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Furfural production from empty fruit bunch – A biorefinery approach

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ABSTRACT

Biofuels production from agriculture residues is gaining much attention in Brazil due to agriculture residue availability, environmental benign properties of the fuel and the capacity to improve rural development. However, for consideration of rational use of biomass resource, a biorefinery approach capable of multiproduct output is desirable. In this context, this study deals with the process optimization of furfural production from oil palm empty fruit bunch using dilute sulfuric acid pretreatment followed by dehydration without any additional catalyst. The reaction conditions were optimized using experimental design. Furfural yield up to 57.6 g/kg dry EFB or 16 g/L could be produced at optimum dehydration process conditions of temperature 198 °C and 11 min residence time. Large quantity of water is utilized in washing process that has to be minimized by alkali or ammonia washing and considerable amount of acetic acid is produced that could be recovered as a product.

1. Introduction

Energy security, climate change and depleting fossil fuels are the main reasons to employ renewable energy in transport and other industries (Asif and Muneer, 2007). Toward this context, there has been a tremendous improvement in bioethanol production processes from lignocellulosic residues in last decade. However, to maximize the profit other additional products that could be produced from the same raw material are being explored in a concept known as biorefinery (World Economic Forum, 2010; Huang et al. (2008); Rødsrud et al., 2012). Lignocellulosic residues, available in abundance from agriculture mainly contain cellulose, hemicellulose and lignin. While cellulose could be used for ethanol production, hemicellulose could be converted to furfural as an alternative to ethanol as a means to diversify the product streams. Lignin can be recovered as a solid fuel for onsite use (Lange et al., 2012).

Furfural produced from hemicellulosic fraction of lignocellulosic residues is considered as one of promising commodity bio-based chemical (NREL, 2004) used in several applications such as fungicide, nematicide, specialist adhesives, flavor compound, refinery lubricants recovery and a precursor for 5-methyl furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol and tetrahydrofuran (Win, 2005). The total production of furfural in the world is around 430,000 ton per year and it is likely to grow due to green chemical initiatives in various industries (Yebu, 2014). At present furfural is produced commercially from the hemicellulose present in biomass, while cellulose and lignin rich solid leftover are used as boiler fuel. Since hemicellulose only makes a fraction of the total composition of lignocellulose, the sole production of furfural from biomass residues would be inefficient, costly and generates more waste (Cai et al., 2014).

Brazil is an agriculturally rich country with crops harvested year round and an interest in expanding oil palm cultivation on abundant degraded land (UNEP, 2011; Villela et al., 2014). The recent initiative from the Brazilian government to expand oil palm production in degraded land for palm oil and biodiesel production has attracted several biorefinery projects to manage and utilize profuse oil palm empty fruit bunch (EFB) to produce bioethanol and biochemicals. In this context this study deals with production and optimization of furfural production from EFB from Brazil with biorefinery approach producing ethanol and lignin as coproducts.

Agricultural residues such as corn stover, sugarcane bagasse, and rice straw are available in many areas around the world depending on the agriculture practices (Ladanai and Vinterbäck (2009)). Choice of biomass depends on the availability and the policy framework of the location. In the literature several biomasses have been used for furfural production; eucalyptus (García-Domínguez et al., 2013), rice husk (Suxia et al., 2012), corn cobs (Sánchez et al., 2013), date-palm tree (Bamufleh et al., 2013), sorghum straw (Vazquez et al., 2007), palm pressed fiber (Riansa-Ngawong and Prasertsan, 2011), sugar cane bagasse (Gamez et al., 2006), olive tree (Romero et al., 2010), wheat straw (Yemiş and Mazza, 2011) and rice straw (Lin et al., 2013). The earlier study

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reported on furfural production from a related biomass (delignified palm pressed fiber) originating from Thailand (Riansa-Ngawong and Prasertsan, 2011). However, there is no study reported on furfural production from Brazilian oil palm empty fruit bunch (EFB) with biorefinery approach.

In the case of conventional furfural production, the objective is to convert the biomass residues to furfural. Therefore, biomass is hydrolyzed and dehydrated in single stage process to convert the hemicellulose to furfural. Whereas, in biorefinery approach as the objective is to convert hemicellulose to furfural and cellulose to ethanol. Hemicellulose and cellulose are first separated from biomass through first stage process (hydrolysis) and the hemicellulose fraction is converted to furfural through dehydration. In the first stage the hydrolysis or pretreatment process is designed to separate hemicellulose as liquid fraction and, cellulose and lignin as solid fraction efficiently, so that these components could be converted in to different products. The disadvantage of conventional process is that the raw biomass is subject to harsh conditions that lead to disintegration of xylose into furfural. However at harsh conditions the cellulose and lignin are also degraded leading to several side reactions that decrease the furfural yield and also generate higher amount of waste (Zhang et al., 2014). In addition the solid fraction left over after furfural production could only be used as a burning fuel which has low value. Whereas in two stage process as furfural is produced from hydrolysis fraction of hemicellulose there is only limited side reactions and high product yield (Mansilla et al., 1998; Punsuvon et al., 2008). In addition the solid fraction rich in cellulose and lignin, remaining after hydrolysis could be valorized into products such as ethanol and lignin derivatives (Vázquez et al., 2007).

In conventional ethanol production process from lignocellulosic biomass, the objective is to convert both hemicellulose and cellulose to ethanol. Therefore, the biomass is pretreated to separate hemicellulose and cellulose, further the pentose obtained from hemicelluose and hexose obtained from cellulose are converted to ethanol by saccharification and fermentation (Chandrakant and Bisaria, 1998). The problem associated with these processes is that, in pretreatment when biomass is hydrolyzed, hemicellulose is converted into furfural and acetic acid and cellulose is converted to HMF. These inorganic acids have an inhibitory effect on the microorganisms that would be used for fermentation to produce bioethanol in the later stage (Jönsson et al., 2013). Therefore, it is necessary to remove these inhibitors (detoxification) that would add additional cost to the process (Klasson et al., 2013; Mateo et al., 2013). On the other hand, the yield of ethanol from hemicellulose with the current microorganism available is less compared to the yield from cellulose that reduces the overall yield of the process (Taniguchi et al., 1997). In addition, the value of ethanol is less compared to that of furfural. In this work a biorefinery approach capable of producing multiple products are examined, therefore, the selection of pretreatment process and the conditions were based on the multiple products (furfural, ethanol and lignin) compared to the conventional single product (furfural) process. On the other hand, the dehydration process conditions for furfural production are not same for all the biomass feedstock, hence the process conditions suitable for Brazilian oil palm EFB was determined through statistical optimization, as there are no data available on furfural production from Brazilian EFB in literature.

Furfural could be produced via hydrolysis and dehydration of hemicellulose using homogenous or heterogeneous catalysts such as H_2SO_4 (Bamufleh et al., 2013; Yat et al., 2008; Rahman et al., 2006), HCl (Herrera et al., 2004,), H_3PO_4 (Lenihan et al., 2010; Vazquez et al., 2007 and Gamez et al., 2006). HNO_3 (Rodriguez-Chong et al., 2004) and solid catalysts (Agirrezabal-telleria et al., 2014). Each process has its own advantages and disadvantages. However, in biorefinery context furfural would be one of the products along with bioethanol and lignin. As pretreatment is the preliminary step for all products, the choice of catalyst should be common to all the products to avoid several chemical uses and process complexity. In the present research work, dilute sulfuric acid pretreatment was designed to achieve an efficient separation of xylose from the EFB and to convert the EFB hydrolysate into furfural without additional catalyst. The required parameters were studied by optimization.

2. Materials and methods

2.1. Raw material

Dried oil palm EFB (*Elaeis guineensis*) was provided by Federal University of Pará, Brazil. The palm plantation from where the fresh fruit bunch (approximate tree age-20–25 years) was harvested was located between Thailand and Moju (about 2°45′S and 48°50′W). The fresh fruit bunch were harvested by the AGROPALMA company for palm oil production. EFB containing 20–25% moisture was collected after pressing fresh fruit bunch in palm oil production plant, later washed, dried for 24 h at 60 °C, ground in a mill to a size range 3–4 cm and stored in a polythene bag until sending to the Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland. At EPFL, the sample was further milled to pass through 80–20 mesh and stored in a zip lock bag until use. HPLC standards furfural, glucose, xylose, cellulase (Cellulast® 1.5 L) and β-glucosidase (powder from almonds) enzymes were purchased from Sigma–Aldrich, Switzerland. *Saccharomyces cerevisiae* strain (BY4741) seed culture procured from EUROSCARF, Frankfurt, Germany was sub-cultured in YPD agar slants at regular intervals and grown in YPD media for fermentation use. All other chemicals were of analytical grade.

2.2. Analysis

Composition of raw EFB, pretreated hydrolysate and pretreated solid fraction samples was determined according to the standard procedures for biomass compositional analysis of National Renewable Energy Laboratory (NREL) (Sluiter et al., 2010; NREL, 2014). High performance liquid chromatography (HPLC) (Agilent Technologies, Germany) equipped with an Aminex HPX-87P column and refractive index detector (RID) was used to analyze sugars. Millipore water was used as the mobile phase at flow rate 0.5 mL/min. The column and detector temperature were maintained at 80 and 55 °C, respectively. Same HPLC equipped with an Aminex HPX-87H column and RID detector was used for furfural, acetic acid and ethanol analysis with 5 mM sulfuric acid as the mobile phase at flow rate 0.6 mL/min. The column and detector temperature were maintained at 65 °C and 55 °C, respectively. Ash and solid lignin were analyzed by gravimetric method. Soluble lignin was analyzed using spectrophotometer method at 320 using 30 L/g cm as the absorptivity coefficient (Sluiter et al., 2011).

2.3. Hydrolysate (first stage)

EFB hydrolysate was obtained by pretreating the raw EFB in a 300 mL high pressure reactor (Parr, USA) using dilute sulfuric acid at statistically optimized conditions carried out earlier (160 °C, 1.025% v/v acid concentration, 10.5 min and 20% solid loading) (Raman and Gnansounou, 2014) and separating the liquid fraction by vacuum filtration. The pretreatment liquid fraction was analyzed for its composition and further processed to produce furfural by dehydration. Whereas the solid fraction was washed with water to increase the pH and to remove liquid fraction attachments in the solids and further processed by saccaharification and fermentation to produce ethanol and lignin.