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Supercritical fluids as a green technology for the pretreatment of lignocellulosic biomass

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HIGHLIGHTS

- The effect of moisture content on supercritical pretreatment of rice husk was evaluated.
- Delignification yields of supercritical pretreatment for rice husk were found at the selected conditions.
- It was assessed and compared the crystallinity index of rice husk after supercritical and diluted acid pretreatments.
- Supercritical and conventional pretreatment effects for enzymatic hydrolysis were compared.
- Techno-economic and environmental performance for supercritical and conventional dilute acid pretreatment was developed.

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ABSTRACT

One of the main drawbacks for using lignocellulosic biomass is related to its recalcitrance. The pretreatment of lignocellulosic biomass plays an important role for delignification and crystallinity reduction purposes. In this work rice husk (RH) was submitted to supercritical pretreatment at 80 °C and 270 bar with the aim to determine the effect on lignin content, crystallinity as well as enzymatic digestibility. The yields obtained were compared with dilute sulfuric acid pretreatment as base case. Additionally a techno-economic and environmental comparison of the both pretreatment technologies was performed. The results show a lignin content reduction up to 90.6% for the sample with 75% moisture content using a water–ethanol mixture. The results for crystallinity and enzymatic digestibility demonstrated that no reductions were reached. Supercritical pretreatment presents the best economical and environmental performance considering the solvents and carbon dioxide recycling.

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1. Introduction

Many studies have demonstrated the potential use of biomass as raw material for bioenergy, biofuels, food, feed, fiber needs as well as a wide family of biomolecules under biorefinery approach (Moncada et al., 2014). According to the information reported by the World Energy Council it is presumed that biomass can provide about 16% of the expected energy consumption of 17208 Mtoe in 2020 (World Energy Council, 2013).

The term biomass is defined by ASTM as “any material, excluding fossil fuel which was a living organism that can be used as a fuel either directly or after conversion process” (ASTM, 2002). This term includes a huge range of materials which can be classified in first, second and third generation raw materials. First generation raw materials refer to edible crops used for food or agribusiness purposes. Second generation raw materials are mainly composed of lignocellulosic materials (cellulose, hemicellulose and lignin rich materials) produced during different extraction or transformation stages such as seeding, cropping, harvesting and processing (Rincón et al., 2014). Other sources of second generation raw materials are the non-edible crops. Finally, Microalgae are recognized as third generation raw materials (Ahmad et al., 2011).

Second generation raw materials do not directly compete with food production which is a positive attribute. These materials are organized in a structure in which lignin and hemicellulose form a complex through covalent cross-linked bounds encapsulating and giving support to the cellulose. Despite the high availability of lignocellulosic biomass the main drawback to be overcome for its practical use is related to biomass recalcitrance. Recalcitrance refers to an arrange of features (epidermal plant issues, structural heterogeneity, constituent complexity and degree of lignifications) which plays a structural protection role against microbial attack (Himmel et al., 2007). Another important aspect contributing to

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the biomass recalcitrance is represented by the cellulose crystallinity. Cellulose crystallinity provides to biomass fibers resistance against chemical and biochemical attack.

1.1. Biomass pretreatments

A number of different processes exist to reduce the recalcitrance and cellulose crystallinity of lignocellulosic biomass. Numerous pretreatment technologies are used to make value-added products from biomass including physical, chemical, hydrothermal and biological methods. This topic is so widely covered in open source literature, that it is difficult to establish all the primary authors for each method.

Physical pretreatments are not widely used given the limited effectiveness. However if some chemicals are added as for example sodium azide together with a buffer solution it is possible to decrease the crystallinity of raw materials through size particle reduction. Kim et al. (2013) reported crystallinity reduction in orders of 32% until 78% using this approach. Chemical pretreatments consider the use of acid, alkaline and organic solvents (organosolv) solutions to increase the raw materials digestibility. A summary of typical effects and conventional reagents used in chemical pretreatments is presented in the Table 1.

Hydrothermal pretreatments (Zhang et al., 2012) involve higher temperatures with the aim to fractionate the hemicellulose as well as to increase the material porosity. Steam explosion, steam treatment and liquid hot water treatment are included in this pretreatment category. These pretreatments use temperatures in the range of 160–240 °C. The main effect observed is related to the hemicellulose hydrolysis and lignin breakdown (Ruiz et al., 2008). The shorter reaction times can be recognized as main advantage of these types of pretreatments. Nevertheless, pH value represents an important constraint: for liquid hot water (LWH) the pH should be restricted to 4.0–7.0 to avoid monomeric sugars release during this pretreatment stage (Ruiz et al., 2008; Kim et al., 2009).

Finally, biological pretreatments use different fungi species such as white-rot, brown-rot and soft-rot to produce enzymes degrading lignin and cellulose. Among these enzymes it is identified lignin peroxidase, lacasse, manganese peroxidase (Wang et al., 2013). However, long times (from days to weeks) are required for these methods to get the desired impacts.

Despite the higher yields obtained through conventional pretreatments, a huge range of disadvantages are presented. Among them, it is possible to highlight the release of inhibitory compounds such as furfural, hydroxymethyl furfural, acetic acid among others, the higher energetic costs associated to high temperatures (above 100 °C) and the biomass recovering costs. Other types of pretreatments have been explored as alternatives to reduce operational conditions in terms of reactions severity, residence time, equipment deterioration and its associated costs. Supercritical pretreatment (Lü et al., 2013) among others are innovative proposals recently discussed. This paper studies the effect of supercritical pretreatment as a green technology (based on an inexpensive solvent as CO_2) on the cellulose crystallinity and lignin removal in rice husk. In this sense the description of the effect is presented below as specific introduction to this work.

Table 1
Chemical pretreatments summary.

Pretreatment	Reagents	Treatment effects
Alkaline[a]	Sodium hydroxide, potassium hydroxide, calcium hydroxide, ammonium hydroxide, lime among others	Lignin removal
Dilute acid[b]	Sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid among others	Hemicellulose fractionation
Organosolv[c]	Ethanol, acetic acid, formic acid, peracetic acid with organic and inorganic catalysts	Lignin removal and hemicellulose fractionation
Ionic liquids[d]	Anions from chloride, formate, acetate or alkylphosphonate	Cellulose crystallinity reduction and partial hemicellulose and lignin removal

[a] Park and Kim (2012).
[b] Chandel et al. (2012).
[c] Amiri et al. (2014).
[d] Li et al. (2010).

1.2. Supercritical pretreatment

A supercritical fluid (SF) is any substance above critical conditions (temperature and pressure), exhibiting properties of liquids such as density and gases such as compressibility. Carbon dioxide is the most used supercritical fluid due to its non-toxic, recyclable, low-cost, environmentally friendly characteristics (considering it in a closed loop as a solvent), and low critical temperature and pressure (31.1 °C and 7.36 MPa respectively).

Supercritical and subcritical fluids have been used in pretreatments since seventies as was reported by Bludworth and Knopf (1993) and Reyes et al. (1989) among others. It is known the delignification effect produced by this kind of pretreatments in different types of raw materials such as corn stover (Narayanaswamy et al., 2011), switchgrass (Narayanaswamy et al., 2011), rice straw (Gao et al., 2010), sugarcane bagasse (Pasquini et al., 2005a) among others (Pasquini et al., 2005b). The most important parameters taken into account are the moisture, temperature, pressure and pretreatment time. Water in the biomass combined with supercritical carbon dioxide generates a carbonic acid mixture which generates a kind of weak acidic environment preliminary promoting the hemicellulose hydrolysis and intensifying the mass transfer conditions (Narayanaswamy et al., 2011). Additionally, when water is mixed with other type of solvents the delignification capability is enhanced; for instance, ethanol improves the solubility of lignin fragments (Lü et al., 2013).

According to authors Pasquini et al. (2005a,b) high pressure enhances the interaction between fluids or solvent mixtures and lignocellulosic biomass increasing and promoting the rupture of the bonds connecting lignin with the lignocellulosic matrix. In addition, authors as Pasquini et al. (2005a,b) and Puech et al. (1990) concluded that short reaction times of 30–15 min including heating or pressurizing were enough to obtain good delignification results in presence of water:ethanol mixture.

The aims of the present study were to evaluate the effects of using supercritical carbon dioxide pretreatment of RH and to perform the techno-economic and environmental assessment of the process. To achieve this, sulfuric dilute acid was considered as the base case to compare the composition and digestibility of RH after pretreatment. All the operational conditions were selected taking into account the most sensitive parameters. In this case short pretreatment times as well as relatively moderate temperatures and pressures were used. Both configurations (supercritical pretreatment and the base case) were simulated using commercial simulators and programming packages (mainly Aspen Plus and MatLab) to calculate the energy and mass balances used to assess the production costs (based on the Colombian context) and the environmental behavior.

2. Methods

2.1. Raw material

RH is a non edible agricultural residue generated during the whole grain de-husking process. Approximately 0.23 ton of RH

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