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Research paper

Fermentable sugars production from peach tree prunings: Response surface model optimization of NaOH alkaline pretreatment

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ABSTRACT

Among lignocellulosic residues, peach tree prunings are widely abundant in Italy, due to an extensive production and a high yield of prunings per cultivated hectare; thus, it represents an interesting feedstock for no food derived ethanol.

In the whole production process, the pretreatment is the most critical step from technical and economic point of view. In this work peach tree residues were submitted to alkaline pretreatment, in order to maximize the fermentable sugar recovery and thus to maximize the theoretical etOH yield evaluating the best operative conditions in terms of NaOH concentration, temperature, and reaction time.

The analysis is carried out by means of Response Surface Methodology approach, in order to optimize the pretreatment step. The optimal predicted conditions to perform the process were NaOH concentration = 0.200 mol dm^{-3}, temperature = 125 °C and reaction time = 35 min, that allowed to obtain a theoretical ethanol yield of 223 L t^{-1} of dry peach tree pruning.

This theoretical yield can be judged satisfactory in the context of forest and pruning biomass and it could be further increased by a future scale up from laboratory to pilot scale.

1. Introduction

In Italy, peach tree pruning represents one of the most widespread residues from agricultural crops and presents the important feature of a high density production, typically ca. 3 t y^{-1} per cultivated hectare. Peach cultivation occupies approximately 90′000 ha, for a total yearly wood availability of 260 kt [1]. Therefore, among the typical Italian hardwood residues studied in the Literature [2,3], it can be considered an interesting feedstock to be investigated for ethanol production. These reasons, together with its low cost, its geographically wide availability, and the scarce information in Literature were at the basis of the choice of investigation on peach tree prunings.

The structure of lignocellulosic biomass mainly consists in lignin, cellulose, and hemicellulose arranged in cell walls, forming a complex network in which lignin builds a physical protection around the sugar fraction [4]. Therefore, in the biochemical conversion of biomass to ethanol, pretreatment represents the crucial step for the performance of the whole process, because it is able to disrupt the matrix and to release the sugars for the subsequent stages of enzymatic hydrolysis and fermentation [5]. Different pretreatment methods are widely studied, including physical, chemical, and biological pathways or a combination of two or more of them [6–8].

The action of alkaline pretreatment, which belongs to chemical methods, is effective for pretreating lignocellulosic biomass. It consists in reactions of solvation and saponification that have two main effects on the lignocellulosic matrix: at the same time the treatment allows the partial solubilization of lignin and the swelling of the fibers, with a consequential decrease in crystallinity and polymerization degree [9,10].

The alkaline source more often used for alkaline pretreatment is the sodium hydroxide (NaOH), that can be active at room temperature or higher, for a duration from minutes to hours, and at alkaline concentration that usually ranges from 0.125 mol dm^{-3} to 3.750 mol dm^{-3} [11,12].

Recently, innovative technologies have been applied to improve the efficiency of alkaline pretreatment, with the goal to enhance the yield of the enzymatic hydrolysis [13,14].

Compared to other pretreatment processes, alkaline pretreatment shows several advantages including low operation cost and milder operative conditions, with reduction of formation of inhibitor compounds

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for downstream processing [15–17]. Moreover, several studies demonstrated that this process could represent a feasible approach to increase the fermentation yield and to simplify the bioconversion scheme [18,19].

On the other hand, the main disadvantages of sodium hydroxide alkaline pretreatment are the high alkali loading, the long pretreatment time, and above all the generation of a large volume of wastewater from washing [20].

In this light, the pretreatment optimization would be a necessary step towards the sustainability of the entire process. This was possible through the implementation of a Response Surface Method in three steps: (1) collect data in input on the basis of a statistically designed experimental plan, (2) correlate the experimental data with a regression model, (3) predict the values of response variables in output [21].

In the present paper, by means of a central composite experimental design, we investigated the effect of the three main operative parameters on the ethanol yield: NaOH concentration (from $0.200\ mol\ dm^{-3}$ to $2.300\ mol\ dm^{-3}$), residence time (from 20 min to 70 min), and reaction temperature (from 75 °C to 125 °C) [22].

The aim of the paper is the optimization of the alkaline pretreatment, in order to find the best operative conditions to maximize the fermentable sugar recovery and to estimate, on this basis, the maximum theoretical ethanol yield from peach tree residues. Pretreatment operating parameters were used as input process variables in a Response Surface Methodology design, assessing the response in output in terms of theoretical ethanol yield.

2. Materials and methods

2.1. Feedstock

Peach tree pruned branches, hereafter called "prunings", were collected after the harvest of 2016 in a local farm in Umbria, center Italy (42°47′45" N, 12°24′33" E). In Fig. 1 a view of the peach tree prunings collection site is shown. Biomass was taken from a 10 years old Red Heaven orchard, a yellow-fleshed peach tree cultivar (*Prunus persica* L.). More specifically, branches of one and two years old having born fruits and leaf free were collected and stored in plastic containers suitable for car transportation to the research centre.

The raw material was mechanically reduced to a particle size of 4 mm with a laboratory hammer mill (Retsch SM2000). Then, the biomass was dried at 40 °C in a climatic chamber until the moisture mass fraction was 10% and stored in sealed polyethylene bags for further use. A fraction was milled to powder, size under 500 μm, with a centrifugal mill (Retsch ZM200). Fig. 2 shows the three different fractions: a) the raw material as collected, b) the biomass after the grinding at 4 mm, and c) the sample after the milling under 500 μm.

The biomass was submitted to a preliminary characterization, comprising a thermogravimetric analysis (LECO TGA701), a CHN elemental analysis (LECO TruSpec CHN), and a calorimetric analysis (LECO AC-350). Characterization activity was performed following a set of widely accepted technical standards [23–27].

In order to analyze the chemical composition, in terms of sugars, NREL-LAPs were adopted and adapted to our equipment [28,29].

2.2. Pretreatment

Pretreatment was conducted in $100\ cm^3$ volume glass flasks. The experiments were carried out with a fixed solid slurry concentration (SL) of $50\ g\ dm^{-3}$.

Industrial plants need to operate with high solid concentration, in order to reduce costs, but, on the other hand, the mixing of the material at laboratory scale by shaking is difficult and results reported at solids concentrations above $100\ g\ dm^{-3}$ are scarce. The solution to this problem has been provided by some recent studies, in which it was found that the relationship between initial solid content and sugar conversion after the enzymatic hydrolysis has a nearly linear behavior in the $50–400\ g\ dm^{-3}$ range of the solid loading. This solution allows to use the results obtained at laboratory scale as reliable information for a future scale up of the process [30,31].

All the samples were heated to fixed temperature and kept in an autoclaving system (Nuve OT 90L) for a fixed residence time, on the basis of the particular experimental model implemented. Fig. 3 shows the color difference between samples before and after the treatment with NaOH.

After the pretreatment, the samples were cooled to room temperature and the pH value was measured; then an aliquot of H_2SO_4 ($0.5\ mol\ dm^{-3}$) was added to the pretreated slurry, in order to adjust the pH to ca. 5.0. The pretreated biomass was recovered by vacuum filtration with filter paper with an average pore size of 20–25 μm (Filter-Lab 1249), washed twice with $200\ cm^3$ of deionized water, and oven dried overnight at 40 °C.

2.3. Enzymatic hydrolysis

Pretreated samples were submitted to enzymatic saccharification in

Fig. 1. View of the peach tree pruning collection site.