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Furfural production from agricultural residues using different intensified separation and pretreatment alternatives. Economic and environmental assessment

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ABSTRACT

Agricultural residues are considered abundant raw materials that can be used to produce valuable chemicals like furfural. Currently, furfural production is characterized by extensive use of energy and low conversions. However, these challenges can be overcome through process intensification in conjunction with a suitable process synthesis. This work proposes the synthesis, design and optimization of furfural production processes using different intensified distillation and pretreatment alternatives. The eco-indicator 99 and total annual cost were considered as metrics to evaluate the performance of furfural processes. To determine the influence of biomass type on energy consumption, costs and environmental impact, four different biomasses are considered raw materials. The design and optimization of furfural processes were carried out using a two-step procedure. Firstly, all possible alternatives were simulated using Aspen Plus, then the best process option for each biomass is optimized using the differential evolution with tabu list method. The results indicate that a dilute acid pretreatment combined with a thermally coupled scheme provides the lowest cost and environmental impact for all feedstocks. Finally, the optimization results show that the best furfural process consists of wheat straw, dilute acid pre-treatment and thermally coupled distillation, owing to its lowest cost and environmental impact which are 13,092,504 dollars/year and 4,536,512 eco-points/year respectively.

1. Introduction

Climate change, pollution, and a continuous increment in the extraction costs of non-renewable fossil resources have encouraged the search and development of renewable and eco-friendly products and chemicals, in order to replace the old chemical building blocks derived from crude oil. Therefore, in recent years, the efforts have been focused on the development and exploitation of new renewable resources, mainly based on biomass to produce these new products. The use of biomass instead of petroleum for producing chemicals and fuels has several environmental benefits such as reductions in polluting emissions, less toxic residues, better waste management, among others. In this sense, the lignocellulosic residues are considered as one the most important and abundant biomass sources [1], for those reasons, their utilization for producing commodities has attracted attention. Lignocellulosic residues have numerous advantages in contrast to other biomass sources, i.e. they are considered cheap feedstocks because their costs are predominantly correlated with collection costs. Furthermore, the lignocellulosic residues do not compete with the food crops avoiding in this way ethical dilemmas. In this sense, the US National Renewable Energy Laboratory (NREL) undertook the task of investigating the 30 chemical products derived from biomass capable of functioning as new building blocks [2]. Furfural stands out in this list owing to its capability to produce a great variety of chemical products. Traditionally, furfural has been used as precursor to produce nematocides, fungicides, extractant for lubricant oils and fuels [3,4]. However, currently several novel applications for furfural have been proposed. Some examples of these new applications are its uses as a monomer to produce tetrahydrofuran (THF) which is used in the fabrication of Nylon 6-6 [5,6], as well as in the synthesis of furonic acid, which is a widely used chemical in the pharmaceutical industry or as a precursor of furan resins that are used as adhesives for sand agglomerators and cement resistant to chemical

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attacks [7].

Furfural is produced by acid hydrolysis of hemicellulose fraction which is contained in the biomass [8]. Furfural production is not new, the oldest furfural production process was invented in 1922 by the Quaker Oats company and even now it is used to produce about 80% of the global production, due to its easy implementation [9]. However, the Quaker Oats process has some important drawbacks such as the low conversion of biomass to furfural, an expensive furfural purification, intensive use of energy and an excessive degradation of other biomass fractions such as cellulose which can be used to produce other chemicals [3,10]. Based on the aforementioned, the researchers have been focused on the development of new processes to improve the furfural production. Fitzpatrick [11] proposed an alternative to Quaker Oats process called Biofine. This process uses different biomasses to produce levulinic acid and furfural through the acid hydrolysis of hexoses and pentoses. However, it has been characterized by high temperatures and pressure conditions, prolongated resident times and high acid concentrations to hydrolysate cellulose, as a consequence of these severe conditions, intensive energy requirements are needed, also an important degradation of main products into undesired by-products like formic acid and resins is observed. Another development is the Suprayield process proposed and patented by Zeitsch [3], which is based on the acid hydrolysis of pentoses. In this process the furfural once formed is removed in situ maintaining the reaction medium at boiling temperature in order to avoid its resinification and increase the yield. Vedernikovs [12] proposed a process which uses a heterogeneous catalytic medium with salts and strong acid aliquots. This technology has increased the furfural yield from 55% up to 75% of the theorical maximum yield. However, the high-temperature conditions of Vedernikov′s process increase the recalcitrance of cellulose, which affects its application to produce other compounds, in addition, important energy amounts are required in order to purify furfural [13]. Finally, Martin and Grossman [14] proposed the conceptual design of a novel biorefinery to produce DMF and furfural simultaneously from algae and switchgrass. They determined the structure and topology for the process required as a function of biomass used, however, important energy consumptions in the separation stage are observed. So far, the advances on furfural production are based on improving the furfural yield or the economic aspects of the process, but without considering reductions on energy consumptions. In this sense, the process intensification can be a powerful tool for reducing energy consumptions and improve the profitability and other environmental aspects of furfural production.

Process intensification (PI) is a philosophy which seeks to generate smaller, cheaper, efficient and eco-friendly processes. Traditionally, PI has been related to the well establish chemical and petrochemical industry, however, due to the need to emigrate towards a more sustainable and environmentally friendly economy, the process intensification has started to be applied in other novel sectors such as biorefineries, pharmaceuticals, fermentation and polymers with good results [15–17]. A good example of process intensification applied to these novel areas is the production process of methyl acetate implemented by Eastman Chemical company, it became famous owing to a highly grade of intensification, in which the number of process equipment was reduced from 28 up to only 3, achieving important capital cost and energy savings. These achievements are obtained due to the development of new process units that are more efficient and allow the integration of different stages such as reactive distillation [18]. Based on several successful implementations of PI, it is unquestionable that the implementation of intensified process generates important energy, environmental and cost enhances. Until now, the possibility of coupling different intensified separation processes and different pretreatment alternatives to improve the furfural production has not been studied. The consideration of a pretreatment stage allows a better sugars' release for furfural production and at the same time, it provides preservation of cellulose which can be used to produce other biochemicals.

This paper presents the development, synthesis and optimization of new furfural production processes using intensified separation arrangements and incorporating a new pretreatment stage to improve the sugars release and consequently the furfural production. Because of the wide variety of raw materials that can be used to produce furfural, this study considers the four most abundant lignocellulosic residues of Mexico. It is important to highlight, that energy consumption and costs of furfural production depend on biomass used, owing to the differences in composition, chemical properties and structure of cellulose, hemicellulose, and lignin among different raw materials. Therefore, the consideration of different biomasses will allow obtaining a panorama of the degree of improvement that will be obtained by the implementation of intensified processes and pretreatments as a function of the raw material [3,13]. The design and optimization procedure of different furfural processes were performed using a two steps procedure. The first step consists in the synthesis and design of different processes considering two different pretreatments and four different purification alternatives. The total annual cost (TAC) and eco-indicator 99 (EI99) are evaluated to determine the best process for each biomass. In the second step, the best option per raw material was optimized using the differential evolution with tabu list method to improve TAC and EI99. It is important to mention, that the procedure and analysis proposed in this work can be effortlessly extended to other countries and raw materials. Finally, it is of utmost importance to emphasize that this work is the first to study the feasibility of producing furfural in Mexico using endemic agricultural residues, which provides important information about the possible implementation and production of renewable biochemicals in this country in order to migrate towards a more sustainable economy. In addition, an study for reuse of residues and subsequent transformation into high value-added is very important from a perspective of circular economy and environmental impact [19,20].

2. Problem statement

The lignocellulosic residues selected correspond to the most abundant agricultural wastes generated in Mexico, according to the information reported by the Ministry of Agriculture of Mexico [21,22]. The capacity of plants was set to produce 8.5 kton/year of furfural (1000 kg furfural/hr). This capacity corresponds with a typical furfural plant size [3,4]. The raw materials selected are corn stover, sugarcane bagasse, sorghum bagasse and wheat straw. These lignocellulosic residues were chosen as potential raw materials due to their great availability in Mexico in order to claim a production of furfural at industrial scale. However, must be taken into consideration that for other countries the raw materials available could be different e.g. the pistachio shells have been considered as a potential lignocellulosic residue to produce furfural in Iran, owing to their high availability [23].

The availability and cost data of each feedstock considered in this work are shown in Table 1. The biomass shows an intrinsic variability in its composition, this variability is caused by many environmental factors like humidity, nutrients and quality of land, the weather conditions, among others. With the aim of considering the composition variability and provide a representative distribution of the biomass components, an average composition was computed from several previous works for each raw material. This average composition considers the most abundant fractions in the biomass, which are: cellulose, hemicellulose, and lignin. The arabinan and galactan fractions contained in hemicellulose

Table 1
Raw materials of agricultural considered for Mexico. (Data from; SAGARPA,2015 and SAGARPA,2019).

Raw Material	Cost USD/Ton	Availability (Ton/year)
Wheat straw	38.85	2,886,528
Corn stover	58.5	48,204,613
Sorghum bagasse	16	8,553,151
Sugarcane bagasse	25	56,841,522

were added to the xylan fraction to simplify the simulation. The average real and simplified mass percent composition for all lignocellulosic wastes are shown in Table 2.

The references used to calculate the average composition are shown in the supplementary material. Owing to the biomass variability, these simplifications on biomass composition are required to provide a representative composition for simulating and designing purposes. Despite, these simplifications can generate some deviations in the results obtained, they are considered negligible, also these simplifications on biomass composition are a common procedure implemented during the simulation and design phases with very good results [24,25].

2.1. Components and thermodynamic properties required

The processes were simulated using the software ASPEN PLUS®. The components used for the simulations are reported in Table 3. The components not predefined in ASPEN were defined in the software using the thermodynamic properties reported by Wooley and Putsche [26]. It is considered that the cellulose and hemicellulose are only formed by the most abundant components, which are glucan and xylan respectively. This simplification has been demonstrated to provide good results in previous works [24,25,27]. The thermodynamic model used in the simulations is the Non-random two-liquids coupled with the Hayden-OConnell equation of state (NTRL-HOC). This thermodynamic package can predict the formation of two liquid phases typical of mixtures with organic compounds and water. Furthermore, the NTRL-HOC can predict in a reliably way the dimerization and the polar solvation, which are characteristic of the mixtures with carboxylic acids [28].

Table 3
Components used in the simulations.

Component available in Aspen	Component not available in Aspen
Glucose	Cellulose
Xylose	Hemicellulose
Water	Lignin
Acetic Acid	
Sulfuric Acid	
Methanol	
Calcium hydroxide	
Calcium sulfate	
Hydroxymethylfurfural	
Furfural	

2.2. Pretreatment stage

To release the pentoses required for producing furfural and avoiding the degradation of cellulose, two pretreatments have been considered. These pretreatments are the dilute acid with hot water (DA) and the ammonia fiber explosion (AFEX). The inclusion of a pretreatment stage provides a better sugars release and at the same time, it allows the preservation of cellulose, which can be used for producing other biochemicals such as glucaric acid. Other studies have evaluated the use of supercritical CO2, but the technology has not been scaleup for pilot or industrial-scale facilities [29,30].

During the DA pretreatment, the biomass is mixed with a dilute acid solution at medium-high temperatures around 150-220°C and pressures about 4.75- 23.15 bar. One of the most common acids used is sulfuric acid. The main aims of this process are the solubilization of hemicellulose fractions and the reduction of cellulosés crystallinity. The dilute acid pretreatment has been widely used and tested in the production of different biochemicals mainly bioethanol [27,31] but also i-butene [14]. One of the most important disadvantages of this pretreatment for producing biofuels is the sugarś degradation into products like furfural and other side products. However, in this case the degradation of pentoses sugars to furfural is an important advantage because it increases the yield. The simulation of dilute acid pretreatment in ASPEN PLUS was performed according to the methodology reported by Conde-Mejia et al [27]. Because of several numbers of reactions that occur during the DA pretreatment, the most representative reactions have been considered according to the information reported in previous works [27,31–33]. These reactions are shown in the Eqs. 1-6.

$$C_5H_8O_4 + H_2O \rightarrow C_5H_{10}O_5 \tag{1}$$

$$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6 \tag{2}$$

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + H_2O \tag{3}$$

$$2C_5H_{10}O_5 \rightarrow 5C_2H_4O_2 \tag{4}$$

$$C_5H_{10}O_5 \rightarrow 4.68CH_4O \tag{5}$$

$$C_{10}H_{13.9}O_{1.3} \rightarrow (C_{10}H_{13.9}O_{1.3})_{Sol} \tag{6}$$

Eqs. 1 and 2 represent the degradation of hemicellulose and cellulose into xylose and glucose respectively. Eq. 3 is the dehydration reaction of xylose to furfural; Eq. 4 represents the formation of acetic acid from xylose. Eq. 5 corresponds with the degradation of xylose to methanol. Finally, Eq. 6 shows the solubilization of lignin into soluble lignin (A physical step). The dehydration of glucose is not considered due to its low yield [3,10]. Due to the lack of consistent data for acetyl groups contained in the hemicellulose fraction, the concentration of acetic acid was set to the average composition reported previously by Zeitsch [3] and other authors considering the acetic acid as a xylosés degradation sub-product. This averaged composition is: Acetic acid; 1-3%wt [3,10, 34].

Each reaction considers a specific conversion value depending on the raw material used. These different conversions are a consequence of the intrinsic variability in the chemical structure of cellulose, hemicellulose and lignin and cellulosés crystallinity [27]. Table 4 shows the operating conditions for DA pretreatment and the respective conversion values for each reaction and feedstock. The conversions values for Eq. 6, were taken according to the data reported by NREL [32] and Humbird et al [31]. The flowsheet of the DA pretreatment is shown in Fig. 1. Please note, that a neutralization step using Ca $(OH)_2$ is necessary to neutralize the output stream from the pretreatment reactor, during this step gypsum is generated and removed from the system by filtration.

The second pretreatment considered in this work is the ammonia

Table 2
Average composition (dry basis) for each biomass in mass percent.

Raw Material	Composition	Cellulose Glucan	Hemicellulose Xylan	Arabinan	Galactan	Lignin Lignin
Wheat Straw	Real	43.18	29.86	3.37	1.20	22.37
	Simplified	43.18	34.44			22.37
Corn Stover	Real	44.38	26.77	3.52	3.33	22.37
	Simplified	44.38	33.63			22.37
Sorghum Bagasse	Real	44.57	29.25	3.20	0.008	22.94
	Simplified	44.57	32.47			22.94
Sugarcase bagasse	Real	44.84	25.06	2.92	2.73	24.43
	Simplified	44.84	30.71			24.43

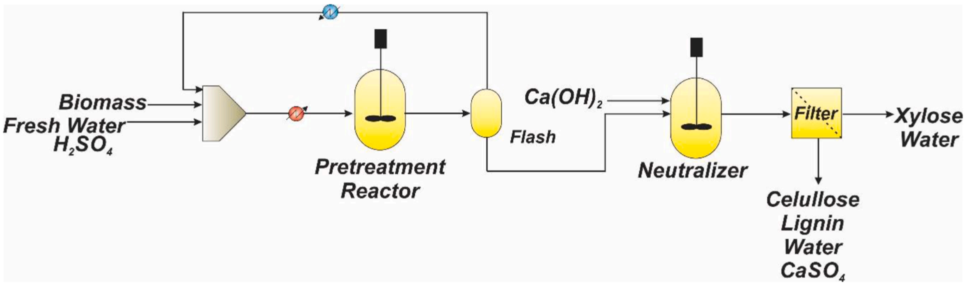


Fig. 1. Flowsheet for dilute acid pretreatment.

fiber explosion, which is commonly known as AFEX. In the AFEX process, the biomass is exposed to ammonia at high-pressure conditions (13.7-20.68 bar) and moderate temperatures (60-160°C) during residences times of 5 min, in order to break the biomass fibers and releasing the sugars. Subsequently, the biomass is treated with enzymes to hydrolysate the chains of polysaccharides and convert them into monomers [35,36]. The AFEX pretreatment offers some special and interesting features compared with other pretreatments, these characteristics are mentioned below [37,38].

- Most the ammonia is recovered and reused.
- The absence of cellulose and hemicellulose degradation increases the sugars conversions.
- Neutralization steps are not required.
- Streams of clean sugars can be produced due to the high selectivity of the enzymes.

Fig. 2 shows the AFEX flowsheet, in this process the biomass with different water ratios and compressed ammonia is fed to the AFEX reactor. During the pressure release the water and ammonia are flashed. The ammonia-water mixture must be separated to reuse the ammonia; hence, this mixture is fed to a distillation column where the ammonia is recovered as top product, then this ammonia is compressed and reused. Thereafter the treated biomass is introduced to an enzymatic hydrolysis reactor to hydrolyze the sugars released during the AFEX reactor. In this case, only the xylan is hydrolyzed because we considered the use of xylanase enzyme to degradation, similar considerations have been used in previous works [39]. The operating conditions for AFEX pretreatment are given in Table 5. The simulation of AFEX pretreatment was performed according to the methodology reported by Conde-Mejia et. al [27]. The chemical reaction of xylan hydrolysis to xylose caused by the enzyme is shown in Eq. 7. The conversions data used for eq.7 are reported in Table 5.

Table 5
Conditions to AFEX pretreatment for the different raw materials.

	Wheat straw	Corn Stover	Sorghum Bagasse	Sugarcane bagasse
Conditions				
Temperature (°C)	95	160	140	140
Pressure (atm)	20.41	20.41	20.41	17.0115
Biomass: ammonia ratio (wt)	1.1	1:1	1:1.43	1:2
Biomass: water ratio (wt) (AFEX Reactor)	1:0.7	1:0.6	1:1.2	1:1.5
Enzyme load (g enzyme/Kg biomass)	60	167.5	19.3	110
Biomass: water ratio (wt) (Enzymatic hydrolysis)	1:6.75	1:7.8	1:7.2	1:6.8
Conversions Eq4.7	76% Xylan	78.32%Xylan	76%Xylan	75.93% Xylan
Reference	Seyed [54].	Uppugundla et al.[55]	Li B. Z. et al.[56]	Krishnan et al.[36]

$$C_5H_8O_4 + H_2O \rightarrow C_5H_{10}O_5 \tag{7}$$

Finally, it is important to highlight, that the operating conditions used to simulate the pretreatments were taken from different sources due to the lack of consistent experimental data. No one group has systematically evaluated all the biomasses and pretreatments. However, the simulation procedure proposed is general, therefore, the experimental data can be easily replaced to improve the simulation data.

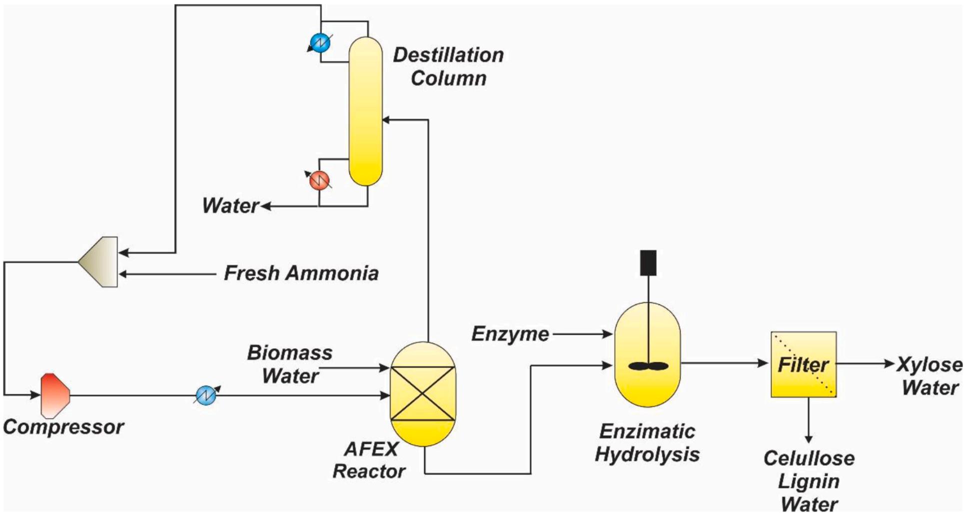


Fig. 2. Flowsheet for AFEX pretreatment.

2.3. Reaction zone for producing furfural

Furfural is produced by dehydration of pentoses (mainly xylose) contained in the hemicellulose fraction. Therefore, biomasses with high content of hemicelluloses are preferred in order to increase the furfural yield. This dehydration reaction is usually catalyzed with mineral acids like hydrochloric acid or sulfuric acid to promote the formation of furfural [3,13]. Fig. 3 shows the chemical mechanism for the acid-catalyzed dehydration reaction of xylose to furfural [40]. The chemical reaction of furfural formation from pentoses can be expressed as follows:

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O \tag{8}$$

A process flowsheet of the reaction zone is illustrated in Fig. 4a. The reactor required to produce furfural consist in a stirred tank in which an aqueous solution of xylose obtained during the DA or AFEX pretreatments is feeding jointly with small amounts of sulfuric acid to promote furfural production, at the same time, a high-pressure steam is feeding through reactoŕs bottom in order to remove furfural from the reaction medium avoiding in this way its resinification and formation of other decomposition products. A vapor stream rich in furfural, water and some impurities (mainly acetic acid and methanol) is obtained. This stream is condensed and fed to separation zone. Finally, a stream rich in water, xylose, furfural and acetic acid leaves from the reactoŕs bottom. This stream is typically neutralized and treated with microorganisms in order to degrade the traces of organic compounds and reuse the water [3,10]. The reaction conditions used are 190°C and 13.14 atm, the flow of sulfuric acid is adjusted according to the mass flow from the pretreatment stage to achieve an acid concentration of 0.1M. These conditions were taken from previous work reported by Oefner et al.,[43]. They found experimentally that the maximum conversion of xylose to furfural is obtained under these conditions. The conversion corresponds to 53% of xylose to furfural. Similar yields have been reported by Binder et al,[44] and De Jong and Marcotullio [10]. It its important to highlight, that this reactor cannot be directly simulated in Aspen Plus because it does not contain a simulation block with those characteristics. For that reason, the reactor is simulated using two blocks a reactor block and a flash tank block, where the sum of energy requirements of each equipment is the energy consumption for the real reactor. The scheme used to simulate the reactor in Aspen Plus is shown in Fig. 4b. Similar considerations to simulate complex equipment are reported in some previous works [41,42].

2.4. Furfural purification zone

This section provides a brief description of different alternatives for purifying the mixture from the reactor which is rich in water, furfural, methanol and acetic acid. Owing to the complexity of mixture, different technologies are addressed to determine the best separation technology.

The furfural purification has two problems: the first one is the large quantity of water contained in the mixture, which generates a dilute solution of furfural; a dilute solution implies higher energy consumptions, larger equipment and longer resident times in order to achieve the furfural purification. The second problem is the complexity and non-ideal behavior of mixture. Furfural and water form a heterogeneous azeotrope when the concentration of furfural is 35.5 wt%. This azeotrope is shown in the ternary diagrams of Fig. 5. This azeotrope implies that furfural is not able to be separated using conventional distillation, therefore, complex distillation schemes such as extractive distillation or azeotropic distillation are required.

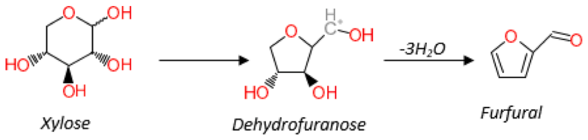


Fig. 3. Pentoses dehydration reaction.

Based on the information provided by the ternary diagrams, it becomes clear that the azeotrope formation is located inside of the two-liquids phase zone, in which the organic and aqueous phases can be separated by precipitation in a decanter. For this reason, a possible process to separate this mixture is the azeotropic distillation [45,46]. In the azeotropic distillation, the mixture is concentrated up to the heterogeneous azeotropés composition, then it is condensed and sent to a decanter where the formation of two liquid phases is promoted.

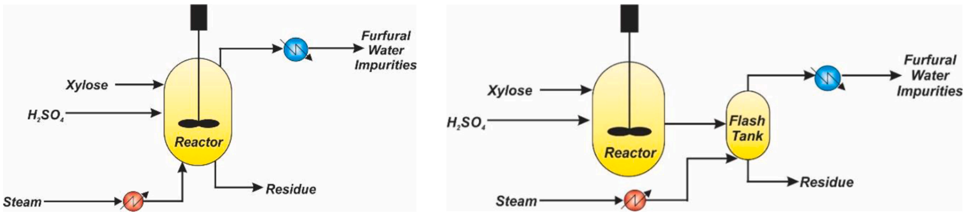
Based on the thermodynamic properties of mixture, another possible process to purify furfural is the hybrid liquid-liquid extraction – distillation process, where a solvent is added to the mixture. The main role of this solvent is promoting the formation of two-liquid phases. This solvent cannot form a new azeotrope with the main component in order to simplify the separation and avoid extra equipment [45,46]. The furfural purification schemes studied in this work are reported in Fig. 6.

Fig. 6 a) corresponds to the typical azeotropic distillation process for furfural purification, this process consists of three columns where the column C1 is called azeotropic distillation column [3]. The main role of this column is to concentrate the mixture up to the azeotrope composition. In this unit, water is the most volatile component, it drags the furfural to the gas phase then furfural is condensate. When furfural is condensed, two phases are formed and sent to a decanter through a side stream, subsequently, a stream rich in water is returned to column C1 for helping to promote the formation of two liquid phases. Finally, acetic acid and water are removed from the bottoms of C1, the recovery of acetic acid is not economically feasible due to it is present in very small amounts. Thus, a common practice is to treat the wastewater using anaerobic digestion in order to degrade the acetic acid [3]. This scheme has been studied by several authors and it is commonly called Quaker process [3,34,47,48].

To reduce the energy consumption, different intensified processes have been considered, including a thermally coupled distillation (TCC) and a divided wall column (DWC). Fig. 6 b) and c) show the TCC and DWC schemes, respectively. TCC scheme is generated from the conventional separation process by removing the condenser of column C1, which is replaced by interconnecting flows between the stripper section of column C2 and column C1. The main objective of interconnecting flows is to mitigate the remixing phenomena of intermediate volatile components, which is associated with thermodynamic inefficiencies in distillation columns [49]. Finally, the rectification zone of column C2 is moving to the top of column C1 to complete thermally coupling.

The divided wall column is one of the best examples of intensification applied to distillation. The divided wall configuration is designed from the conventional azeotropic scheme merging the columns C1 and C2 in a single shell, which are divided by an internal wall. In this case, the height of wall can be determined by the number of trays of C1. In this case, the wall must be extended up to the bottom of the column in order to achieve two different bottom streams, one bottom stream corresponds to wastewater stream and the other one corresponds to a stream a rich in furfural. A more extended explanation about the design of TCC and DWC is provided by Nhien et al., [47] and Contreras-Zarazúa et al.,[48]. Both intensified schemes were chosen due to their better control properties, energy savings, better safety issues and less environmental impact [50,51].

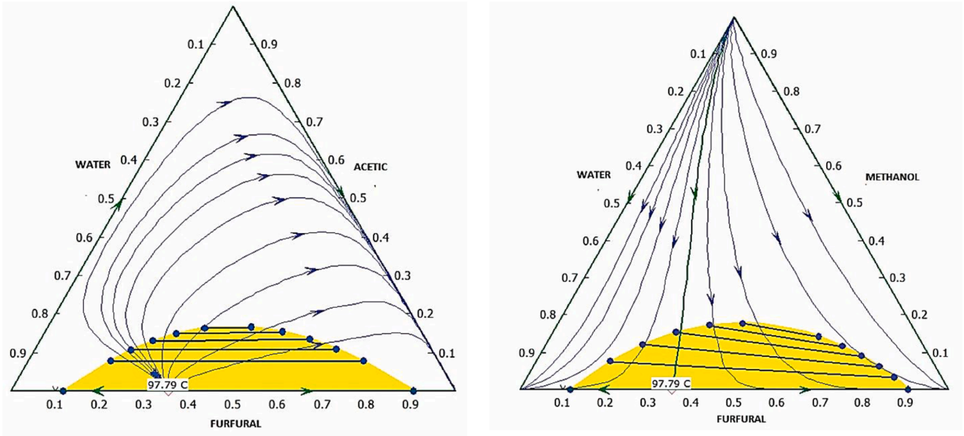
The last alternative is the liquid-liquid extraction process coupled to a distillation sequence (ED), which is shown in Fig. 6 d). This process is based on previous work reported by Nhien et al.,[9]. Nhien and coworkers investigated different solvents to purify furfural using the software CAMD, they found that butyl chloride is best solvent. Butyl chloride has especial features that make it a good solvent to purify furfural such as less toxicity and inflammability compared with other solvents as benzene or toluene. The ED process consists mainly of four equipment: E1 is the liquid-liquid extraction column in which the solvent is introduced by the bottom and the feed stream coming from



a)

b)

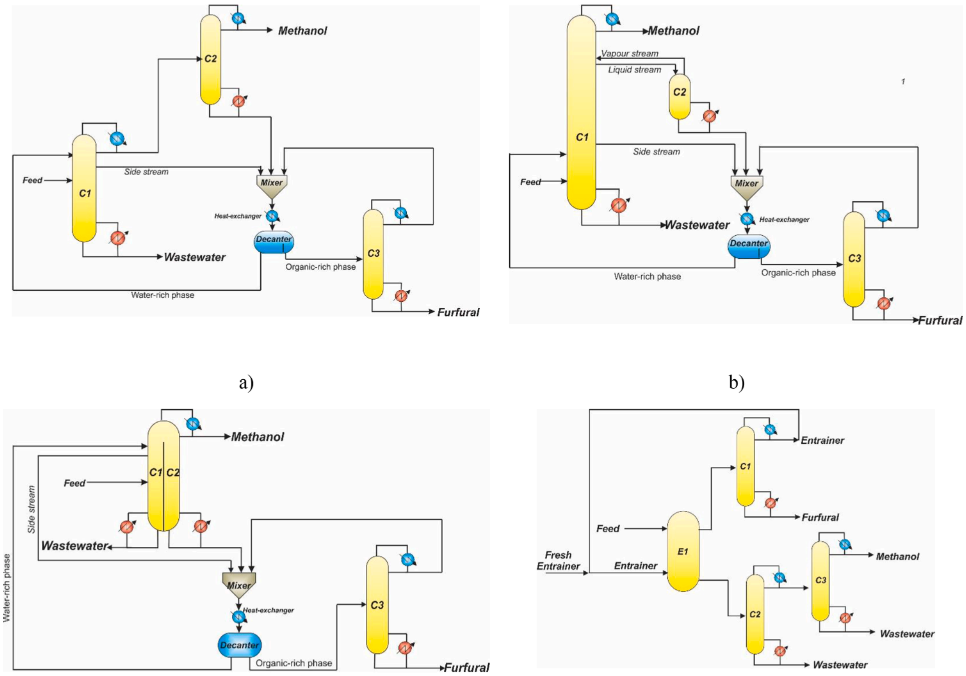
Fig. 4. a) Process flowsheet of the reactor zone. b) Process flowsheet of the reactor zone used in Aspen Plus.



a)

b)

Fig. 5. Ternary diagrams for the mixture Water-Furfural- Methanol- Acetic Acid.



a)

b)

c)

d)

Fig. 6. Processes separation schemes. a) Convectional Quaker Oats process b) Thermally coupled scheme c) divided wall column scheme d) Extractive liquid-liquid scheme.

furfural reactor is introduced by the top. In this case, butyl chloride carries the furfural to the top of extractive column E1, afterwards furfural is purified in the conventional distillation column C1. On the other hand, a stream rich in water leaves from the bottom of E1. This stream is fed to column C2 where the methanol is pre-concentrated. Subsequently, the top products of C2 are purified in the column C3 where the methanol is obtained as the most volatile component. Finally, the design parameters used to simulate all the process separation alternatives are reported in Table 6. These design parameters were taken from previous work of Contreras-Zarazúa et al., [48].

3. Optimization procedure

Based on the previous information, it becomes clear that all the possible options generated a superstructure. Fig. 7 shows the superstructure diagram, which contains all the process alternatives considered in this work, which consist of 32 possible alternatives. A two-step procedure is used to solve this superstructure.

In the first stage, all the alternatives are simulated in Aspen Plus using the design data from previous studies and the costs and environmental impact of each process are evaluated. This step is called the prescreening stage. Subsequently, the best alternative per biomass is optimized using a hybrid platform which links Aspen Plus and the optimization method of differential evolution algorithm with tabu list (DELT), which was programmed in Visual basic inside of EXCEL. The optimization was carried out in order to improve the environmental impact, costs and satisfying the purity and mass flowrate constraints for furfural and methanol. The purity requirements are 99.2% and 99% for furfural and methanol respectively, these compositions are the minimum required for subsequent applications. On the other hand, the minimum mass flows were set in 1000 kg/hr and 200 kg/hr for furfural and methanol, respectively.

The total annual cost (TAC) and the eco-indicator 99 were chosen as metrics to evaluate the economic and environmental impact issues, respectively. These indexes were selected according to their importance in the selection of sustainable processes [52]. The TAC consists in the sum of the costs for each process equipment, the operating costs associated with the use of utilities as steam, electricity, cooling water among others, and the costs of the raw material. The EI99 is a life cycle methodology, which has been used successfully by several authors to evaluate the environmental impact and sustainability of several chemical processes. This methodology has proved to be a powerful tool for selecting processes with low environmental impact during the design and synthesis stages [52]. The complete description and parameters used to evaluate the TAC and EI99 as well as the optimization method are provided in the supplementary material.

It is important to mention, that the procedure and metrics considered in this work can be applied to analyze the production of other biochemicals from different biomasses and using other routes e.g. thermochemical conversion or fermentation. In order to implement this procedure to other processes, at least data of biomass composition, types of chemical reactions, conversions, temperatures and operational flows are required for pretreatments and reactors. Furthermore, other more rigorous data such as chemical kinetics or non-equilibrium models can be effortlessly implemented. In addition, depending on the type of process, product or other specific considerations further metrics such as safety issues, control properties, water usage, jobs and economic development impact models can be included in the procedure to evaluate in a more integral way the sustainability of processes.

4. Results

This section provides the results for prescreening stage, where the 32 possible biorefineries are jointly evaluated considering the total annual cost, energy consumption and eco-indicator as metrics. A deep analysis of 32 alternatives will justify the best alternatives chosen for the optimization phase. Finally, the results of the optimization phase are presented in this section. In this step, the process specifications are improved by the optimization procedure to minimize the costs and environmental impacts. All the optimizations were performed using a computer with AMD Ryzen^{TM} 5-1600 @3.2GHz, and 16GB of RAM @2400MHz. Each optimization required a computational time of around 504h.

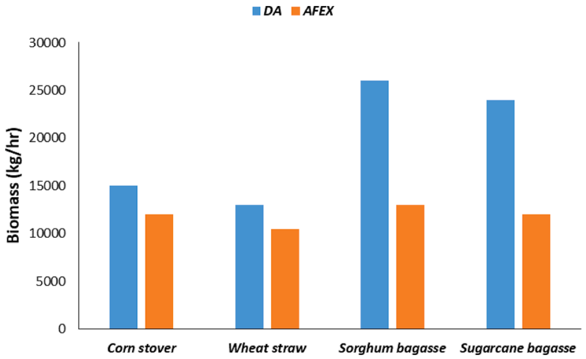


Fig. 8. Amount of biomass for each pretreatment and Quaker Oats process.

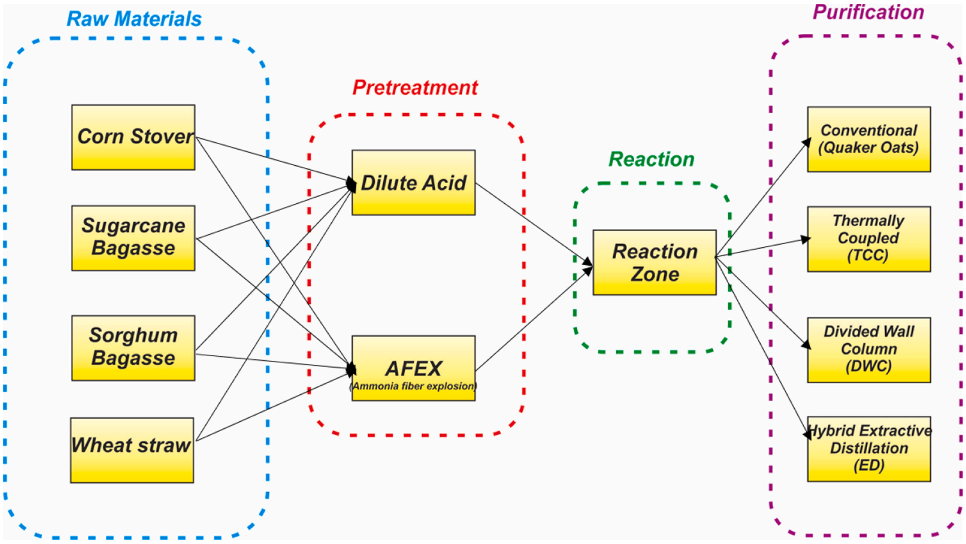


Fig. 7. Superstructure considered for the process production of furfural.

4.1. Prescreening results

Fig. 8, shows the amount of biomass required to produce furfural using the two pretreatments and the Quaker Oats process as a representative case. The biomass consumption is the same for the other separation options because the biomass required only depends on the pretreatment technology and its ability to release sugars. Based on the results, please note, how the dilute acid pretreatment requires greater amounts of biomass for all the cases compared with the AFEX pretreatment. These results can be explained, because the DA pretreatment generates a degradation of pentoses into by-products as methanol and acetic acid. The AFEX pretreatment does not produce by-products because it is focused on breaking the fibers to release sugars instead of degrading the fibers. For this reason, the AFEX is more efficient in the use of biomass. Note, that sorghum and sugarcane bagasse require more biomass, because the grade of crystallinity of cellulose for both is higher than the wheat straw and corn stover. Cellulose with a higher grade of crystallinity implies an increment on water- biomass ratio to achieve the solubilization of sugars, hence, more biomass is required (Krishnan et al., 2010; Li B. Z. et al., 2010). This can be easily corroborated by analyzing the dilute biomass ratios required to achieve the sugars solubilization in Tables 4 and 5.

Fig. 9, summarizes the energy consumption for the 32 alternatives. Please note, that the dilute acid pretreatment shows a remarkably lower energy consumption compared with AFEX for all cases, which contrasts with the result of biomass required by the pretreatments. The results can be explained owing to the AFEX process requires a recompression stage and a distillation column to purify and reuse the ammonia, which increases the costs and energy consumptions. Additionally, the AFEX pretreatment needs an enzymatic hydrolysis step. The water added during the enzymatic hydrolysis must be removed from furfural, which implies an increment in the costs and energy requirements used by the separation process.

Fig. 10., shows the environmental impact chart for all the biorefineries considered. The environmental impact is directly associated with energy consumption. Therefore, a higher energy consumption implies more emissions and stronger environmental impacts. It is for this reason, that the EI99 and energy consumption have the same tendency, as consequence, the biorefineries with DA pretreatment have lower environmental impacts.

With the purpose to demonstrate since energy consumption is the factor with the strongest contribution to environmental impact, Fig. 11 shows the broken-down chart of EI99 for corn stover biorefineries considering both pretreatments and Quaker Oats process as representative cases. Please note, that the steam used for heating and the electricity used for pumping have the stronger contributions, in contrast to the steel which is the factor with the less contribution. The same tendencies can be observed considering other separation schemes and raw materials.

Table 4
Conditions and conversions to DA pretreatment for the different raw materials.

	Wheat straw	Corn stover	Sorghum Bagasse	Sugarcane bagasse
Conditions				
Temperature (°C)	160	158	122	160
Pressure (atm)	7	5.5	2.32	6.6
Biomass load	40%wt	30%wt	10%wt	16%wt
Water load	60%wt	70%wt	90%wt	84%wt
Acid load kg acid/ 1000kg water	1	0.7714	2	3.43
Conversions				
Eq. 1	80% xylan	90% xylan	78.96% xylan	75.5% xylan
Eq. 2	4% glucan	9.9% glucan	17.49% glucan	4.37% glucan
Eq. 3	13.98% xylose	9% xylose	4.8% xylose	8.79% xylose
Eq. 4	7% xylose	8% xylose	7.98% xylose	10.7% xylose
Eq. 5	7% xylose	8% xylose	7.98% xylose	10.7% xylose
Eq. 6	5% Lignin	5% Lignin	5% Lignin	5% Lignin
Reference	Schell et al.,[57]	Humbird et al.,[31]	Tellez-Luis et al.,[58]	Neureiter et al., [59]

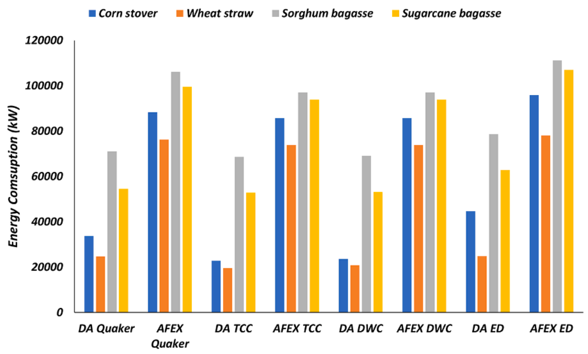


Fig. 9. Energy consumption for the different biorefineries.

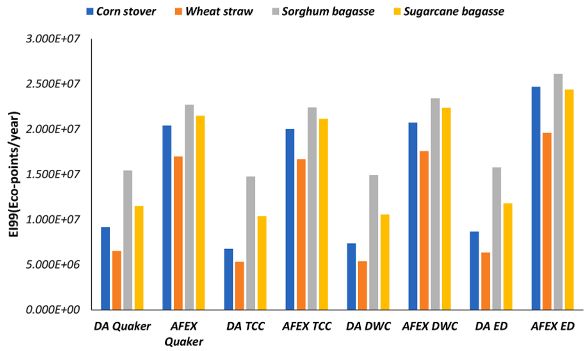


Fig. 10. Eco-indicator for the different biorefineries.

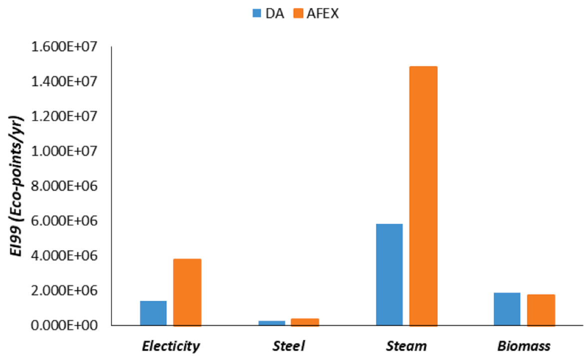


Fig. 11. Break down Eco indicator for biorefinery of corn stover and Quaker oats process.

A comparison of the total annual cost for all alternatives, is shown in Fig. 12. The operating cost depends on utilities such as the electricity used for pumping cooling water, and the steam for providing energy to the process. Therefore, TAC, EI99 and energy consumption follow the same trend. Note, that the biorefineries with AFEX pretreatment consume more energy than biorefineries with DA, hence, the AFEX alternatives are more expensive. Please note, that wheat straw is the cheapest raw material for all cases due to its lowest solid load. A lower solid load is associated with a less crystallinity of cellulose, which allows less severe pretreatment conditions, fewer acid concentrations, less enzyme load and fewer amounts of water reducing the cost for heating

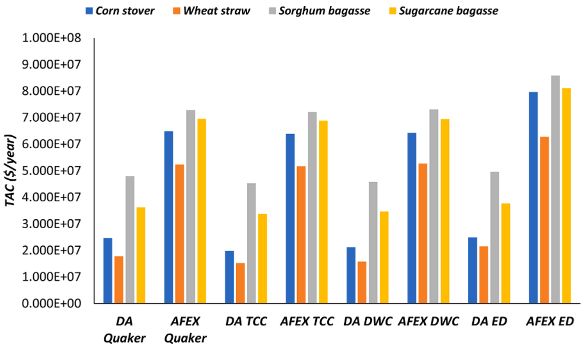


Fig. 12. Comparation for the different biorefineries

and separation.

For sugarcane and sorghum bagasse, the production costs for both are higher, which is caused by their more severe conditions during the DA pretreatment and higher water loads in AFEX. Both raw materials require great water quantities, which increases the heating and purification costs. On the other hand, note that the extractive distillation processes (ED) have higher environmental impacts and total annual costs, in contrast to other options. This increment on EI99 and TAC in ED processes is caused by the entrainer. The furfural separation requires great amounts of entrainer, subsequently, this entrainer and furfural must be separated. The entraineŕs purification increases the energy requirements, the costs and the eco-indicator, it is for these reasons that the ED purifications processes are not the best options.

On the other hand, in Fig. 9 the energy savings generated by TCC and DWC alternatives with respect to the conventional Quaker Oats processes are observed. These energy savings also generated reductions in total annual cost and eco-indicator. These energy savings indicate as DWC and TCC have a better distribution of the components avoiding the remixing phenomena, which is the main cause of inefficiency in distillation [49]. There are no significant differences in energy consumption, cost and environmental impact between DWC and TCC schemes, because both schemes are thermally equivalent, which means that both alternatives have similar energy consumption. However, smaller TAC and EI99 are observed for TCC scheme, the difference is caused by the size of column C2. In the DWC scheme, column C2 needs to be beyond the standard in diameter and the number of trays to integrate column C1 in a single shell. On the other hand, in the TCC process column C2 is considerably smaller. These differences in the number of trays and size are showed in Table 6. For this reason, the DWC is a little expensive. In addition, the TCC separation scheme is considered the best alternative separation to the biorefinery.

Table 6
Design parameters for separation processes.

Design Variables	Conventional	TCC	DWC	ED
Number of trays E1	—–	—–	—-	17
Number of trays, C1	55	97	81	53
Number of trays, C2	12	27	83	50
Number of trays, C3	6	9	11	50
Feed stage of water-rich phase C1	22	26	6	—–
Feed tray, C1	27	65	39	35
Tray of side stream C1	16	43	33	—-
Feed tray C2	8	1	—–	27
Feed stage C3	3	3	4	9
Diameter of C1, m	.44	1.02	—–	0.907
Diameter of C2, m	.42	0.36	2.57	1.844
Diameter of C3, m	1.63	0.8	1.23	0.521
Top pressure (atm)	1	1	1	1
Reflux ratio of C1	18.5	24.5	—–	0.2
Reflux ratio of C2	0.21	—–	25.14	18
Reflux ratio of C3	0.208	0.455	0.233	5
Furfural stream	6308.37	6304	6300.8	—-
Entrainer Flowrate, kg/hr	——	——	—–	6490
Side stream flowrate, kg/hr	3882	11668	3821.96	—-
Liquid Stream flowrate, kg/hr	—–	22603.8	4696	—-
Vapour Stream flowrate, kg/hr	—–	179.8	38790.3	—-

In summary, Figs. 9–12 showed as the AFEX pretreatments are more efficient in the use of biomass; nevertheless, the ammonia compression and subsequent purification joined to the water added in hydrolysis stages raise the processes costs and increase the environmental impact. In contrast, the DA pretreatment required more biomass. However, DA pretreatments require fewer quantities of water, which reduce the operating cost caused by purification and the environmental impacts. At the same time a reduction on water consumption generates a more sustainable process.

4.2. *Optimization results*

Based on the lowest TAC and EI99 values shown by the dilute acid pretreatment coupled with the thermally coupled process, these technologies were selected as the best options to produce furfural for all lignocellulosic wastes. The process flowsheet for complete biorefinery is presented in the Fig. 13. Therefore, this process structure will be optimized with the DETL method. The optimization of biorefinery requires a computational time of 504h per biomass, for this reason, the complete set of alternatives is not optimized.

The optimization results are presented through Pareto front charts EI99 vs TAC. The Pareto fronts are presented in Fig. 14. These Paretós front correspond to 120 solutions of the last generation (generation 810). Each point represents a furfural plant design for each feedstock. Fig. 15. shows the evolution of wheat strawś Pareto front during the optimization as a representative case. This chart is obtained by plotting the Pareto front points (designs) for representative generations (Gen), this Figure represents as the objective functions are improved through the optimization process. Note as in Fig. 15., the designs obtained with the optimization method converge to a single point, this point is called utopia point. This point represents the solution that has the best tradeoff for both objectives [53]. The convergence to the utopia point indicates that the solutions reported in this work are in the vicinity of global optimum, similar behaviors are showed in the optimization of the other raw materials.

Based on Fig. 14., the biorefinery with wheat straw shows the lowest environmental impact and cost followed by the corn stover, sugarcane bagasse and sorghum bagasse, respectively. This tendency is the same as the tendency showed during the prescreening, which confirmed as the cost depends strongly on pretreatment conditions specifically of biomass-water ratio. The pretreatment conditions are important because they determine the amount of biomass to be treated and the amount of water added. The sugarcane and sorghum bagasse require a larger water-biomass ratio, which means that for these processes it is necessary to add more water, which must be removed. Therefore, large amounts of water increase separation costs and energy consumption. The design parameters obtained during the optimization method are reported in Table 7. In addition, in the supplementary material (Tables S5-S8) the complete mass flows and energy consumptions for each biorefinery are provided.

Based on the results a biorefinery with wheat straw as raw material is the best alternative to produce furfural because it provides the lowest cost and environmental impact. In contrast, the sugarcane and corn stover are noticeably more abundant in Mexico, which can represent an advantage when supplying raw material to the process, however, these processes have higher TAC and EI99. Finally, the sorghum bagasse process is the most expensive and it has the highest environmental impact due to the high water-biomass ratio, for this reason it is considered the worst option.

5. Conclusions

The production of chemicals derived from biomass aid to mitigate

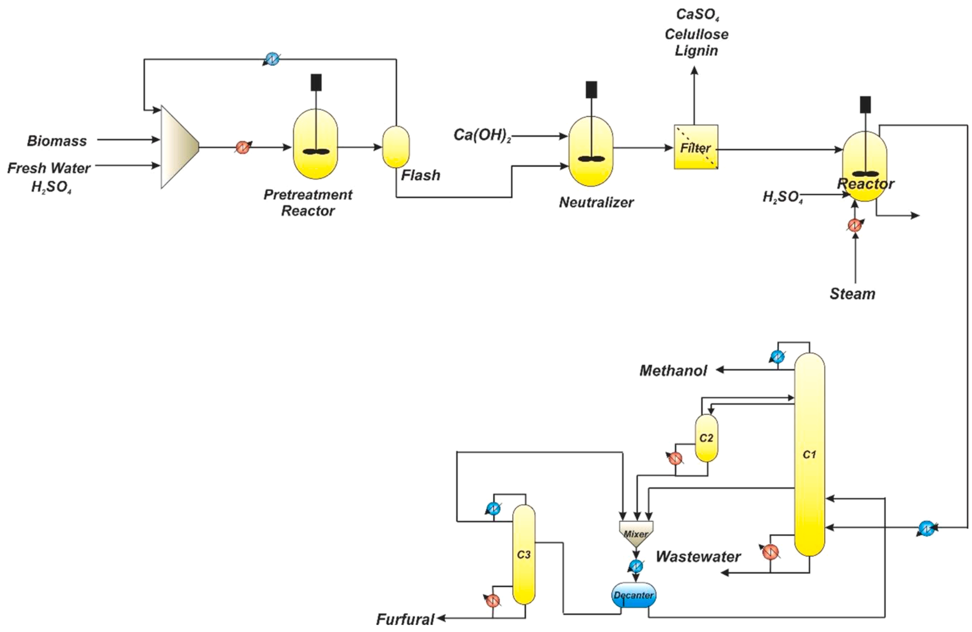


Fig. 13. Process scheme selected for furfural production.

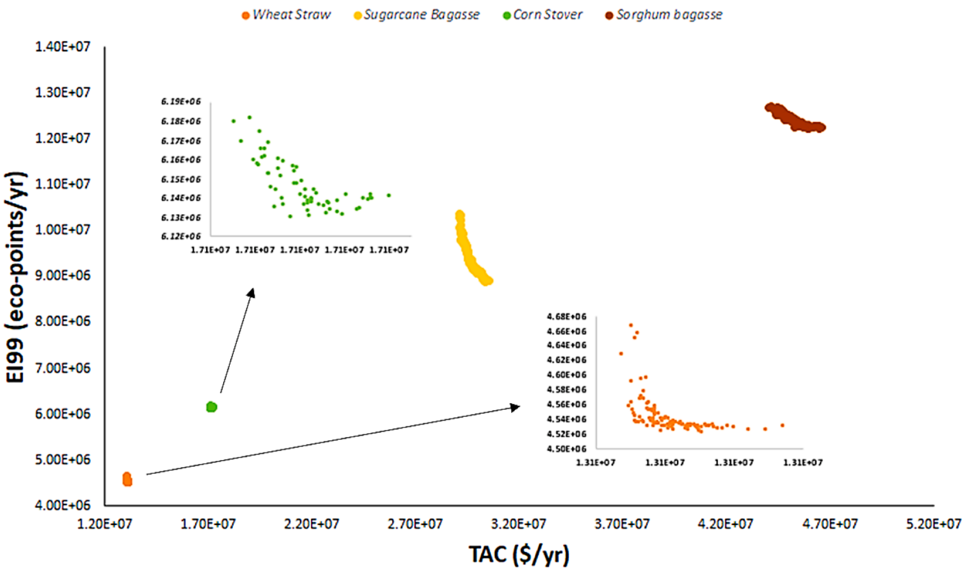


Fig. 14. Pareto fronts for furfural production biorefinery using DA and TCC scheme.

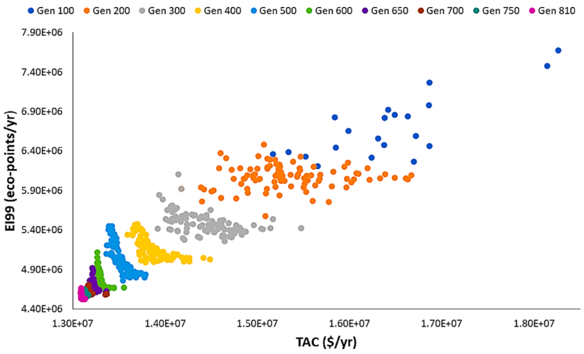


Fig. 15. Evolution of Pareto front through generations for wheat straw process using DA pretreatment and TCC separation scheme.

the strong dependence on petroleum products reducing in this way, the polluting emissions, and toxic residues. In this work, the design of several furfural production processes considering different biomasses was performed. In the same way, different novel technologies such as thermally coupled schemes and different pretreatment options have been considered for reducing the energy requirements, the excessive use and degradation of biomass, and the emissions generated. To generate processes for furfural production with the lowest environmental impact and cost. The results show that dilute acid pretreatment and a thermally coupled separation process are the best options for furfural production for the four feedstocks due to this configuration has less cost and environmental impact. During the optimization phase it is possible to decrease the cost of the process by around of 15% for TAC and EI99. This improvement is caused by a reduction in the mass flows of recycling streams and a lower use of biomass and water during the processes. The water used in the pretreatment step has the strongest influence on the cost and environmental impact because, the water added determines the

Table 7
Design parameters obtained during the optimization for furfural processes using DA and TCC.

Design Variables	Wheat straw	Corn stover	Sugarcane Bagasse	Sorghum Bagasse
Biomass flow (kg/hr)	12213	15981	22040	24183
Sulfuric acid flow Pretreatment(kg/hr)	183.19	287.64	397.21	446.63
Pressure flash pretreatment (atm)	3	1	3	1
$Ca(OH)_2$ flowrate (kg/hr)	138.235	217.055	299.83	336.46
Sulfuric acid flowrate reaction zone(kg/hr)	14.85	28.20	113.48	220.78
steam flowrate reaction zone(kg/hr)	10843.9	13680	7278.99	11924.1
Pressure steam reaction zone (atm)	12.86	13.85	18.68	15.60
Pressure reactor reaction zone (atm)	1.0084	1.052	1.047	3.18
Number of trays, C1	105	102	115	104
Number of trays, C2	22	17	16	14
Number of trays, C3	8	9	10	9
Feed stage of water-rich phase C1	47	44	21	26
Feed tray, C1	65	57	83	71
Tray of side stream C1	28	21	52	33
Feed tray C2	1	1	1	1
Feed stage C3	7	6	5	7
Diameter of C1, m	1.1	1.4	1.7	1.8
Diameter of C2, m	0.46	0.67	0.7	0.78
Diameter of C3, m	0.611	1.11	1.2	2.34
Top pressure (atm)	1	1	1	1
Reflux ratio of C1	26.43	20.69	23.19	31.26
Reflux ratio of C3	0.30	1.20	1.88	1.07
Side stream flowrate C1, kg/hr	2876.36	4551.34	5861.35	4540
Liquid Stream flowrate, kg/hr	924.43	2539.87	1958.8	3315
Vapour Stream flowrate, kg/hr	178.81	25.02	628.8	498.1
Reboiler Duty C1 (kw)	2890	3906.75	4161	5382.6
Reboiler Duty C2 (kw)	74.77	12.08	257.3	206.05
Reboiler Duty C3 (kw)	82.68	113.50	93.25	238
Furfural mass purity %	99.8%	99.3%	99.3%	99.9%
Methanol mass purity %	99.3%	99.6%	99.3%	99.5%
Investment cost ($)	24,347,000	24,653,220	25,837,520	27,084,320
Total Annual Cost ($/yr)	13,092,504	17,122,917	29,729,476	45,398,620
Eco-Indicator 99 (Eco-points/yr)	4,536,512	6,130,272	6,199,056	12,283,218

energy consumed during the reaction and separation stages. Therefore, during the optimization the amount of biomass and other process parameters are improved to minimize the effect of excessive use of water. The results indicate that a biorefinery to produce furfural with wheat straw as raw material is the best option, based on the lowest cost and eco indicators. This work is a good example of how the implementation of different novel technologies to a current process can improve the efficiency on the use of resources, energy savings and generating in this way, a cleaner production technology with the lowest environmental impact and energy consumption.

This work considers that the total amount of lignocellulosic residues generated each year in Mexico are available to produce furfural. However, some lignocellulosic residues are left on the ground to avoid erosion and provide nutrients to the soil. For this reason, it is usual to consider that only 25% to 40% of the residues are available. Considering 8500hr of operation per year and based on the information provided in Table 7, the results indicate that only around 3.59- 0.281% of the total available residues are required. However, to ensure an industrial scale production of furfural and avoid these erosion issues, it is suggested to develop a supply chain analysis for this process. In this sense, the results obtained in this work provide valuable information such as process yield, cost and environmental issues, for a subsequent supply chain analysis for the production of this platform chemical at the country-level. Finally, the procedure proposed in this work can be extended to other raw materials, products and processing pathways using their corresponding data of biomass composition, types of chemical reactions, conversions, temperatures and operational flows.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cep.2021.108569.

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