolysis. During steaming, hemicelluloses are subjected to partial degradation by autohydrolysis. The lignin is delocalized and coagulated, thereby opening the structure and increasing the pore size of the cell wall (Excoffier et al., 1991; Michalowicz et al., 1991). Furthermore, steam pretreatment is an energy-efficient method to reduce the particle size and increase the accessible surface of the raw material (Holtzapple et al., 1989). The defibration of the material is usually achieved by an explosion at the end of the treatment as can be seen in several patents and publications (Mamers and Rowney, 1978; Pschorn et al., 2008, 2011; Sun and Cheng, 2002). Refining of the pretreated material in a laboratory defibrator is a possible alternative to the explosion. This kind of equipment was used for pretreatment for enzymatic hydrolysis and for the production of chemicals (Klupsch et al., 2001; Puls et al., 1985).

There are controversial opinions in the literature, whether explosion after the steaming does increase the efficiency of the enzymatic hydrolysis. Brownell et al. (1986) found no significant differences in the overall sugar yield after enzymatic hydrolysis after steam treatment of aspen wood at 240 °C for 3 min, whether the explosion was from full steam pressure or most of the steam was vented through a needle valve. Li et al. (2005) compared steam explosion of wood chips with steam treatment of wood meal in an autoclave and got higher sugar yields for steam exploded wood. However, the raw material and the severity of the treatments differed substantially between the different methods.

The present study aimed to compare the pretreatment with a steam explosion and a steam refining unit, using the same raw material and the same steaming conditions. It should be answered if the different methods lead to significant differences in the overall mass balance and in the carbohydrate yields after enzymatic hydrolysis.

It is generally challenging to compare processes that are carried out in different laboratories with different equipment. One particular problem in batch-wise steaming experiments is the correct collection and analysis of all by-products of the process. Especially volatile compounds such as furans and organic acids are difficult to determine, since losses occur during decompression of the reactor. However, it is of interest to determine the generated amount of these compounds, as they should be collected and used as by-products in an industrial-scale process.

A thorough mass balance of the products and by-products was therefore carried out to determine the effects of both steaming methods.

## 2. Methods

### 2.1. Raw material

Poplar (*Populus balsamifera*) wood chips were obtained from a short rotation plantation in Methau, Saxony (Germany). The

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**Table 1**
Carbohydrate composition and extractives content of the raw material.

| | Wood [%] | Bark [%] | Total raw material [%] |
|---|---|---|---|
| Extract f. Soxhlet | 4.4 | 21.7 | – |
| Glucose | 43.7 | 24.6 | 42.1 |
| Xylose | 14.3 | 8.1 | 13.7 |
| Other sugars[a] | 6.1 | 6.3 | 6.2 |
| Residue | 23.5 | 30.4 | 24.0 |

[a] Mannose, arabinose, galactose, cellobiose, rhamnose, glucuronic acid.

delivered wood chips were up to 20 mm in length and 8 mm in thickness; the material contained ca. 17% bark. Prior to the steaming experiments, the wood chips were further milled in a Retsch mill (Retsch, Haan, Germany) over a 6 mm sieve.

The wood and the bark fractions were analyzed separately by Soxhlet-extraction with acetone according to Tappi standard test method T280 pm-99 and a two-stage acid hydrolysis optimized for monomeric sugar recovery (Puls, 1993). Two hundred milligrams of dry material were hydrolyzed with 2 mL of 72% $H_2SO_4$ at 30 °C for exactly 1 h to break up the crystalline structure of the cellulose. The samples were then diluted with water to a concentration of 4% $H_2SO_4$ and put in an autoclave for 30 min at 120 °C for hydrolysis to monomeric sugars. After cooling, the samples were filtered on a No. 4 sintered glass crucible. The residue was weighed as the acid-insoluble lignin content. The extract content and the carbohydrate composition of the raw material are shown in Table 1.

### 2.2. Steam pretreatments

Steam pretreatment of the poplar wood was studied by varying the temperature (205–215 °C) and the residence time (10–20 min). Severity factors were calculated according to Overend and Chornet (1987) as $\log R_0 = t * \exp(T - 100/14.75)$, where $t$ is the time (min) and $T$ is the temperature (°C) of the treatment.

#### 2.2.1. Steam refining

Steam refining pretreatments were performed in a cylindrical horizontal 10 L reactor with a diameter of 22 cm and a length of 25 cm. The reactor is closed at the front with a cap which is screwed pressure-tight to the reactor. The material input was 300 g air-dried wood (89% dry matter content) per batch. The reactor was equipped with a blade system with four blades reaching over the whole length of the reactor, which could be rotated at 1455 rpm by an electric motor with a rated power of 6.8 kW. The mountings of the motor shaft in the rear wall and in the cap were cooled with water to prevent the shaft from getting stuck. The wall of the reactor contained five sets of bars. At the end of each steam pretreatment, the blade system was rotated for 30 s while the reactor was still under pressure. Thus, a defibration of the softened material occurred between the blades and the bars at the wall of the reactor. After steaming, the pressure was released through a valve, which took about 2–3 min. A flexible pipe was attached to the valve, which was cooled and led into a bin filled with ice water to condense the steam. Two experiments (R210_15D and R210_15E) were carried out without refining at the end of the treatment.

#### 2.2.2. Steam explosion

The steam explosion unit (Cambi, Asker, Norway), described in detail elsewhere (Horn et al., 2011), was equipped with a 20 L reactor and a flash tank with a removable bucket to collect the pretreated material. Defibration of the pretreated material was achieved by a sudden release of the pressure. In the flash tank, the steam exploded material was divided by a cyclone into the fibrous material and the steam containing volatile compounds. The steam was directly led to a cooling circuit with a spray cooler and a condensation tank to recover volatile compounds from the steam. The water in the condensation tank was changed after each experiment to be able to detect the accumulation of volatile compounds depending on the steaming conditions.

Two experiments (E210_15D and E210_15E) were carried out, where the steam was gently released to a pressure of 6 bar before opening the explosion valve. The sudden pressure release from 6 bar was necessary to empty the reactor.

### 2.3. Fractionation of the slurry

The refining reactor was emptied by flushing with additional water. Thereby, a thorough washing of the fibers occurred. The extract formed during the reaction through condensation of the steam was separated from the fibers together with the wash water. Separation of the slurry into the solid fraction (fibers) and the water soluble fraction (extract) was carried out in a spin dryer.

The slurries from steam explosion had substantially higher dry matter contents due to less condensation during the reaction. A portion of the fibers was washed later with 30–40 mL of water $g^{-1}$ of fibers to divide the slurry into the soluble and the non-soluble fraction. The yields of both fractions were calculated based on the raw material input by considering the total weight and the dry matter contents of the fractions. Dry matter contents were determined by drying of the fibers at 105 °C and by freeze-drying of the extracts.

### 2.4. Acid hydrolysis of fibers and extract

Hydrolyses of fiber material and extracts were carried out as follows. The fibers were air dried at 20 °C and 60% air moisture before further analysis. For carbohydrate analysis the fibers were hydrolyzed in a two step hydrolysis, as specified in Section 2.1 for the raw material.

Hydrolysis of the extracts was carried out after freeze-drying. Lyophilized samples (100 mg) were dissolved in 10 mL water, spiked with 1.8 mL of 2 N $H_2SO_4$ (1.5% $H_2SO_4$) and autoclaved at 120 °C for 30 min.

### 2.5. Enzymatic hydrolysis of the fibers

Enzymatic hydrolysis of the fibers was conducted with 300 μL Celluclast 1.5L (Novozymes A/S, Bagsvaerd, Denmark; measured activity of 73 filter paper units (FPU) $mL^{-1}$) and an addition of 50 μL Novozym 188 (Novozymes A/S, Bagsvaerd, Denmark; β-glucosidase) per g substrate. All experiments were carried out at 4% dry matter content in phosphate citrate buffer pH 4.8 for 72 h at 45 °C. Filter paper activity of Celluclast was determined according to the NREL laboratory analytical procedure (Adney and Baker, 1996).

### 2.6. Analyses

For steam explosion experiments the content of furfural and 5-hydroxymethylfurfural (5-HMF) in the extracts and in the condensed vapour phase were analysed by RP-HPLC on an Agilent system Infinity 1290 with separation on a Zorbax Eclipse Plus C18, 2.1 × 50 mm (Agilent Technologies, Santa Clara, CA, USA), conditioned at 25 °C with a gradient of water and acetonitrile as eluent and 0.6 mL $min^{-1}$ flow rate. For the steam refining experiments the same compounds were separated on an Aquasil C18 4.6 × 250 mm (Thermo Scientific, Waltham, MA, USA), conditioned at 35 °C with a gradient of 1 mM phosphoric acid and acetonitrile as eluent and 1 mL $min^{-1}$ flow rate. Both systems were equipped