



# Study of process configuration and catalyst concentration in integrated alkaline extrusion of barley straw for bioethanol production



A. Duque\*, P. Manzanares, I. Ballesteros, M.J. Negro, J.M. Oliva, F. Saez, M. Ballesteros

Biofuels Unit, Energy Department-CIEMAT, Avda. Complutense, 40, 28040 Madrid, Spain

## HIGHLIGHTS

- Barley straw was alkali-pretreated and neutralized in a single extrusion process.
- Alkali level and two process configurations (filtration, yes or not) were tested.
- Filtration allows to obtain better enzymatic digestibility of extrudates.
- Good ethanol production by liquefaction plus SSF of pretreated materials.

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## ABSTRACT

Barley straw was pretreated with alkali (NaOH) at increasing NaOH/DM ratios (6–10%) and neutralized in a twin-screw extruder, obtaining a substrate ready for the incubation with enzymes. Two process configurations were evaluated: with and without filtration inside the extruder. The enzymatic digestibility of the pretreated substrates was evaluated and filtration was proved to be beneficial for the enzymatic hydrolysis. A maximum enzymatic hydrolysis yield of 71% was attained for the barley straw pretreated with 8 g NaOH/100 g dry barley straw and filtration inside the extruder. The ethanol production was evaluated on this substrate for increasing solid loadings, 2.5, 15 and 20% (w/v). A global process yield based on ethanol production, including hydrolysis and fermentation, was calculated over the pretreated material in experiments at 20% (w/v) solids, reaching 53% of the maximum theoretical. The concentration of ethanol reached up to 29 g/l in these conditions.

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## 1. Introduction

Lignocellulosic biomass is increasingly being recognized as an important feedstock for the production of biofuels and chemicals by contributing to environmental sustainability and not competing with food production [1]. Particularly, bioethanol produced from lignocellulose by biochemical pathway (*cellulosic ethanol*) is foreseen to become one of the most credible alternatives to meet bioethanol supply targets in the next years in a sustainable way [2]. A great effort has been devoted in the past decades to overcome the technological and process-based barriers present in the different stages of the cellulosic ethanol value chain, i.e., pretreatment, hydrolysis, fermentation and distillation. However, the highly-structured and recalcitrant nature of lignocellulose remains as an important bottleneck in the conversion process and thus any advances in the pretreatment step will undoubtedly contribute to optimize hydrolysis and further processing downstream opera-

tions [3]. Several pretreatment approaches based on elevated temperatures and/or high concentration of chemicals such as solvents, acids, etc. have been proven to effectively fractionate lignocellulosic biomass and extensive literature has been published on this subject in past years [4–8]. Recently, thermo-mechanical extrusion process has been claimed as an interesting and alternative method for fractionation of lignocellulosic biomass based on it can be applied at relatively mild process conditions and operates in continuous way [9]. It provides high shear, rapid heat transfer, effective and rapid mixing, and a continuous throughput and adaptability for many different process configurations [10–12]. One consequence of its versatility is that extrusion can be used alone or combined with other pretreatments or chemicals (reactive extrusion) to enhance its performance.

Concerning reactive extrusion with alkali, two different forms of combining alkaline pretreatment with extrusion have been described in the literature on different biomasses. One is the impregnation of the raw biomass in an alkali solution for a determined period of time, followed by the introduction of this wet biomass into the extruder [10,13–16]. Another way is the addition of

\* Corresponding author. Tel.: +34 91 346 6054.

E-mail address: [aleta.duque@ciemat.es](mailto:aleta.duque@ciemat.es) (A. Duque).

the alkaline solution directly into the extruder [17–20], which allows one-step process operation. The second alternative is more advantageous, considering the reduction in the process time and the higher integration level of this strategy. Particularly for barley straw biomass, the authors proved in a previous work [17] that twin-screw extrusion in combination with alkali directly fed into the extruder effectively fractionates barley straw (BS) biomass into its constituents. Mild temperature and chemicals conditions were used, preventing the formation of inhibitory byproducts coming from the degradation of hemicellulose/lignin. However, it was also shown that the so produced materials (hereinafter, extrudates) need a washing or pH-adjusting step before they can be submitted to enzymatic hydrolysis (EH). Therefore, downstream operations become complicated, meaning a significant drawback from an industrial point of view.

The process strategy followed in the present work is the alkaline extrusion of barley straw by performing continuous alkaline-extrusion at reasonably low NaOH/DM (w/w) ratios ( $R$ ) ranging from 6% to 10% (w/w), with neutralization inside the extruder. These  $R$  values were selected considering the effective results obtained in the former work of alkaline extrusion of BS [17].

The fact that neutralization is performed during extrusion run increases the integration of the pretreatment and allows generating a substrate ready for the enzymatic hydrolysis [21]. However, in this integrated concept the addition of both alkali and acid inside the extruder implies the formation of inorganic salts that remain in the substrate for its subsequent hydrolysis and/or fermentation. Thus, in this work the inclusion of a filtration step inside the extruder was studied aimed at evaluating if a partial removal of such soluble solids affects the yield of carbohydrate hydrolysis upon further incubation of the extrudate with cellulolytic enzymes. The strategy including filtration is compared to one without filtration. The effect of increasing NaOH/DM ratio in the integrated alkaline pretreatment of BS and the inclusion of the filtration step in the performance of enzymatic hydrolysis of extrudate was evaluated in laboratory tests using commercial enzymes.

Moreover, this paper deals with one of the less studied areas in the assessment of the extrusion pretreatment: the evaluation of the ethanol production potential from alkaline extrudates [9]. For this purpose, simultaneous saccharification and fermentation (SSF) experiments at increasing solids loading levels, including a 24 h liquefaction step, were carried out on extrudates generated on the best process conditions. The production of ethanol was measured and the yield of the fermentation process calculated.

## 2. Materials and methods

### 2.1. Raw material

Barley straw biomass (6% moisture content), was provided by Centre for the Development of Renewable Energy Sources (CEDER), (Soria, Spain). Biomass was coarsely-crushed to 5 mm particle size using a laboratory hammer mill (Retsch), homogenized and stored until used.

### 2.2. Alkaline extrusion pretreatment

Extrusion experiments were carried out in a twin-screw extruder (Cletral Processing Platform Evolum<sup>®</sup> 25 A110, Cletral, France) described elsewhere [17]. The extruder was continuously fed with 0.6 kg/h of BS. A solution of NaOH (10% w/v) was pumped into the extruder at variable feeding flows, in order to achieve alkaline ratios of 6, 8 and 10 g NaOH/100 g BS. After alkaline treatment and in the same extrusion run, a solution of H<sub>3</sub>PO<sub>4</sub> (0.1 M) was

introduced for neutralization purposes, in a proportion enough to obtain a pH about 5 at the output, which is an adequate value for the hydrolytic enzymes action in the subsequent step comprised in this work. Temperature was set at 68 °C along the extruder and the speed of the screw was 150 rpm, as in the previous work [17], which means a residence time inside the extruder of about 2 min.

Two process configurations were considered in order to carry out the alkaline pretreatment and neutralization of the biomass: the complete configuration (C) (Fig. 1), in which alkali and acid are sequentially added to the extruder and then extrudate comes out, and the filtered configuration (F) (Fig. 2), which includes a filtration step previous to the output of the extrudate. The position of the inputs and barrels, as well as the screw profile, were adapted and optimized to each of the configurations. In C, alkali is introduced in barrel 1 and acid in barrel 5, while in F alkali is also introduced in barrel 1, but acid is added in barrel 4 and barrel #5 is replaced by a filtering module. Transport screws, bi-lobal paddles and reverse screws were used in order to provide transport, mixing and shearing effects along the extrusion.

An important factor, influencing the effectiveness of the pretreatment is the liquid to solid ratio inside the extruder ( $L/S$ ) [9]. This parameter is calculated as the sum of the liquid flows (NaOH solution for the reaction zone, soda plus acid solution flow in the neutralization zone) entering the extruder, plus the moisture of the raw material, divided by the amount of dry weight barley straw fed to the equipment. It is especially important in the reaction zone (barrels 1–4 in C and 1–3 in F). The values for the  $L/S$  in the reaction and in the neutralization zone for the three soda levels are shown in Table 1.

To stabilize operation conditions, the extruder was operated for 30 min before any sampling was taken. After this time, the extrudates in configuration C and F and the filtrate from configuration F, were collected for at least 30 min to avoid variation in output flow rates. Extrudates were kept in sealed plastic bags and stored at 4 °C until use. A portion of extrudates and filtrates were analyzed for main components and the content in monomeric and oligomeric sugars and potential inhibitors (furfural, hydroxymethyl furfural – HMF, and phenols), respectively, as described below.

### 2.3. Raw and pretreated material characterization

The composition in carbohydrates, acid-insoluble lignin and ash content was determined in raw material and extrudates, according to the laboratory analytical procedures (LAP) for biomass analysis [22] of the National Renewable Energy Laboratory (NREL, CO).

### 2.4. Enzymatic hydrolysis tests

Extrudates from both configurations (C and F) were submitted to enzymatic hydrolysis in 0.05 M sodium citrate buffer (pH 4.8) at 50 °C and 2.5% (w/v) dry extrudate load. Experiments were performed in 100 ml Erlenmeyer flasks on a rotary shaker (Certomat-R B-Braun, Germany) at 150 rpm. Enzymatic cocktail consisting of commercial cellulase boosted with commercial xylanase in a proportion 9:1 (protein content basis) was added in a dosage of 20 mg protein (8 FPU of cellulase)/g dry extrudate. The enzymes were kindly provided by Novozymes A/S (Denmark). Samples were taken at 0 h and then at 24 h and 48 h, when the hydrolysis of the extrudates is completed. After withdrawal, samples were boiled for 10 min to deactivate enzymes before chromatographic analysis. The sample at 0 h is used to determine the amount of sugars coming from the solubilization during extrusion and from the enzymatic preparation. These sugars do not result from the hydrolytic action of enzymes during incubation and therefore, they are sub-

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