



# Dilute alkali pretreatment of softwood pine: A biorefinery approach



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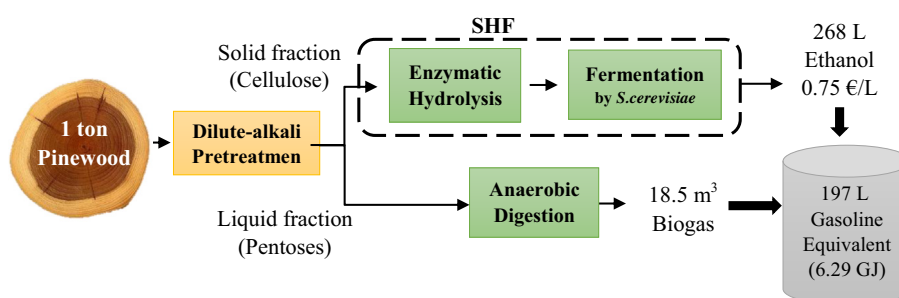
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## HIGHLIGHTS

- Dilute alkali pretreatment enhanced the yield and economy of biofuel production.
- Biogas was produced from hemicelluloses that were not fermentable by *S. cerevisiae*.
- The maximum ethanol yield from the solid fraction of pretreated pinewood was 78%.
- The maximum total energy of 6.29 GJ/ton can be generated from pretreated pinewood.
- Biogas yield and the economic viability were reduced at higher NaOH concentration.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Dilute alkali pretreatment was performed on softwood pine to maximize ethanol and biogas production via a biorefinery approach. Alkali pretreatments were performed with 0–2% w/v NaOH at 100–180 °C for 1–5 h. The liquid fraction of the pretreated substrates was subjected to anaerobic digestion. The solid fraction of the pretreatment was used for separate enzymatic hydrolysis and fermentation. High ethanol yields of 76.9–78.0% were achieved by pretreatment with 2% (w/v) NaOH at 180 °C. The highest biogas yield of 244 mL/g volatile solid (at 25 °C, 1 bar) was achieved by the pretreatment with 1% (w/v) NaOH at 180 °C. The highest gasoline equivalent (sum of ethanol and methane) of 197 L per ton of pinewood and the lowest ethanol manufacturing cost of 0.75 €/L was obtained after pretreatment with 1% NaOH at 180 °C for 5 h. The manufacturing cost of ethanol from untreated wood was 4.12 €/L.

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## 1. Introduction

Ethanol and biomethane are two renewable fuels that can be used in the transportation sector. Currently, ethanol is industrially produced from sugar- or starch-based raw materials. However, due to limited resources of corn and wheat, this has led to a food vs. fuel dilemma (Noori and Karimi, 2016a; Kumar et al., 2016). Lignocellulosic materials such as agricultural and forest residues

are available to a large extent at low prices. These materials have been considered non-food based feedstocks for biofuel production. However, they resist enzymatic or microbial attacks, and a pretreatment step is necessary prior to their enzymatic or biological conversion (Shafiei et al., 2015; Karimi and Taherzadeh, 2016a, 2016b). Alkaline pretreatment by sodium hydroxide is one of the most effective chemical pretreatments for ethanol production (Kim et al., 2016; Karimi et al., 2013). This pretreatment modifies cellulose structure and partially solubilizes hemicellulose and lignin, and thus increases the accessibility of lignocelluloses. Hemicellulose and lignin removal were shown to enhance the

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hydrolysis of lignocelluloses (Karimi et al., 2013; Hendriks and Zeeman, 2009; Menegol et al., 2016). Pretreatment by sodium hydroxide can be performed at severe (0.5–4% NaOH at high temperature) or moderate conditions (at least 6–8% NaOH and low temperature) (Karimi et al., 2013). Considering the high cost of sodium hydroxide, using lower concentrations is economically more favorable. Several NaOH pretreatments of softwoods have been studied by Mirahmadi et al. (2010), Noori and Karimi (2016a), and Salehian and Karimi (2013) with 7–8% NaOH. These studies have revealed that pretreatment with higher concentrations of NaOH was most efficient for agricultural residues and hardwood rather than for softwood of which maximum hydrolysis yields were less than 55% (Mirahmadi et al., 2010; Salehian and Karimi, 2013). Zhao et al. (2008) have investigated presoaking spruce with 12% urea and 3% NaOH. Pretreatment of the presoaked wood with 3% NaOH for 24 h at  $-15^{\circ}\text{C}$  yielded 60% glucose. To our knowledge, no previous investigation has been reported on pretreatment of softwood with dilute NaOH at high temperatures. Additionally, previous studies which were performed at higher alkaline concentrations or lower temperatures did not result in high saccharification yields. Thus, the first aim of this study was to investigate dilute alkali pretreatment of softwood pine at elevated temperatures.

After completion of the pretreatment by NaOH, a slurry containing solid and liquid fractions is produced. The solid fraction is filtered from the liquid fraction (called pre-hydrolysate) and enzymatically hydrolyzed for ethanol fermentation. However, a portion of carbohydrates which are recovered in the pre-hydrolysate are not fermentable by ordinary ethanolic microorganisms, e.g., *Saccharomyces cerevisiae* (Shafiei et al., 2015; FazeliNejad et al., 2016).

In order to have an economically viable process, the pre-hydrolysate portion should be converted to byproducts or products, such as ethanol, methane, or biomass (FazeliNejad et al., 2016; McMillan et al., 1999; Dien et al., 2003). Pre-hydrolysate contains solubilized monomer or short chain carbohydrates. The carbohydrates are mainly solubilized hemicelluloses which have been released during the pretreatment (Karimi et al., 2013). For the conversion of both pentoses and hexoses to ethanol, separate hydrolysis and co-fermentation (SHCF) or simultaneous saccharification and co-fermentation (SSCF) was suggested (McMillan et al., 1999; Dien et al., 2003). Xylose assimilation in the former process suffers from glucose and ethanol inhibition (Taberzadeh and Karimi, 2011; Jin et al., 2012). SSCF process can be performed by two different or one recombinant microorganism (Kumar et al., 2016; Talebnia, 2015). In SSCF, glucose inhibition is reduced; however, ethanol yield in SSCF from both glucose and xylose is considerably lower than that formed from glucose by ordinary yeasts (e.g., *Saccharomyces cerevisiae*) (McMillan et al., 1999; Koppram et al., 2013). Furthermore, differences in the optimal fermentation condition of the two strains, e.g., pH and temperature, and the challenges of using genetically modified organisms, i.e., safety issues and gene instabilities, are practical bottlenecks (Ho et al., 2001; Dien et al., 2000). Therefore, simultaneous conversion of both hexoses and pentoses to ethanol on an industrial scale is still challenging (Kumar et al., 2016; Dien et al., 2003). In this paper, biogas production was suggested as an alternative method to maximize biofuel production since methane contributes to 50–70% of the biogas. A biorefinery for combination of ethanol production from solid fraction and biogas production from pre-hydrolysate was used to maximize the conversion of the available sugars in softwood pine to biofuels. Although many researches were performed on ethanol and biogas production from the solid fraction of pretreated materials; however, to our knowledge, no previous research on biogas production from the pre-hydrolysate obtained in dilute alkali pretreatment has been reported in the literature.

This study was aimed at optimizing dilute sodium hydroxide pretreatment for maximized biofuel production in a biorefinery based on softwood pine. To find the optimum pretreatment conditions, total amounts of energy produced in terms of gasoline equivalent were determined and compared. Furthermore, the effects of alkali pretreatment on the wood structure were investigated. Finally, a preliminary economic assessment for the biorefinery was carried out for determination of the most economically viable pretreatment condition.

## 2. Material and methods

### 2.1. Raw materials

Pinewood (*Pinus eldarica*) was obtained from the city of Delijan (Delijan, Iran,  $33^{\circ}59' \text{N}$ ,  $50^{\circ}41' \text{E}$ ). The wood was debarked, ground, and milled to powder. Afterwards, the milled wood was screened and sieved through 20- and 80-mesh screen to obtain particles less than 1 mm. The dry weight of pinewood powder was measured by oven drying at  $105^{\circ}\text{C}$  (Sluiter et al., 2008a, 2008b).

Two commercial enzymes, Cellic<sup>®</sup> CTec2 (VCNI0013) (as the main source of cellulase and  $\beta$ -glucosidase), and Cellic<sup>®</sup> HTec2 (VHN00002) (as the source of hemicellulase and cellulase) were kindly provided by Novozymes A/S (Bagsvaerd, Denmark). The cellulase activities of the enzymes were measured to 122 and 34 filter paper units (FPU), respectively, based on the filter paper method (Adney and Baker, 1996). A mixture of 90% Cellic<sup>®</sup> CTec2 and 10% Cellic<sup>®</sup> HTec2 was prepared and used in enzymatic hydrolysis. A block flow diagram (BFD) of the procedure that presents the experiments is depicted in Fig. 1. The procedure includes pretreatment, enzymatic hydrolysis, fermentation and anaerobic digestion, which are discussed in the next sections.

### 2.2. Pretreatment

A Pretreatment with dilute sodium hydroxide was performed in a 500 mL high pressure stainless steel batch reactor (Kayhan Steel Sanat Co., Isfahan, Iran) equipped with pressure indicator and thermometer (Amiri et al., 2010). Sodium hydroxide solutions of 0, 1, and 2% w/v were prepared and used for the pretreatment of pinewood powder at the concentration of 10 wt% wood in the final slurry. The pretreatment experiments were performed for 1, 2, and 5 h at 100, 140, and  $180^{\circ}\text{C}$ . Afterwards, the reactor was cooled to about  $70^{\circ}\text{C}$  in an ice chamber. The pretreated solids were separated from the liquid phase by filtration and washed with distilled water until they reached pH 7. Finally, the solid fractions were dried at room temperature for one day and stored in plastic bags.

### 2.3. Neutralization

For biogas-producing bacteria to survive, it is desirable to decrease the alkaline pH to about neutral. Removing the  $\text{Na}^+$  ions from the slurry was also necessary, since these ions at high concentrations have an inhibitory effect on the bacterial consortia even at neutral pH. For neutralization,  $\text{H}_3\text{PO}_4$  was used ( $3 \text{ NaOH} + \text{H}_3\text{PO}_4 \rightarrow \text{Na}_3\text{PO}_4 + 3 \text{ H}_2\text{O}$ ) because of the low solubility of  $\text{Na}_3\text{PO}_4$  salt in water (5.4 g/100 mL). Furthermore, the temperature was decreased to  $0^{\circ}\text{C}$  to further increase salt precipitation.

Neutralization of pre-hydrolysates was performed by the addition of 2 M  $\text{H}_3\text{PO}_4$  to obtain pH 7. Ice chamber was used to decrease the temperature of the mixture. The precipitated lignin and salts of  $\text{Na}_3\text{PO}_4$  were removed by centrifugation and the liquid fractions were kept frozen until use.

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