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Review

Sub- and supercritical water hydrolysis of agricultural and food industry residues for the production of fermentable sugars: A review

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ABSTRACT

Bioethanol has been researched as a potential alternative to substitute liquid fossil fuels due to its eco-friendly characteristics and relatively low production cost when compared to other bio-based fuels. First generation bioethanol is produced from raw materials rich in simple sugars or starch, such as sugarcane and corn, which are food sources. To avoid the fuel versus food dilemma, second generation bioethanol aims at using non-edible raw materials, as lignocellulosic agricultural residues, as source of fermentable sugars. Hydrolysis with sub/supercritical water has demonstrated great potential to decompose the lignocellulosic complex into simple sugars with several advantages over conventional processes. This review provides an overview of the state of the art on hydrolysis with sub- and supercritical water in the context of the reuse of agricultural residues to produce suitable fermentation substrates for the production of second generation bioethanol. Recent applications and advances are put into context together, providing an insight into future research trends.

Contents

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1. Introduction

Our society is largely dependent on fossil fuels as energy source. Problems arise from this fact: (i) fossil fuels are non-renewable; (ii) the production of energy from fossil fuels presents some serious environmental consequences; and (iii) only a few countries are self-sufficient in terms of oil production. Considering these aspects, renewable and abundant sources of energy are undoubtedly the key for a sustainable energy supply model. Biofuels derived from biomass are considered the most promising alternative in short to medium term. The current fossil fuel-based manufacturing philosophy is based on the massive production of throwaway products with large requirements of raw materials and energy. On the other hand, for a biomass chemical industry, the philosophy may be moved to local production taking into account the distributed nature of biomass resource available in each region (Cantero et al., 2015e). From the biofuels that can be obtained from biomass, ethanol is usually considered an efficient and economical fuel substitute, or additive, thus representing one of the most important renewable energy sources (Zaldivar et al., 2001).

The first generation ethanol production from sugarcane and corn has seen wide development in the last decades, and tends to continue improving its economic feasibility (Berni et al., 2013). However, the raw materials used in these processes are food sources, which generates controversy on the competitive use of farmable lands by food and fuels industries. To avoid this problem, second generation bioethanol aims at using non-edible raw materials as source of fermentable sugars. The cheapest and most abundant source of non-edible sugars is lignocellulosic agricultural residues.

Agricultural and food industry wastes have a plethora of phytochemicals with commercial interest that can be recovered to decrease the waste generation and to improve the economic feasibility of the main process, by producing secondary streams of value added compounds (Bergeron et al., 2012; Galanakis, 2012, 2013, 2015; Vardanega et al., 2015). Another valuable product present in lignocellulosic materials is sugars.

Several technologies have been developed to recover sugars from lignocellulosic feedstock, but transferring them to industrial scale has proven a challenge. Only in 2013 the first commercial size plant that converts biomass to bioethanol has been launched in Italy; three more plants are under construction in Brazil and another one is planned in China (Vardanega et al., 2015). The process is far from optimized, mainly due to the difficulty of making sugars available for fermentation, since it requires breaking the lignin-hemicellulose bonds to allow direct access for enzymes to cellulose, which further convert it so simple sugars. This is usually achieved by high energy-consuming conversion processes.

The hydrolysis can be carried out by chemical routes, using acid or alkaline catalysts, or by biological routes, using enzyme catalysts. Although acid and alkaline hydrolysis are relatively fast methods that produce high sugars concentrations, the reaction medium must be neutralized after the process, generating solid waste. Other drawbacks include equipment corrosion, poor catalyst recyclability, and sugars degradation. Due to environmental problems posed by these techniques, the enzymatic process is preferred. Besides not generating solid residues, no sugars are degraded during the process, thus no inhibitors of the subsequent fermentation microorganisms are formed. In contrast, the process is slow, which makes it high energy consuming, and the enzymes are difficult to recover and reuse. Furthermore, the enzymes cannot break down the lignocellulosic complex, so this process requires a pretreatment that allows for the enzymes to access the cellulose and the hemicellulose. Different approaches are being tested for the pretreatment: acid, alkali, sulfite, liquid hot water, steam explosion, carbon dioxide explosion, ammonia fiber explosion, ozonolyzis, wet oxidation, ionic liquids, organosolv, microwave and ultrasound (Alvira et al., 2010; Eggeman and Elander, 2005; Huang and Fu, 2013; Langan et al., 2011; Tadesse and Luque, 2011; Taherzadeh and Karimi, 2008; Tomás-Pejó et al., 2011; Yu et al., 2007).

As there is increasing understanding of the processes taking place during biomass hydrolysis, new techniques are being exploited. A physicochemical approach is using sub/supercritical water as reaction medium. This process degrades less sugars than acid and alkali hydrolysis, it does not generate solid residues, it is extremely fast when compared to both acid and enzymatic routes, and it may avoid the pretreatment step required for the enzymatic process. The sub/supercritical water hydrolysis (SCWH) concept was developed in the early 1990s, and is still not optimized. Therefore, the objective of this work is to present the progress that has been made toward making the SCWH process technically feasible for converting lignocellulosic agricultural residues into fermentable sugars.

2. Sub/supercritical water hydrolysis of lignocellulosic biomass

The basic concept of the hydrolysis step in the second generation bioethanol production is the breakdown of