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Synthesis and Optimization of a Furfural Production Process. A case Study of Mexico Considering Different Lignocellulosic Feedstocks

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Abstract

In this work the design, synthesis and optimization of a furfural production plant, considering the most abundant and common lignocellulosic wastes of Mexico is proposed. For the process, different pretreatment technologies and different purification process including intensified schemes are considered giving a total of 32 possible process alternatives. The pretreatment technologies are the dilute acid (DA) and ammonia fiber explosion (AFEX) respectively, for the separation zone we considered an azeotropic distillation process, a thermally coupled scheme distillation, a dividing wall column and one liquid- liquid extraction process. A two-stage procedure is used to determine the best process per biomass type. First, the processes are modelled in Aspen plus. Next, the best option per biomass is optimized using the differential evolution with tabu list in order to minimize the total annual cost and the environmental impact. The prescreening results indicate that the dilute acid pretreatment and the thermally coupled distillation provide the lowest cost and environmental impact for furfural production for all the raw materials. The optimization results indicate that a biorefinery with wheat straw as raw material is the best option to produce furfural due to its low cost and environmental impact which are 13 M$/yr and 4,536,512 eco-points/year respectively.

Keywords: Furfural, Process Design, Multi-Objective Optimization, Process Intensification, Biorefinery

1. Introduction

Every year in Mexico the agricultural activities generate approximately 640 billion tons of lignocellulosic residues. However, only 5% of these wastes are used. This small percentage is used as food for livestock, compost or burned as fuel mainly, while the rest is incinerated at the harvest sites, which provokes several environmental problems. The lignocellulosic residues can be used to produce high-added value biochemicals. The use of waste has several advantages with respect to other biomasses. The two most important are that these residues do not compete with food avoiding ethical problems and the second reason is because these wastes are cheap. Furfural had been listed by The National Renewable Energy Laboratory (NREL) of the United States as one of the most important biochemicals produced from lignocellulosic residues due to its wide range of applications as fungicides, extractant for lubricant oils and its ability to compete with chemicals derived from petroleum (Marcotillio, 2011).

Traditionally Furfural has been synthesized by the acid hydrolysis and dehydration of hemicellulose fraction contained inside biomass. For this reason, raw materials with high content of hemicellulose are considered better raw materials. In this work is proposed the synthesis, design and optimization of furfural production processes considering the four most abundant agricultural residues of Mexico. The synthesis phase considers two different pretreatment options and four different process separation schemes including two intensified alternatives in order to generate the most energetic efficient process resulting in 32 possible designs. The best process scheme for each raw material was optimized using the differential evolution with tabu list. Two different indexes, which are the total annual cost (TAC) and eco-indicator 99 (EI99) have been used as performances criteria in order to determinate which are the best raw materials, and which is the best process structure for a furfural plant located at Mexico.

2. Methodology

The selection of raw materials is realized according to the four most abundant agricultural wastes generated in Mexico per year (SIAP, 2019), which are corn stover, wheat straw, sorghum bagasse and sugar cane bagasse. The furfural plants were designed considering a typical size production of 1000 kg/hr furfural (Marcotullio, 2011). We considered that the biomass is formed by cellulose, hemicellulose and lignin the most abundant fractions. An average for these three main fractions composition obtained from different works was used in order to consider the biomass variability.

The design and simulations of the processes were carried out using the software ASPEN PLUS®.The thermodynamic model used at the simulations is Non-random two-liquids coupled with the Hayden-O´Connell (NTRL-HOC) equation of state in order to predict the formation of two liquid phases characteristics of processes with organic compounds and water. The processes are divided in three sections, pretreatment, reaction and purification. For the pretreatment zone, to release of pentoses, two pretreatments have been considered. These pretreatments are the dilute acid with hot water (DA) and the ammonia fiber explosion (AFEX). During the DA pretreatment, the biomass is mixed with a dilute solution of acid in medium-high temperatures around 150-220°C and pressures of 4.75- 23.15 bar. One of the most common acid used is sulfuric acid. The main objective of this process is the solubilization of hemicellulose fractions and the reduction in the crystallinity of cellulose. During the AFEX pretreatment the biomass is exposed with ammonia at high pressure conditions (13.7-20.68 bar) and moderate temperatures (60-160°C) during residence times of 5 min in order to break the fibers inside biomass and release the sugars. Then the biomass is treated with enzymes to hydrolysate the chains of polysaccharides and convert them into monomers like glucose or xylose. Both pretreatments were simulated according with the methodology proposed by Conde-Mejia et al., (2012).

For reaction zone where the furfural is produced, the aqueous solution rich in pentoses produced during the pretreatment stage is introduced into a CSTR reactor with thermal conditions of 190°C and 13.14 atm. Sulfuric acid is fed to the catalyzed the reactor, the concentration of the acid inside the reactor needs to be 0.1M. Under these conditions the conversion of pentoses to furfural is 53%wt, which, represents an efficiency of 82.82% with respect to the theoretical value. A scheme of the reactor and a more detail about the conditions are reported by Zeitsch, (2000).

Different processes have been considered for the purification stage in order to reduce the energy consumption and determinate which is the best option to purify the furfural. The processes are Convectional azeotropic distillation (Quaker oats), which is the typical process used to purify the furfural. In order to reduce energy costs and consumption and improve the thermodynamic efficiency two intensified schemes have been considered: a thermally coupled scheme (TCC) and a divided wall column scheme (DWC). Finally, a liquid-liquid extraction coupled with distillation has also been considered (ED). The distillation schemes were designed in order to get a purity of furfural of 99.2% by mass, that is the minimum purity required to use the furfural in the production of fuels and polymers. The design parameters used for simulating were taken from the previous work,Contreras-Zarazúa et al., (2019). Figure 1 shows the superstructure diagram, which contains all the process alternatives considered in this work. Due to the magnitude of the problem a two-step procedure was used to solve the superstructure. In this case only the best process flowsheet with the less total annual cost and environmental impact for each raw material. These processes are selected to be optimized within Aspen Plus using the differential evolution algorithm with tabu list, which was programed in Visual basic inside EXCEL.

The Total annual cost (TAC) was chosen as a parameter to evaluate the processes economics and this metric was calculated using Guthrie method, the parameters for the equipment's were taken from Turton et al. (2008). We assume steel stainless steel as the construction material for all the equipment, and payback period of 10 years. The trays type sieve are selected with spacing between trays of 2 ft are considered. 8500 hours of yearly operation for each configuration were defined cooling water, heating and electricity are considered has operating cost. **The Eco-indicator** (EI99) was the index used to evaluate the environmental impact of biorefineries, it is a lifecycle method that evaluates different categories (steel, electricity, and vapor) where individual scores are assigned depending of amount of water used, emission produced during the operation of the plant among others.

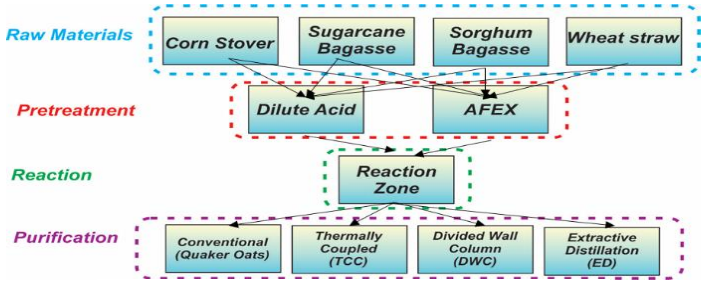

Figure 1. Superstructure for furfural production.

The Differential Evolution with Tabu List Algorithm proposed by Sharma and Rangaiah 2010 has been used at this work. The parameters required by DETL algorithm are the following: Population size (NP): 120 individuals, Generations Number (GenMax): 834, Tabu List size (TLS): 60 individuals, Tabu Radius (TR): 0.01, Crossover fractions (Cr): 0.8, Mutation fractions (F): 0.3. These values were determined through a previous tuning process of the algorithm. The implementation of the multi-objective optimization strategy involved a hybrid platform, which linked Aspen Plus^{TM} and Microsoft Excel^{TM} . The decision variables for each reactive distillation configuration are reported in Table 1. Finally, the multi-objective optimization problem can be expressed mathematically as in Eq. (1) and Eq. (2):

$$\min \quad Z = \{TAC; EI99\} \tag{1}$$

Subject to:
$$\begin{aligned} y_{i,PC} &\geq x_{i,PC} \\ w_{i,FC} &\geq u_{i,FC} \end{aligned} \tag{2}$$

The objective function is constraint to fulfill the purity and the mass flowrate vectors for the components in the mixture. For example, the values of the purities for the components obtained during the optimization process $y_{i,PC}$ must be either greater or equal to the specified values of purities for the component $x_{i,PC}$. Furthermore, the mass flowrates obtained $w_{i,PC}$ must also be either greater or equal to the specified values of the mass flowrate $u_{i,PC}$.

Table 1. Desion variables and optimization results for fufural production biorefineries.

Decision variables	**Discrete variables**	**Continuous variables**
Amount of raw material (kg/hr)	---	X
Number of stages extraction column, E1	X	---
Number of stages columns,	X	---
Feed stage, columns	X	---
Steam flowrate reaction zone (kg/hr)	---	X
Pressure steam in the reaction zone (atm)	---	X
Discharge pressure in AFEX pretreatment (atm)	---	X
Pressure reactor AFEX pretreatment (atm)	---	X
Entrainer mass flow (kg/hr)	---	X
Interlinking flow (kg/hr)	---	X
Reflux ratios	---	X
Heat duties equiments	---	X
Diameter columns	---	X

Finally, it is important to mention that this methodology is not exclusive for this process and it can be applied to different raw materials, chemical products and regions of Mexico and the world. Only data of conversion, pretreatment conditions or product specifications are required to apply this methodology to other raw materials and products.

3. Results

In this section are the prescreening results of 32 possible biorefineries are showed. Figure 2 shows a comparison of the TAC for all alternatives, the EI99 follows the same tendency that cost, due to the environmental impact depends strongly of utilities the electricity used for pumping cooling water, and the steam to provide energy to the process. The results indicate that biorefineries with AFEX pretreatment have higher energy consumption than biorefineries with DA. The AFEX pretreatment needs the compression and purification of ammonia which increases considerably the cost. The DA only requires the addition of sulfuric acid, which is a cheaper alternative, for this reason the AFEX alternatives are considerably more expensive. In the case of processes separations, the Extractive liquid -liquid processes are expensive compared with the Quaker Oats, TCC and DWC options. These results are due to the need for solvents since it involves additional energy consumption, environmental impact and solvent recovery/separation units. In Figure 2 the TCC and DWC processes have similar cost with respect to the conventional Quaker Oats processes, because these alternatives does not have important energy savings, which is reflected on the total annual cost and eco-indicator. The large amounts of water inside the processes avoiding the elimination remixing phenomena, which is the main cause of inefficiency in distillation columns on DWC and TCC processes. However, the DA TCC has the lowest energy for all the raw materials. For this reason, DA pretreatment with the thermally coupled processes are considered as the best option because they show the lowest total annual cost and environmental impact.

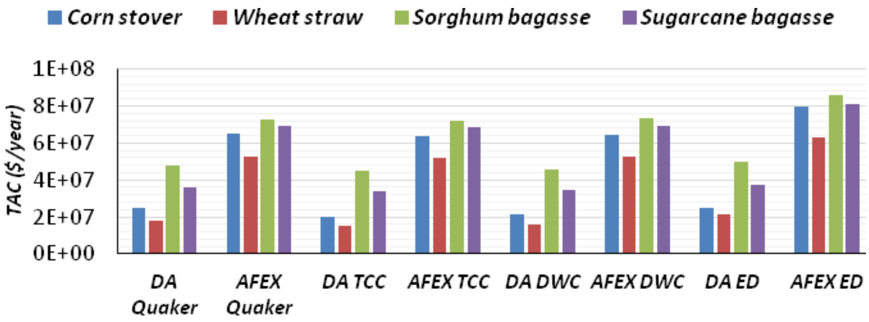

Figure 2. Total anal cost for all the alternatives.

In the Figure 3a the Pareto front of the DA using a thermally coupled column to process wheat straw is shown as a representative case, while in Figure 3 b are showed all the pareto fronts are presented. Note that in Figure 3 the designs obtained with the process optimization method converges to a single point, this point is called utopia point. This point represents the solution that has the best equilibrium for both objectives. Based on the results and considering only the total annual cost and the environmental impact as criteria, wheat straw is the best raw material to produce furfural. In contrast, sugarcane and corn stover are noticeably more abundant in Mexico, which can represent an advantage when supplying raw material to the process, however this process have higher TAC and EI99.

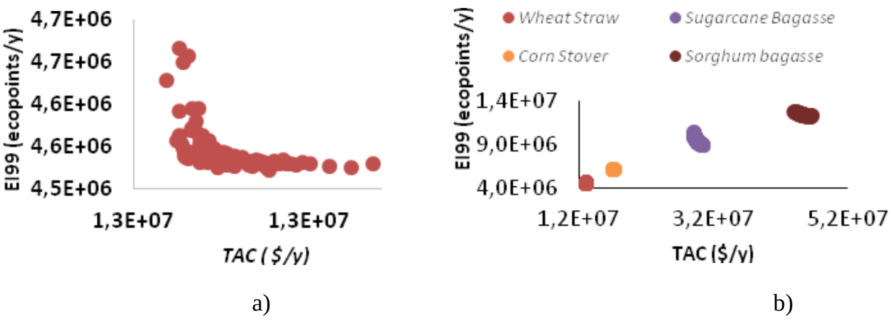

Figure 3. Pareto Fronts for DA coupled with TCC separation.

A scheme of the optimal process selected is presented in the Figure 4 that correspond DA pretreatment coped with a thermally coupled distillation. Some design parameter for wheat straw and corn stover processes as a representative case are showed in Table 2 using DA and TCC. Note, that the amount of biomass and water required in the wheat process is fewer than corn stover process which explain the lowest cost an environmental impact.

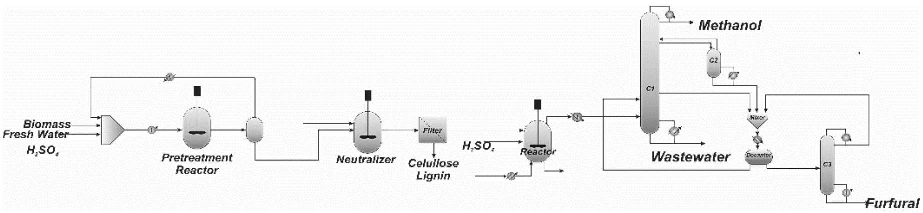

Figure 4. Scheme of the process selected.

Table 2.Representative parameter for bio refineries with wheat straw and corn stover.

Decision variables	Wheat straw	Corn Stover
Amount of raw material (kg/hr)	12213	15981
Amount of water (kg/hr)	10843.9	13680
Energy consumption (kW)	24,681	33,716
Total Annual cost ($/y)	13,092,504	17,122,917
Eco.indicator 99 (Eco-points/y)	4,536,512	6,130,272

4. Conclusions

This work has performed the synthesis, design and optimization of furfural production plants, considering different lignocellulosic wastes produced in Mexico. A two-stage procedure of synthesis and optimization is used to select the process alternative. Based on results of prescribing and optimization phases, we considered that a biorefinery to produce furfural with wheat straw as raw material is the best option based on lowest cost and eco indicators which correspond to values of 13M$/yr and 4,536,512 eco-points/year respectively.

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