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Production of furfural from pentosan-rich biomass: Analysis of process parameters during simultaneous furfural stripping

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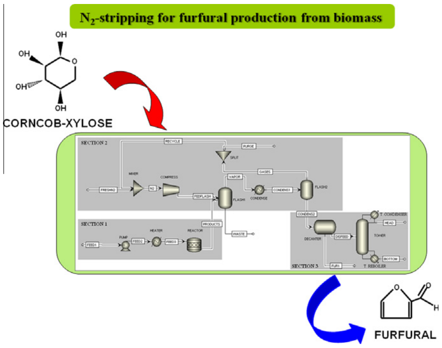
HIGHLIGHTS

- The use of N_2-stripping shows higher yields than steam-stripping.
- A one step hydrolysis–dehydration achieves higher furfural yields.
- The modeling data using N_2-stripping show higher furfural concentration.
- The annual utility costs are considerably reduced compared to steam-stripping.

GRAPHICAL ABSTRACT



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ABSTRACT

Among the furan-based compounds, furfural (FUR) shows interesting properties as building-block or industrial solvent. It is produced from pentosan-rich biomass via xylose cyclodehydration. The current FUR production makes use of homogeneous catalysts and excessive amounts of steam. The development of greener furfural production and separation techniques implies the use of heterogeneous catalysts and innovative separation processes. This work deals with the conversion of corncobs as xylose source to be dehydrated to furfural. The results reveal differences between the use of direct corncob hydrolysis and dehydration to furfural and the prehydrolysis and dehydration procedures. Moreover, this work focuses on an economical analysis of the main process parameters during N_2-stripping and its economical comparison to the current steam-stripping process. The results show a considerable reduction of the annual utility costs due to use of recyclable nitrogen and the reduction of the furfural purification stages.

1. Introduction

The interest for the design of novel chemical processes for the production of biobased chemicals has increased in the past years. The integration of refineries and biomass feedstock shows interesting potentials for the development of biorefineries (Karinen et al., 2011). In this sense, the integrated use of cellulose, hemicellulose and lignin is very important for the economical feasibility of the biorefining industry. Among the furan-based chemistry, furfural (FUR) is a widely used chemical for applications such as industrial solvent or precursor for high value-added products (Mamman et al., 2008). During the initial stage, the hemicellulose is hydrolyzed to xylans, which generate pentose carbohydrates to be further cyclodehydrated to FUR. Commercially, FUR is produced using sulfuric acid as homogeneous catalyst. Moreover, high steam to product ratio is used in order to strip the FUR and to avoid its further degradation. However, its usual production yield is still around 50% (Zeitsch, 2000). These conditions lead to a process showing several corrosion and toxic effluent issues, as well as high separation and purification costs. For these reasons, the improvement of appropriate catalyst design and chemical technology remains of great interest for the integration of the furan-based industry in biorefineries.

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The different FUR production parameters have been varied in several research studies to optimize its production. Reactions conditions operated using water at high temperature (Jing and Lu, 2007) or with different stripping agents (Agirrezabal-Telleria et al., 2011) showed significant FUR yield improvement. Recently, the use of steam in combination with acetic acid and $FeCl_3$ achieved to selectively separate FUR (Mao et al., 2012). Moreover, the use of biphasic water/organic solvent systems (Dias et al., 2005) or ionic-liquids (Lima et al., 2009) allowed to achieve high FUR yields. Most of these works were based on the synthesis of novel heterogeneous catalysts to study the cyclodehydration reaction mechanism and to selectively produce FUR using xylose as model compound (Antal et al., 1991; Zeitsch, 2000) or using glucose as co-carbohydrate (Agirrezabal-Telleria et al., 2012b). Most of the studied materials featured strong acid-sites as well as proper textural properties to increase the selectivity to FUR. Recent studies proposed several catalysts, ranging from sulfated zirconia (Dias et al., 2007), exfoliated nanosheets (Dias et al., 2006b) or functionalized micro-mesoporous catalysts (Agirrezabal-Telleria et al., 2012c; Dias et al., 2005, 2006a,c). Other studies focused on the use of zeolitic structures (Kim et al., 2011; Moreau et al., 1998), vanadium phosphates (Sádaba et al., 2011) or sulfonated silica-shells (Jeong et al., 2011), showing high FUR yields.

The development of studies applied to upgrade raw biomass, such as corncobs or bagasse, feedstocks should be focused on robust and efficient processes. Given the broad range of sub-products generated by the decomposition of biomass, the proposed systems should allow to selectively separate the desired compounds. In this sense, the use of co-solvents in the production of furfural would difficult further separation stages, as well as an increase of the production cost. The studies based on sophisticated catalysts might be focused under biphasic conditions, however, the most suitable reaction medium during xylose dehydration is water, already present at high quantities in the raw biomass.

This work will focus on the study of the furfural production from pentosan-rich biomass, such as corncob, as well as model compounds present in the biomass, such as xylose and glucose. The novelty of this work will be provided by the use of nitrogen as the stripping agent to immediately remove the FUR produced. The tests will be performed using different feedstocks and loads. The modification to be performed on the current FUR manufacturing process would then be minimized by changing the stripping agent from steam to nitrogen. Finally, the proposed process will also be modeled and economically evaluated to compare its potential with respect to the steam-stripping process.

2. Methods

2.1. Corncob composition

The raw material was first grounded in a mill to a particle size of 0.4 mm. The chemical composition was quantified using TAPPI standards in terms of moisture (TAPPI T264 cm-97), ash (TAPPI T211 om-93), extracts (TAPPI T204 cm-97), Klason lignin (TAPPI T222 om-98), α-holocellulose (Wise et al., 1946), cellulose, hemicellulose (Rowell, 1983).

2.2. Catalytic tests and product analyses

Xylose and biomass conversion batch catalytic tests were performed in a temperature-controlled stain-steel reactor (*Autoclave Engineers*) stirred at 500 rpm. Biomass feed was previously dried to remove physisorbed water. In order to keep the reaction medium in liquid phase (200 mL of reaction total solution), the system was pressurized at 15 bar. The water/toluene tests were performed with 1:1 v/v ratio (mol ratio of 5.9 water/toluene). The corresponding xylose solution was pumped with a Waters 515 pump to obtain an initial xylose load of 20 g L^{-1} (0.44 M). Catalyst load was fixed at 60 wt.% with respect to initial xylose load and reaction time was set at 20 h. Reaction samples were taken at different intervals with a needle valve. Xylose conversion (X_X) on mol basis was calculated at different intervals and FUR yield (FUR_Y) calculated as mol of FUR obtained per mol of converted xylose. Furfural yield for biomass was calculated based on the hemicellulose content and its hydrolysis to xylose.

The N_2-stripping tests were carried out in a 2 L reactor (Autoclave Engineers), with controlled electric-heating and stirred at 500 rpm (see Scheme 1). In a typical semi-continuous (SC) experiment operating at 180 °C and 10 bar, the reactor was loaded with the corresponding amount of catalyst and substrate (xylose, glucose or corncob) and heated up to 180 °C with deionized water (1.5 L initial volume). During the N_2-stripping tests, mass-flow controlled nitrogen was bubbled into the liquid bottom at 150 mL min^{-1} (STP) until reaching 80% of initial volume as condensate. This gas flow stripped the water–furfural vapor stream. The gaseous flow was later fed to a condenser (cooled by Peltier effect at 10 °C), where gas and liquid streams were separated. The condensate was continuously weighted. Automatic control valves were used to regulate the reactor-pressure and liquid level in the condenser.

The reaction products were diluted, and FUR and HMF quantified in a 1260 Infinity module from *Agilent*. The products were separated using a Zorbax SB-C18 column (3.5 μm, 3.0 × 150 mm) at 1 mL min^{-1} and 35 °C using water as eluent. Secondary-products were also identified by GC–MS (6890 GC and 5973-Mass Selective Detector from *Agilent*) using a DB-FFAP column, helium as carrier gas at 1 mL min^{-1} and an injection volume of 1 L.

3. Results and discussion

3.1. Biomass characterization

According to the biomass composition procedure described in Section 2.2, the corncobs showed an average moisture content of ∼10% and the composition on dry-basis was as follows:

As mentioned in Section 1, corncobs and bagasse are the most common biomass in the furfural manufacturing (Mamman et al., 2008). As observed in Table 1, the high pentosan-content of corncobs proved its application for furfural production.

3.2. Activity of Amberlyst 70 during FUR production from corncobs

The activity during the hydrolysis of hemicelluloses and the subsequent conversion of pentoses to furfural was evaluated under hydrothermal conditions at 180 °C and different extraction configurations.

Toluene was reported as a very efficient furfural extracting solvent to isolate it from the yield-loss reaction medium (Agirrezabal-Telleria et al., 2012a). As observed in Table 2 using water/toluene systems, the biomass-derived furfural yield using Amberlyst 70 showed high values compared to feeds containing xylose or the sugar mixture. The hemicellulose conversion was assumed as complete after the batch reactions (Chareonlimkun et al., 2010a), so furfural yield calculations were carried out based on the initial hemicellulose content. Previous data showed that furfural resinification reactions were negligible in toluene and mainly occurred in the water-phase (Agirrezabal-Telleria et al., 2011). However, the presence of biomass particles in the water solution could avoid the contact between furfural, adsorbed on the particle surface, and the catalyst. This effect could reduce the furfural yield-loss