

From wood wastes to hydrogen – Preparation and catalytic steam reforming of crude bio-ethanol obtained from fir wood



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ABSTRACT

Fir wood wastes were used to produce crude bio-ethanol by two methods: simultaneous saccharification and fermentation (SSF) and acid hydrolysis followed by the fermentation of the acid hydrolyzate. The main components of crude bio-ethanol are ethanol and acetic acid. In addition, low concentrations of a wide range of alcohols, acids, esters, ethers and aldehydes are also present. Ethanol concentration is higher in the SSF process than in the acid hydrolysis: 43.69 g/L compared to 37.53 g/L, respectively. Opposite to ethanol concentration, the acetic acid concentration is higher in the acid hydrolysis process: 16.36 g/L compared to 10.24 g/L, respectively. The crude bio-ethanol was used to produce hydrogen by catalytic steam reforming. The tested catalysts were the common Ni/Al₂O₃ and two rare earth oxides promoted Ni catalysts: Ni/La₂O₃–Al₂O₃ and Ni/CeO₂–Al₂O₃ prepared by successive wet impregnation. The characterization techniques revealed that the addition of rare earth oxides improves the Ni dispersion and the reducibility of the promoted catalysts. The best feed rate which assures the optimal ratio between conversion and catalyst deactivation is 0.8 mL/min bio-ethanol. The addition of extra oxide (La₂O₃ and CeO₂) to the support improves the ethanol conversion especially at 250 °C, but no significant effect on the acetic acid conversion was observed. At 250 °C the ethanol conversion is almost 90% for Ni/La₂O₃–Al₂O₃ and Ni/CeO₂–Al₂O₃, but the acetic acid conversion is below 30% for all catalysts. At 350 °C both ethanol and acetic acid present maximum conversion. At this temperature the best hydrogen production is obtained for Ni/La₂O₃–Al₂O₃ due to better ethanol conversion and better selectivity for hydrogen formation. At 350 °C the promoted catalysts are stable for 4 h time on stream, different degrees of deactivation being obtained at lower temperatures.

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1. Introduction

Woody biomass is the most abundant biomass in the world. In the actual context of intensive quest for environmental friendly energy sources, the woody biomass and especially the wood wastes resulted from forest activities is of special interest. A superior way to add value to these wastes is their transformation in the second generation bio-ethanol, as a way for further transformation in hydrogen and/or syngas. In the actual technologies, the hydrogen generation from lignocelluloses biomass is a two stage process: in the first step raw biomass is converted to hydrogen substrate (i.e. ethanol) and in the second step this is catalytically transformed into hydrogen [1]. Hydrogen is often called “the fuel of the future”

although it is not exactly a fuel but an energy vector. Hydrogen is foreseen by many researchers as a very suitable and environmentally friendly energy carrier [2] due to its possibility to be used in fuel cells for stationary and mobile power generation with practically no hazardous emissions [3]. The so called “hydrogen economy” seems to be a viable alternative in the future to replace the actual fossil fuel based one [4].

Woody biomass has a complex structure having as main components cellulose, hemicellulose and lignin. Generally, the process of the bio-ethanol production includes four steps: pretreatment, hydrolysis, fermentation and distillation [5]. Autohydrolysis pretreatment with compressed hot water is an environmental friendly process in which the selective depolymerization of hemicellulose takes place [6]. Hemicellulose is easily recovered in the liquid fraction as mono- and oligosugars, and cellulose and lignin are separated in the solid fraction (cellulose is more susceptible to hydrolysis). The remaining lignin fraction has a higher affinity for cellulolytic enzymes components, thus resulting in reduced

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hydrolysis efficiency. Therefore, the intercalation of an intermediate step of delignification may be an effective method to promote enzymatic digestibility of wood [7]. The hydrolysis of cellulose is primarily performed either through a chemical or an enzymatic route; in this hydrolysis step cellulose is broken into monomers. The acid hydrolysis is much faster than the enzymatic hydrolysis, this representing an economic advantage. Potential acids that can be used in acid hydrolysis are sulfuric and hydrochloric acids, in concentrate or dilute form [8]. Previous studies showed that dilute acids significantly improve the cellulose hydrolysis, but require high temperature and neutralization of pH [9]. The resulted sugars are fermented to ethanol. Enzymatic hydrolysis and fermentation can be performed together in the so-called simultaneous saccharification and fermentation (SSF) or separately, in two steps: hydrolysis and fermentation (SHF).

The usual route for ethanol transformation into hydrogen is the steam reforming (ESR). Being a catalytic process, the importance of the catalytic materials is well established. The most used catalysts are noble (Rh, Pt, Pd, Au, Ag) [10,11] and non-noble (Ni, Co, Cu) [12,13] metals supported on various oxides (Al_2O_3 , ZrO_2 , CeO_2). Noble metals have the advantage of high catalytic activity and stability, their main drawback being the high production costs. Ni based catalysts are very active for reformation reactions and often used for ESR, their main drawback being the relatively rapid deactivation due to carbon deposition. A series of approaches have been taken to overcome this problem: (i) the addition of small quantities of noble metal to Ni, the resulting bimetallic catalysts presenting improved stability and selectivity for H_2 formation [14]; (ii) the modification of support by addition of other oxides (CaO, MgO, CeO_2 , La_2O_3 , etc) [15–17].

This paper reports for the first time to our best knowledge a comprehensive study of crude bio-ethanol production from fir wood wastes and its subsequent transformation in hydrogen by ethanol steam reforming. Epron et al. reported the steam reforming of a model raw bio-ethanol mixture obtained by the addition of the most common impurities to a solution of ethanol; the composition of crude bio-ethanol obtained in our work is very different from that reported by the group of Epron [18]. In previous papers, the term of bio-ethanol usually defines the pure ethylic alcohol obtained by crop fermentation followed by distillation. In our paper the term of crude bio-ethanol defines the liquid part of the fermentation broth, which contains all the fermentation products, not only ethanol.

2. Materials and methods

2.1. Bio-ethanol production

2.1.1. Materials

The fir (*Albies alba*) wood wastes were collected locally and used as raw material. The dried material was stored in plastic bags at room temperature. Yeast from *Saccharomyces cerevisiae* YSC2 and peptone from animal tissue P5905 were purchased from Sigma–Aldrich (St. Louis, MO, USA). H_2SO_4 (98%), $\text{CH}_3\text{—COOH}$, NaOH, KH_2PO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$ citric acid ($\text{C}_6\text{H}_8\text{O}_7$) were

purchased from Merck (Darmstadt, Germany). NaClO_2 (80%) was purchased from Alfa Aesar GmbH & Co (Karlsruhe, Germany). All chemicals were analytical reagent grade. Ultrapure water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA).

The scheme for bio-ethanol production considered in this work is presented in Fig. 1.

2.1.2. Autohydrolysis pretreatment

The pretreatment of wood was carried out in a steel pressure Parr reactor with a Parr 4523 temperature controller (Parr Instruments, Illinois, USA). The raw material was loaded into a 1 L reaction vessel and was supplemented with an appropriate amount of deionized water to obtain a final solid to liquid ratio of 1:7. The mixture was heated at 190 °C and 60 bar pressure for 10 min residence time. At the end of the reaction, the reactor was cooled and the mixture was separated by filtration into the solid residue and the liquid phase. The pretreatment conditions were selected based on preliminary results, according to our previously published method [19].

2.1.3. Delignification of cellulosic materials

The solid materials recovered after pretreatment were delignified using acid-chlorite method, according to Hallac et al. [20]. The experiments were carried out in 250 mL conical flasks using sodium chlorite (0.6 g/g biomass), acetic acid (0.6 mL/g biomass) and deionized water (84 mL/g biomass). The reactions were carried out at 70 °C for 2 h (repeated for 3 times). The suspension was filtered, washed with water and acetone until neutral pH.

The delignified materials were hydrolyzed with dilute acid followed by fermentation (route II in Fig. 1), or subjected directly to simultaneous saccharification and fermentation (SSF) (route I in Fig. 1) in order to obtain the crude bioethanol.

2.1.4. Dilute acid hydrolysis followed by fermentation of acid hydrolyzate

Acid hydrolysis experiments of the solid residue recovered after delignification of wood were carried out in two steps: (i) in 500 mL conical flasks containing 2% H_2SO_4 at 100 °C for 60 min, and (ii) in 15% H_2SO_4 at 100 °C, for 90 min. After the hydrolysis process, the liquid fractions were separated from unreacted solids and then fermented to bioethanol. The amount of acid used for cellulosic fraction hydrolysis was 38 g of H_2SO_4 to 2 g of dry solid. The fermentation of acid hydrolyzate was performed in 1 L flasks containing 700 mL hydrolyzate obtained above, 70 mL nutrient solution (medium content per liter: 5 g of yeast extract, 20 g of KH_2PO_4 , 10 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 20 g of $(\text{NH}_4)_2\text{SO}_4$ and 1 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), and 70 mL inoculum solution (medium content per liter: 10 g of yeast extract, 20 g of peptone and 50 g of glucose). The initial pH was adjusted to 5.0 by adding NaOH (2 M). All the experiments were carried out at 30 °C for 72 h. The nutrient solution and the inoculum solution were activated and grown at 30 °C for 24 h in an incubator. During the fermentation process, samples were collected to determine the content of ethanol and acetic acid.

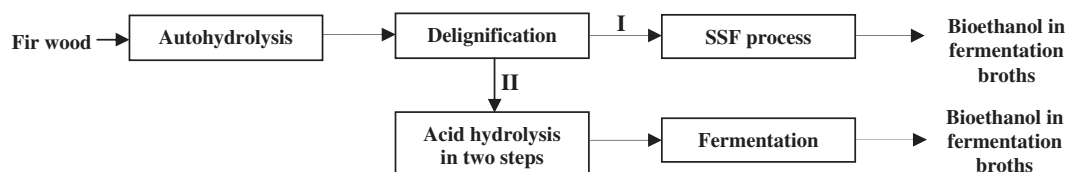


Fig. 1. Schematic representation of different treatments performed for bio-ethanol production from wood wastes.

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