



# Comparison of pretreatment methods for rye straw in the second generation biorefinery: Effect on cellulose, hemicellulose and lignin recovery



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## HIGHLIGHTS

- Comparison of three water-based pretreatments for bioethanol production from straw.
- C6-, C5-sugar and lignin yields as most important comparison parameters.
- Mass balances for three important components: cellulose, hemicellulose, lignin.
- OS shows the best performance followed by SE and LHW with similar yields.
- All processes showed satisfactory results for the pretreatment of lignocellulose.

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## ABSTRACT

The increasing interest in lignocellulose-based biorefineries boosts the further development of the needed pretreatment methods for preprocessing biomass. There are a large number of different processes that are being investigated; however research is made mostly based on different types of biomass with the same pretreatment or several modifications of the same process for a given type of biomass. In this work a comparison of promising chemical pretreatments using the same biomass was performed. Organosolv (OS), Steam (SE) and Liquid-Hot-Water (LHW) processes were used for the pretreatment of rye straw and the treated solids further enzymatically hydrolyzed. Best results for carbohydrate and lignin yield were found for the OS pretreatment followed close by the LHW and SE with similar results. All of the processes showed satisfactory performance for the pretreatment of lignocellulosic biomass for application in the second generation biorefinery.

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## 1. Introduction

With the further developing of the lignocellulose-based biorefinery, there is an increasing interest in finding the optimum pretreatment conditions for each of the different methods and processes as well as for suitable biomass candidates. This is not an easy task, given the amount of modifications that can be made to a process and the infinite choice in lignocellulose-based materials. Several overviews of pretreatment methods for biorefineries can be found in literature (Hayes, 2009; Himmel and Bayer, 2009; Hu et al., 2008). As mentioned in Kamm and Kamm (2007) the most important characteristics for chemical methods are that they *selectively* and *efficiently* isolate the different components of lignocellulose: cellulose (hexoses for ethanol fermentation), hemicellulose (mainly pentoses) and lignin (phenolic biopolymer).

Selectivity and efficiency are the main requirements for such pretreatments and this is often connected to the use of additives or chemical substances in the pretreatment in order to achieve this goal. This generates a large list of available methods that could be used for the treatment of lignocellulose; however *technical simplicity* and *non-hazardous environments* are highly important as well. In this work, a comparison was made using the same biomass (rye straw) for different promising pretreatment methods, selected due to their selectivity, efficiency, but also because of their technical simplicity and non-hazardous environment.

Ethanol-based Organosolv (OS), water-based Steam (SE) and Liquid-Hot-Water (LHW) pretreatments were tested for rye straw, a common agricultural waste in European countries. The OS pretreatment was originally developed as an alternative pulping method (Chum et al., 1999). A water/solvent mixture is used for the fractionation of the different components of the lignocellulose.

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Mostly operated batchwise, the main variables in process parameters are temperature (180–195 °C), pretreatment time (30–90 min), addition of a catalyst (acid or base mostly) and the liquid-to-biomass ratio (4:1–10:1) (Arato et al., 2005). Under this range of operating conditions, the hemicellulose and lignin go into solution, leaving behind a highly purified cellulose pulp, which can be further hydrolyzed to glucose with an enzymatic treatment.

Another advantage of Organosolv pretreatment is the relatively easy recovery of solvent which can be done through distillation. However, there is a limit on the liquid-to-biomass ratio that can be achieved and the addition of solvents and catalyst represent additional costs and environmental effort. For this, the water-based pretreatments represent another interesting line of chemical processes for modification of lignocellulose using only water.

Due to the changes in its ionic product depending on temperature, water can induce an initial breaking of hemicellulose bondings and a consequent autohydrolysis reaction (Kruse and Dinjus, 2007). There are mainly two types of hydrothermal pretreatments: one based on water as steam (SE) and the other on liquid water under pressure, Liquid-Hot-Water (LHW).

The main parameters of SE treatment are temperature (190–220 °C) and duration (from few seconds to several minutes) (Taherzadeh and Karimi, 2008). SE is mainly operated as batch in laboratory scale; the biomass is loaded in a tank and then brought into contact with steam at the desired temperature. In contrast, the design in industrial scale is based on a continuous reactor followed by an explosion (sudden expansion) or a refining step. In SE, hemicellulose is initially hydrolyzed through the action of steam and this reaction is further catalyzed by the presence of the organic acids formed during treatment (Mosier et al., 2005).

Similar conditions can be found in LHW; an advantage of this method is its operation as semi-batch, which allows a physical separation between the hemicellulose and the pretreated solids streams. Process parameters are temperature (190–220 °C), flow rate and water to biomass ratio (5:1–10:1) (Zetzl et al., 2011). During LHW pretreatment, pressure is kept above the vapor pressure of water in order to keep it in the liquid state. The pre-heated liquid is then passed through a packed bed of biomass (Mosier et al., 2005) starting the hydrolyzing reaction and consequent auto catalyzed extraction of hemicellulose and lignin as in SE. In this work, rye straw was used as lignocellulose feedstock for obtaining optimal operating conditions of the three pretreatment methods (OS, SE and LHW), allowing a direct comparison of their performance.

## 2. Methods

### 2.1. Materials

Rye straw was obtained from a local distributor with the mean particle length of 3–5 mm and 10% humidity. The straw was stored in closed containers at room temperature and was used directly as obtained. The compositional analysis was based on the method explained in Section 2.3 and the material consists of: glucose, 41.6%w; xylose, 25.2%w; other sugars, 3.7%w; lignin, 21.7%w; ashes, 3.9%w and protein, 1.6%w.

Ethanol (94% denaturated) was purchased from AppliChem, sulfuric acid (1 M) from SigmaAldrich and both were used directly as obtained.

### 2.2. Pretreatment methods and enzymatic hydrolysis

#### 2.2.1. Organosolv pretreatment (OS)

Ethanol was used as the organic solvent. The varied process parameters were temperature, acid concentration and duration of

the pretreatment. The biomass load was kept at 1:8 (62.5 g rye straw in a dry basis to 500 g solution) through all the experiments. The water/ethanol ratio in the mixture was kept at 1:1 (50%w). A statistical software (JMP 9.0.0<sup>®</sup>) was used for the design of experiments and for data analysis. The variation of the parameters was selected to cover a range of values so that the experiments were performed at three different levels (high-middle-low) for each of the parameters selected: temperature (190, 180 and 170 °C), sulfuric acid concentration (0, 0.65 and 1.3%w) and time (3, 2 and 1 h). The pretreatment was done in a 1 L batch reactor immersed in a 15 L autoclave filled with water. At the end of the experiment, the 15 L autoclave was cooled down to 100 °C, the pressure released and the autoclave opened. The reactors were taken out, cooled in water and opened. The content of the reactor was then filtered with a Büchner funnel equipped with a filter paper. The pretreated straw was washed with 2 kg of an ethanol–water mixture (50%w) and further treated as described in Section 2.2.4. From the liquid fraction after pretreatment a sample was taken for sugar analysis and the solution then diluted 1:1 with water in order to precipitate the dissolved lignin. The solution was cooled overnight (8 °C) and filtered afterwards. The obtained solids were washed with de-ionized water at 40 °C, air dried overnight and then vacuum-dried at 40 °C. The obtained solids were called “Organosolv (OS) lignin”.

#### 2.2.2. Steam pretreatment (SE)

For SE, the varied parameter was processing time, which was set to 10, 20 or 30 min. The procedure is similar as in Schütt et al. (2011, 2012). Temperature was kept at 200 °C and no addition of catalyst was made. The straw (ca. 100 g in dry basis) was loaded in a 10 L reactor (22 cm diameter and 25 cm length). Once it achieved the required pressure, the steam was fed to the reactor for the amount of time required. A four blade system can be found within the reactor, as well as bars on the walls. The blades can be rotated thus putting the straw through a mechanical stress between the blades and the bars. This was done with the reactor under pressure for the last 30 s. of each treatment. After this, the reactor was depressurized, opened and the pretreated straw was collected with the liquid by washing and further separated by centrifugation. The separated solids were further treated as described in section 2.2.4 and the liquid fraction stored for further analysis.

#### 2.2.3. Liquid-Hot-Water pretreatment (LHW)

LHW pretreatment was performed at three different temperatures 180, 200 and 220 °C, the flow rate and biomass to hydrolyzate ratio was kept the same for all experiments (4 mL/min and 1:10). The pressure was kept above 50 bar to assure water was still liquid. Temperature was controlled with an oven. Straw was loaded in a 50 mL fixed bed reactor and heated up to the desired temperature. At this point, pre-heated water was passed through the reactor, cooled down after the reaction zone, depressurized and collected. After the required time, the water flow was stopped, the reactor cooled down, depressurized and the pretreated straw collected. These solids were further treated as described in Section 2.2.4 and the liquid fraction was given a freeze–thaw treatment to induce precipitation of the extracted lignin. The obtained solids were then separated by centrifugation and dried under vacuum at 40 °C. This fraction was called “Aquasolve-Liquid” (AL) Lignin.

#### 2.2.4. Enzymatic hydrolysis of pretreated solids (EH)

The pretreated straw from each experiment was then enzymatically treated. A 5:1 mixture of Celluclast 1.5 (cellulase complex, filter paper activity of 52.1 FPU mL<sup>-1</sup>) and Novozyme 188 (β-glucosidase, activity of 189 CBU mL<sup>-1</sup>, where CBU means “cellobiase units”) were added to 1 g of pretreated straw in 25 mL universal buffer at pH 4.8 and 50 °C for 72 h. The exact amount of the

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