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Sustainable Design of an Optimal Supply Chain for Furfural Production from Agricultural Wastes

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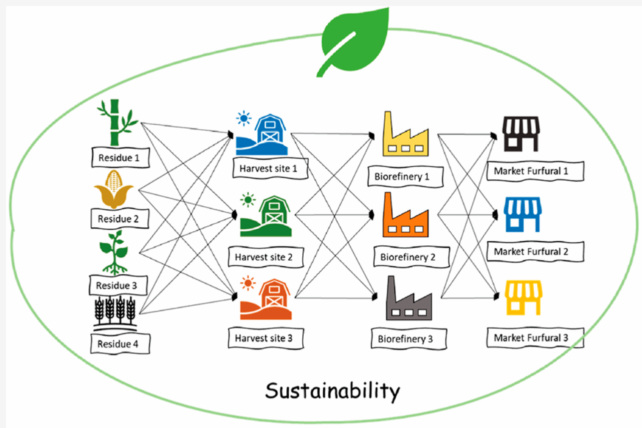
ABSTRACT: Biochemicals produced from lignocellulosic residues appear to be a feasible solution to replace traditional fossil resources. However, their implementation must overcome some challenges such as biomass seasonality; feedstock selection; harvest selection; potential geographical biorefineries location; and numerous economic, environmental, and social restrictions. This work proposes a multiperiod supply chain model for the use of agricultural wastes toward the production of platform biochemicals, such as furfural. The most abundant of Mexico's lignocellulosic residues are considered. The demand of furfural was chosen so that it can replace the feedstocks required to produce the terephthalic acid imported to Mexico. Economic, environmental, and social objectives were considered to evaluate the supply chain solution. The economic aspect consists of the maximization of net profit. The environmental impact is the minimization of eco-indicator 99, and the social objective is the maximization of jobs generated. The results show that furfural production for replacing current raw materials in Mexico is feasible. The supply chain solution with the best trade-off consists of a profit of 1 billion USD/year, 19 000 jobs generated/year, and 370 million eco-points/year. Finally, the supply chain model proposed a distributed furfural production scheme, where several small furfural plants are installed and distributed over all of the country.



■ INTRODUCTION

Nowadays, climate change, pollution, resource depletion, and other important environmental problems have forced mankind to search for renewable and environmentally eco-friendly products for replacing the old commodities derived from petroleum. In this way, biomass and especially the lignocellulosic residues are some of the most abundant renewable raw materials in the world. Estimations from the U.S. Department of Energy[1] indicate that the worldwide biomass availability is around 5 billion tons per year. The lignocellulosic residues have several advantages over other biomass sources; i.e., they are cheap because these kinds of raw materials are considered wastes, thus their costs are only associated with the collection costs and transport. Besides, they avoid the use of food crops for producing biochemicals, solving, in this way, possible ethical dilemmas. It is clear that the use of lignocellulosic residues for producing biochemicals provides important benefits associated with the incorporation of these wastes into the value chain, such as the generation of profits for farmers from the sales of wastes; reductions of toxic residues and emissions; and the generation of renewable ecofriendly products, chemicals, and materials. In this way, the U.S. National Renewable Energy Laboratory (NREL) has listed the 30 most important biochemicals produced from biomass.[2] In this list, the furfural and two of its derivates (furan dicarboxylic acid and levulinic acid) stand out owing to their several industrial applications. Furfural is an important and versatile biochemical platform; it is used in the production of nematicides, lubricant oils, diols, solvents, furan resins, and fuels.[3,4] Additionally, furfural has proved to be an important precursor in the production of many plastics such as nylon-6-6, polyethylene terephthalate (PET), and polyester.[5−7] Despite the enormous potential implied in the conversion of lignocellulosic wastes to biochemicals, one the major barriers preventing the implementation of these eco-friendly alternatives is the seasonal biomass availability and variability.[8] This biomass variability depends on many factors such as harvest

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Figure 1. Furfural market locations in Mexico.

location, seasonality, the land's nutrients, weather conditions, farmers' sowing decisions, etc. These factors can provoke an inconsistent production of biochemicals, resulting in several problems to cover the demand required for these chemicals. However, this problem can be overcome through suitable design and analysis of the supply chain (SC) involved in the production of the biochemicals.[9] The SC provides a flexibility in the provision of raw materials to the biorefinery; in addition, it gives the capability to generate an optimal inventory planning and operational schedule for a biorefinery in order to satisfy the demand.[10,11]

In recent years, different supply chain works for producing a wide range of different biochemicals have been reported. Marufuzzaman et al.[12] reported the design and optimization of a supply chain for syngas production from woody residues; their study consists of mixed-integer linear programming (MILP) which was implemented considering nine states of United States. The target of this work is to determine the optimal biogasification facilities and chipping terminal locations in order to achieve a continuous production of syngas and minimize the costs. Čuček et al.[13] present a regional supply chain based on MILP for the generation of different types of biofuels, energy, and food. The idea of this work is the maximization of the biomass resources considering competition between energy and food production and minimizing the carbon footprint generated by the supply chain activities. Paolucci et al.[14] proposed a two-tier supply chain model applied to the north of Italy for producing bio-oil; their first tier consists of the analysis and design of SC considering average territorial demands and biomass data. Their second tier consists of designing an SC using detailed data. The idea of this work is to evaluate the data's quality and how it affects the supply chain solutions. Furthermore, Marvin et al.[15] analyzed an SC for bioethanol production using different biomasses in the Midwestern United States; in addition, they studied the feasibility of meeting governmental biofuel mandates in 2015 using installed corn stover facilities. They found that the mandates could be satisfied with important reductions in the bioethanol costs and using the installed facilities.

In the specific case of Mexico, some SC works have been reported; most works are focused on biofuel production purposes from biomass. Murillo-Alvarado et al.[16] proposed an MILP SC model with the aim of producing solid fuels and ethanol from lignocellulosic residues generated by the tequila industry. They consider the maximization of net profit and the minimization of environmental impacts; their results indicate that several small processing plants are required in order to minimize the environmental impact, and even with this configuration important profits are obtained. Domínguez-Garcia et al.[17] studied the feasibility of replacing the demand of jet fuels with biofuels produced from lignocellulosic residues in airports of Mexico; they analyzed different scenarios and demands. Additionally, they considered economical and carbon emissions as objectives functions. Their results showed that in Mexico there is sufficient biomass to satisfy all airport demand for jet fuel, obtaining, in this way, important profits and reductions of CO_2 emissions up to 93%. Rendon-Sagardi et al.[18] proposed a dynamic supply chain model for bioethanol production. The aim of this work was to produce the ethanol for blending (90% gasoline with 10% of ethanol). They used a dynamic model in order to consider the changes in gasoline demand. Their results indicate that, because of the current situation in Mexico, it is only feasible to cover 0.8% of the total demand of blends.

Traditionally, biorefinery supply chain works have focused on biofuels and the minimization of costs or maximization of profit. However, up to now, the feasibility for producing and distributing other biochemicals produced in biorefineries has not been broadly addressed. In this work, using a supply chain model, the feasibility of producing furfural in Mexico is studied with the aim of replacing the current raw materials imported for producing terephthalic acid (TA). TA was chosen according with its high demand in Mexico and in the wide market, which is valued at 110.6 billion USD.[19,20] The contribution of this work is important, because this study allows determination of the feasibility of replacing the current raw materials for important commodities with biochemicals in order to achieve a more sustainable and renewable way of producing them. Economic, environmental, and social aspects were considered as objective functions to evaluate the supply chain solution. The economic objective consists of the maximization of net profit, whereas the environmental impact

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and social aspects correspond to the minimization of eco-indicator 99 and the maximization of jobs generated, respectively. These indexes were selected because the new SC works must be focused on improving sustainability, not only the economic aspects. These indexes are in accordance with the principles of sustainability and green chemistry proposed by Jiménez-González and Constable[21] and with the challenges and sustainability indexes in SC that must be addressed according to the suggestions of Garcia and You[22] and Perez et al.[23]

2. PROBLEM STATEMENT

Mexico has an important availability of lignocellulosic residues, the Ministry of Agriculture of Mexico (SAGARPA) reports that each year are generated 5.86×10^8 tons of lignocellulosic residues in the 20 million of hectares used for agricultural purposes in the country.[24,25] Despite Mexico having an enormous generation of lignocellulosic residues, only a small fraction, less than 5%, of the total amount is used, mainly for cattle food purposes; the rest of the residues are burned, generating several environmental problems such as pollution, fires, and novice emissions. Data from the Ministry of Ecology and Climate Change (IECC) indicate that 5% of the total emissions of CO_2 generated yearly in Mexico are originated by the burn of lignocellulosic residues.[26,27] Those lignocellulosic residues can be used to produce high value chemicals such as furfural. Furfural is an important raw material in the production of terephthalic acid (TA) by green routes. Owing to the lack of feedstock, Mexican chemical factories cannot meet the demand of TA required in Mexico. According to the most recent data provided by the Mexican National Association of Chemical Industry (ANIQ), in 2019 were imported 79 270 tons of terephthalic acid, despite Mexico having the installed capacity to produce it.[19] The demand of furfural required in Mexico for producing all of the imported terephthalic acid has been estimated using the yields data reported by Tachibana et al.[5] The locations of potential furfural markets (TA producers) are shown in Figure 1. The location and demands required in each market were obtained from ANIQ.[19] The sales of byproducts (mainly methanol) generated during the process production of furfural are also considered. Because the TA producers locations correspond with the most important chemical complexes of Mexico, the market locations of methanol are considered the same as those for the furfural markets. Table 1 shows the cities where the potential markets are located and their respective demands per year for furfural and methanol.

Corn stover, wheat straw, sorghum bagasse, and sugar cane bagasse were considered as raw materials owing to being the most abundant lignocellulose residues generated yearly in Mexico.[25] The annual availability and costs of these residues are showed in Table 2. One important point to be considered is the variable production rate of these wastes caused by some natural conditions such as seasonality and location, the land's nutrients, etc. In this sense, Figure 2 shows the availability of corn stover for each Mexican state during different seasons as representative cases; these data were taken from Ministry of Agriculture of Mexico (SAGARPA).[25] The maps for the other raw materials are shown in Figure S1 of the Supporting Information.

Table 1. Demand of Furfural and Methanol for Each Market

market city	market (Mi)	furfural demand (ton/y)	methanol demand (ton/y)
Camargo	M1	3310	0
Coatzacoalcos	M2	384 622	261 000
Puebla	M3	11 715	0
Poza Rica	M4	26 475	0
Tampico	M5	39 713	29 000
Salamanca	M6	13 237	0

Table 2. Raw Materials of Agricultural Considered for Mexico[24,25,28]

lignocellulosic residue	cost USD/ton	total availability (ton/year)
wheat straw	38.85	2 886 528
corn stover	58.5	48 204 613
sorghum bagasse	16	8 553 151
sugar cane bagasse	25	56 841 522

In order to consider the biomass variability caused by harvest location and seasonality, multiperiod inventory planning with a within one-year horizon is proposed for the supply chain; this horizon has been divided into the four different time periods ($t \in T$). The consideration of multiperiod inventory planning allows managing of the storage and shipments of biomass and products in order to satisfy a continuous demand of markets. Figure 3 shows the super-structure considered for solving the supply chain. The conversions from lignocellulosic wastes to furfural and methanol are known; these data were taken from the previous work of Contreras-Zarazua et al.[29] In order to provide a more realistic biomass distribution, the Mexican territory has been discretized into 59 different regions. This discretization was based on population data, where the zones with less population have greater lignocellulosic waste availability. The discretization of Mexican territory and the availability data of wastes for each zone are reported in Figure S2 and Tables S1−S4 of the Supporting Information, respectively. The aim of this work consists of determining which is the best raw material to produce furfural, the harvest site where this raw material is collected, the location and capacity of the biorefinery facilities and the best shipment routes to transport the raw material from harvest sites to biorefineries and the furfural and methanol from biorefineries to markets in each period of time t.

Economic, environmental, and social issues have been considered the objective functions to evaluate the supply chain performance solution. The economic index is the maximization of the net profit. The environmental index is the minimization of eco-indicator 99, and the social index consists of the maximization of jobs generated during the different activities involved in the supply chain (e.g., recollection, transportation, workers in biorefinery, etc.). The jobs generated are calculated using the Jobs and Economic Development Impact methodology (JEDI).[30]

3. ASSUMPTIONS

In this paper, some assumptions are considered in order to simplify the problem's solution. It is assumed that the centroid area of each zone generated during the discretization of Mexico (see Figure S2) is the place where all of the lignocellulosic wastes of the region are located; for this reason each point is considered as the harvest location. This assumption could be

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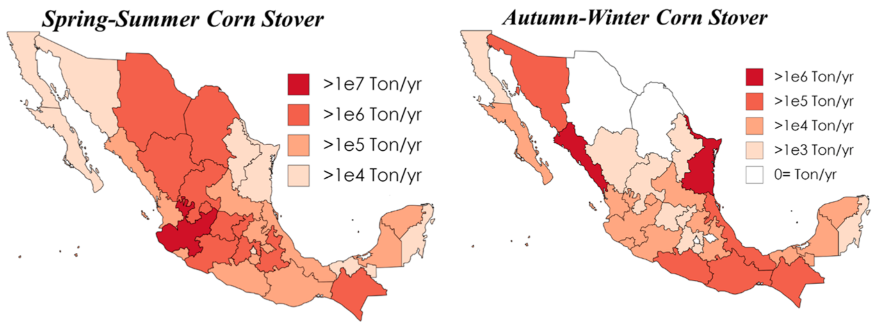

Figure 2. Map for biomass availability of corn stover.

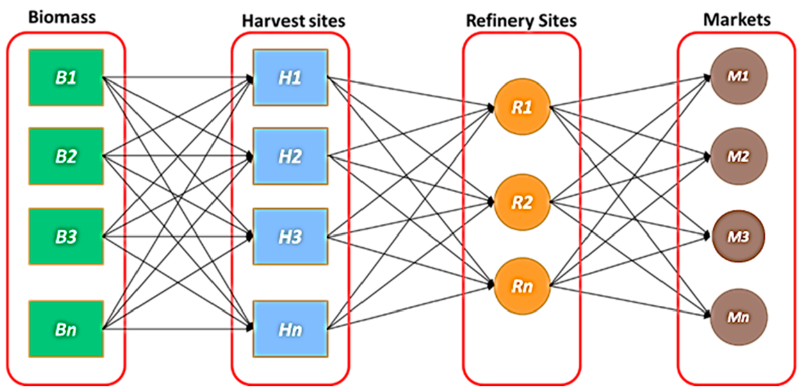

Figure 3. Supply chain super structure.

easily relaxed only dividing each discretization zone into smaller subsites. The possible biorefineries' locations are given by the position of the centroid but displaced 14 km; it avoids a zero distance in the case that a centroid could be selected as a biorefinery and harvest location at the same time.[31]

It is assumed that all of the biomass is storage only at the harvest site. If the biomass is storage during long periods of time, it suffers losses due to degradation by natural processes. Therefore, this assumption avoids the monetary losses caused by the transportation of biomass that never will be used due to its degradation in the biorefineries. It is important to highlight that the biomass degradation only occurs before the transportation of biomass. In this way, a biomass degradation factor of 10% is considered per period. This is a reasonable value for degradation losses; similar values were used in previous works presented by Ng and Maravelias.[32] This degradation factor is considered independent of the location; for this reason, it is the same for all of the harvest sites.

Finally, it is considered that only one biorefinery can be constructed by each zone. The biorefineries are characterized by the use of important amounts of water. This consideration avoids the excessive use of water of a specific region, and at the same time, this assumption avoids the depletion of the total biomass located by zone, which can be used for other purposes such as cattle feed.

4. MODEL FORMULATION

In this section, the mathematical formulation of the supply chain model for furfural production and the respective objective functions are developed. The mathematical model is formulated as a multiperiod Mixed Integer Lineal Programing (MILP) problem in order to consider the biomass seasonality. It is important to highlight that the calculation of the transportation distances was carried out using the Rhum line method, which is explained in the Supporting Information.

5.1. Mass Balance at the Harvest Sites. The mass balance at the harvest sites was realized considering a cyclic inventory. The biomass inventory level ($A^{RM}_{i,j,t}$) at a harvest site for a specific time t is calculated according to the next equation:

$$A^{RM}_{i,j,t} = A^{RM}_{i,j,t-1}(1 - \alpha_{j,t}) + b^{RM}_{i,j,t} - \sum_{k} S^{RM}_{i,j,k,t} \qquad i, j \in J^{RM}, t \tag{1}$$

where $A^{RM}_{i,j,t-1}$ is the inventory level of a previous time period. $\sigma_{j,t}$ is the loss factor coefficient due to biomass deterioration, which is considered as 10% of the raw material. $S^{RM}_{i,j,t}$ represents the shipments of biomass j from a harvest site i to a biorefinery k. $b^{RM}_{i,j,t}$ is the biomass used from a specific harvest site in a period of time, which must be lower than or equal to the biomass availability of the harvest site. This variable is calculated as follows:

$$b^{RM}_{i,j,t} \le \varphi_{i,j,t} \qquad i, j \in J^{RM}, t \tag{2}$$

where $\phi_{j,t}$ is the availability of biomas j in a harvest site i at a period t.

The shipments of raw materials from harvest to the refineries are constrained according to eq 3.

$$\sum_{t} b^{L}_{i,j,t} \cdot y_{i,j,k} \le \sum_{t} S^{RM}_{i,j,k,t} \le \sum_{t} y_{i,j,k} b^{U}_{i,j,t} \qquad i, j \in J^{RM}, k \tag{3}$$

where $b^{L}_{i,j,t}$ and $b^{U}_{i,j,t}$ are the lower and upper bounds of the biomass required in a harvest. $y_{i,j,t}$ is the binary variable for the selection of shipments in the arc $i \rightarrow k$ (shipments from harvest to biorefinery). If $y_{i,j,t} = 1$, the arc $i \rightarrow k$ is selected to ship biomass; otherwise it is not chosen.

The cyclic inventory used for guaranteeing a constant supply to refineries is implemented considering that the biomass storage in the last period ($t = T$) is equal to the storage at beginning period ($t = 0$), which can be expressed mathematically as follows:

$$A^{RM}_{i,j,t=T} = A^{RM}_{i,j,t=0} \quad i, j \in J^{RM}, t \tag{4}$$

where each period t corresponds to 3 months in order to achieve one year of time horizon.

5.2. Mass Balance at the Refineries. The mass balance for biorefineries is obtained in an analogous way to harvest sites considering cyclic inventory. The mass balance equation for biorefineries is given by

$$A^{P}_{j,k,t} = A^{P}_{j,k,t-1} + PP^{P}_{j,k,t} - \sum_{m} S^{P}_{j,k,m,t} \quad j \in J^{P}, k, t \tag{5}$$

where $S^{P}_{j,k,m,t}$ is the total sales of products (furfural and methanol shipments) from biorefinery k to the market m at time t. $A^{P}_{j,k,t}$ and $A^{P}_{j,k,t}$ are the inventory levels of product j in the current and previous period of time, respectively, for the biorefinery k. $PP^{P}_{j,k,t}$ represents the amounts of products (methanol and furfural) produced at biorefinery k during period t, which is determined using the next equations:

$$BC^{RM}_{j,k,t} = \sum_{i} S^{RM}_{i,j,k,t} \quad i, j \in J^{RM}, k, t \tag{6}$$

$$PP^{P}_{j,k,t} = \sum_{j \in RM} \eta^{RM}_{j,j'} BC^{RM}_{j,k,t} \quad j \in J^{P}, k, t \tag{7}$$

$BC^{RM}_{j,k,t}$ is the biomass consumed at each biorefinery k. $\eta^{RM}_{j,j'}$ is the conversion factor of each raw material $j \in J^{RM}$ to products $j' \in J^{P}$. The conversion data from different raw materials to furfural and methanol are show in Table 3. The implementation of the cyclic inventory for biorefineries is analogous to that of harvest inventory. Therefore, the cyclic inventory is expressed as follows:

Table 3. Conversion Data for Each Raw Material

lignocellulosic waste	conversion furfural (t output/t input)	conversion methanol (t output/t input)
corn stover	0.077	0.01
wheat straw	0.082	0.011
sorghum bagasse	0.035	0.007
sugar cane bagasse	0.046	0.009

$$A^{P}_{i,j,t=T} = A^{P}_{i,j,t=0} \quad i, j \in J^{P}, t \tag{8}$$

The sales of biorefineries $S^{P}_{j,k,m,t}$ (shipments to markets) are constrained according to the next equation:

$$\gamma^{L} \le \sum_{k} S^{P}_{j,k,m,t} \le \gamma^{U} \quad j \in J^{P}, m, t \tag{9}$$

Equation 9 indicates that the shipments ($S_{j,k,m,t}$) are constrained between upper (Υ^{U}) and lower bounds (Υ^{L}). For furfural, the lower bound is satisfied by the demand required by the markets, whereas the upper bound was set for satisfying up to an additional 10% of the total demand. In the case of methanol, its demand is higher than that of the furfural market; it is for this reason that the methanol sales are only constrained with a lower bound which corresponds to the total amount of methanol produced at the biorefineries.

5.3. Refinery Capacity Constrains. The capacity constraints for a biorefinery k are defined based on the amount of biomass consumed j at time t ($BC_{j,k,t}$). The capacities of the biorefineries are constrained by

$$\beta^{L} W_{j,k} \le \sum_{t} BC^{RM}_{j,k,t} \le \beta^{U} W_{j,k} \quad j, k \tag{10}$$

where $W_{j,k}$ is the binary variable for the selection (installation) of a biorefinery at a certain location k, while β^{L} and β^{U} are the lower and upper bounds of biomass consumed, which corresponds to 10 000 tons/y and 1 500 000 kg/h, respectively. These bounds correspond to furfural productions of 850 tons/y (100 kg/h) and 51 0000 tons/y (6000 kg/h). These limits were selected in order to fit them to the smallest and largest furfural plants reported by Zeitch[33] and Marcotullio.[4] The conversion data from biomass to furfural are reported in Table 3.

Connectivity Capacity Constrains. The connectivity constraints limit the number of biorefineries allowed by zone and how these biorefineries receive and ship the products. The connectivity constraints are expressed mathematically as follows:

$$\sum_{j \in RM} W_{j,k} \le 1 \quad k \tag{11}$$

$$\sum_{j \in J^{P}} \sum_{m} U_{j,k,m} \ge \sum_{j \in J^{RM}} W_{j,k} \quad j \in J^{P}, k \tag{12}$$

where $W^{P}_{j,k}$ is the binary variable for installing a bioenergy in a certain zone. Equation 11 establishes that at most one refinery is allowed for each zone. $U_{j,k,m}$ is the binary variable for the selection of shipments in the arc $k \rightarrow m$ (shipments from biorefinery to market). If $U_{i,j,t} = 1$, the arc $k \rightarrow m$ is selected to ship biomass; otherwise it is not selected. Therefore, eq 12 indicates that at least one shipment arc from refinery to market ($k \rightarrow m$) must be used if a refinery is selected in a specific location k for a specific biomass j. Additionally, when an arc is selected the mass flows (shipments) related to this arc can be nonzero, which is represented as follows:

$$\sum_{t} S^{P}_{j,k,m,t} \le \varepsilon^{U} U_{j,k,m} \quad j \in J^{P}, k, m \tag{13}$$

where ε^{U} is the yearly upper bound of shipments, which is given by the maximum production capacity allowed of a furfural plant of 51 000ton/y. $U_{j,k,m}$ is the binary variable for selecting the arc $k \rightarrow m$ (biorefinery to market).

5.4. Transportation and Raw Material Costs. On the basis of the data provided by the Ministry of Communications and Transports of Mexico (SCT), the main means of transport of products in Mexico is the truck; in this sense, the Ministry reports that the costs associated with the transport of products using trucks are divided into two types: variable costs which are a function of the travel distance and fixed costs related with the amount of material transported.[34,35] In this way, the equations used to calculate fixed and variable transportation costs were obtained from the data provided by the Ministry of Communications and Transports of Mexico.[34] The costs equations (in USD dollars) are shown as follows:

$$\mathrm{VTC}^{i-k} = 0.856 \sum_i \sum_{j\in \mathrm{RM}} \sum_k \sum_t y_{i,j,k} D_{j,k,t}^{i-k} \tag{14}$$

$$\mathrm{FTC}^{i-k} = 3.126 \sum_i \sum_{j\in \mathrm{RM}} \sum_k \sum_t S_{i,j,k,t}^{\mathrm{RM}} \tag{15}$$

$$\mathrm{VTC}^{k-m} = 0.856 \sum_k \sum_{j\in P} \sum_m \sum_t U_{j,k,m} D_{k,m,t}^{k-m} \tag{16}$$

$$\mathrm{FTC}^{k-m} = 3.126 \sum_{j\in P} \sum_k \sum_m \sum_t S_{j,k,m,t}^{\mathrm{P}} \tag{17}$$

where $\mathrm{VTC}^{i\text{-}k}$ is the variable transportation cost between harvest i and biorefinery k. $\mathrm{VTC}^{i\text{-}k}$ is the variable transportation from biorefinery k to market m. $D_{j,k,t}^{i\text{-}k}$ is the transportation distance from harvest to refinery, and $D_{k,m,t}^{k\text{-}m}$ is the distance from the refinery and market. $\mathrm{FTC}^{i\text{-}k}$ and $\mathrm{FTC}^{i\text{-}k}$ are the fixed transport costs from harvest i to biorefinery k and from biorefinery k to market m, respectively.

Because all of the raw materials considered in this work are agricultural wastes, their costs are only associated with their respective recollection cost. Therefore, the amount of biomass is the only variable that affects the cost; thus, the total raw materials costs (RMC) can be expressed by the following equation:

$$\mathrm{RMC} = \sum_i \sum_{j\in \mathrm{RM}} \sum_k \sum_t \mathrm{CBT}_j \cdot S_{i,j,k,t}^{\mathrm{RM}} \tag{18}$$

where CBT_J is the cost of biomass per ton ($USD/ton) and $S_{i,j,k,t}^{\mathrm{RM}}$ represents the shipments of biomass j from harvest i to refinery k in a specific time period t. The costs for each biomass are provided in Table 2.

5.5. Calculation of Capital and Utilities Costs. The biorefinery cost data reported by Contreras-Zarazúa et al.[29] were used as a reference to calculate the capital and utilities costs of biorefineries. This work reports the annualized utilities and capital costs for furfural biorefineries using different biomasses like corn stover, wheat straw, sorghum bagasse, and sugar cane bagasse. In order to consider the scale economy of furfural plants, the furfural processes proposed by Contreras-Zarazúa et al.[29] were scaled to different plant sizes, and their annualized costs were recalculated. The processes were scaled to furfural productions of 850 ton/y, 4250 ton/y, 8500 ton/y, 25500 ton/y, and 51000 ton/y, and their respective capital costs were calculated using the Guthrie method considering a payback period of 10 years, which was used to annualize the capital costs according to previous works reported by Contreras-Zarazúa et al.[29] and Turton et al.[36] The main idea is to use cost data for different plant sizes to generate a continuous function that allows calculation of annualized capital costs in the supply chain. However, because the annualized capital costs have a nonlinear behavior they cannot be used within a linear model. For this reason, the nonlinear equation for the annualized capital cost is simplified to a pseudo-continuous linear function using a piecewise linear approximation. This technique consists of the approximation of annualized capital costs using a set of linear equations.[37] Therefore, the five plant capacities considered in this work were used to generate the piecewise function; using these five production capacities, four linear intervals (n) were obtained. The parameters for these linear equations are given in Tables S8 and S9 of the Supporting Information. Once the linear intervals (n) have been generated, the piecewise function is implemented as follows:

$$\sum_n V_{j,k,n}^{\mathrm{RM}} = \sum_t \eta_j \mathrm{BC}_{j,k,t}^{\mathrm{RM}} \quad j \in J^{\mathrm{RM}}, k \tag{19}$$

$$\mathrm{ACC}_{j,k,n}^{\mathrm{RM}} = a_{j,n}\tau_{j,k,n} + m_{j,n} V_{j,k,n}^{\mathrm{RM}} \quad j \in J^{\mathrm{RM}}, k, n \tag{20}$$

where $V_{j,k,n}^{\mathrm{RM}}$ is the piecewise variable, which depends on the amount of biomass consumed in each biorefinery $\mathrm{BC}_{j,k,t}^{\mathrm{RM}}$, and its respective conversion factor $\eta_{j,j}^{\mathrm{RM}}$. Please note how the variable $V_{j,k,n}^{\mathrm{RM}}$ is analogous to the furfural produced at a biorefinery ($\mathrm{FP}_{j,k,t}^{\mathrm{P}}$). Note that the subindex n is the number of piecewise intervals (number linear equations). The piecewise function is shown in eq 20, where $\mathrm{ACC}_{j,k,n}^{\mathrm{RM}}$ represents the annualized capital cost obtained using the piecewise function for each refinery. $a_{j,n}$ and $m_{j,n}$ are parameters of linear equations obtained during the fitting of different capacities. Please note that both parameters depend only on the type of biomass and plant size, which is represented by the interval n. $\tau_{j,k,n}$ is the binary variable for the selection of a specific linear equation (segment or interval n) of the piecewise linear approximation. Because the piecewise function is used to quantify the capital cost of biorefineries, it is necessary to connect the binary variable $\tau_{j,k,n}$ with the binary variable for the selecting of biorefineries ($W_{j,k}$), which is carried out using the next equation:

$$W_{j,k} = \sum_n \tau_{j,k,n} \quad j \in J^{\mathrm{RM}}, k \tag{21}$$

Finally, the total annualized capital cost (TACC) is given by the sum of individual capital costs of each biorefinery, which can be expressed mathematically as follows:

$$\mathrm{TACC} = \sum_{j\in \mathrm{RM}} \sum_k \sum_n \mathrm{ACC}_{j,k,n}^{\mathrm{RM}} \tag{22}$$

In order to choose only one segment, the piecewise function needs to be constrained appropriately. In this case, the piecewise linear approximation has been constrained to each interval as follows:

$$850\cdot\tau_{j,k,n=1} \le V_{j,k,n=1}^{\mathrm{RM}} \le 4250\cdot\tau_{j,k,n=1} \quad j \in J^{\mathrm{RM}}, k, n = 1 \tag{23}$$

$$4250\cdot\tau_{j,k,n=2} \le V_{j,k,n=2}^{\mathrm{RM}} \le 8500\cdot\tau_{j,k,n=2} \quad j \in J^{\mathrm{RM}}, k, n = 2 \tag{24}$$

$$8500\cdot\tau_{j,k,n=3} \le V_{j,k,n=3}^{\mathrm{RM}} \le 25500\cdot\tau_{j,k,n=3} \quad j \in J^{\mathrm{RM}}, k, n = 3 \tag{25}$$

$$25500\cdot\tau_{j,k,n=4} \le V_{j,k,n=4}^{\mathrm{RM}} \le 51000\cdot\tau_{j,k,n=4} \quad j \in J^{\mathrm{RM}}, k, n = 4 \tag{26}$$

where the lower and upper bounds of the constraints correspond with the number of plants scaled from the previous work reported by Contreras-Zarazúa et al.[29]

Similarly, the annualized utilities costs for each biorefinery ($\mathrm{AUC}_{j,k}^{\mathrm{RM}}$) depend on plant size. In this case, the utilities costs can be easily associated with the plant size through the amount of raw material processed; for this reason, the utilities costs are calculated per ton of biomass processed yearly. These costs were calculated using the data reported by Contreras-Zarazúa

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et al.,[29] and the data were generated during the scaled function, obtaining a linear equation as follows:

$$\mathrm{AUC}_{j,k}^{\mathrm{RM}} = c_j W_{j,k} + d_j \sum_t \mathrm{BC}_{j,k,t}^{\mathrm{RM}} \quad j \in J^{\mathrm{RM}}, k \tag{27}$$

where c_j and d_j are coefficients that depend on raw material. $\mathrm{BC}_{j,k,t}^{\mathrm{RM}}$ is the biomass consumed in the biorefinery. The coefficients for eq 27 are reported in Table S10. It is important to mention that the utilities costs include the costs of cooling water, heat steam, and electricity. Finally, the total annualized utility costs for biorefineries (TAUC) are calculated using the next equation:

$$\mathrm{TAUC} = \sum_k \sum_{j \in \mathrm{RM}} \mathrm{AUC}_{j,k}^{\mathrm{RM}} \tag{28}$$

6. OBJECTIVE FUNCTIONS

In this section, the metrics used to evaluate the supply chain performance are explained. Economic, environmental, and social aspects have been considered to evaluate the supply chain. The economic metric is the maximization of annual profit; the environmental consists of the minimization of eco-indicator 99 in order to minimize the environmental impact. Finally, the social objective is represented by the maximization of jobs generated during different activities of the supply chain. These indexes and their mathematical formulation are explained below.

6.1. Economic Objective Function: Profit. The economic objective function considered in this work is the maximization of annual net profit (USD/y), which is given by the annual sales of products (furfural and methanol) minus the total annual costs due to different activities of the supply chain such as transportation cost, raw material cost, processing cost, annualized capital cost of biorefineries, etc. Mathematically, the profit can be expressed according to the next equation:

$$\mathrm{Profit} = \mathrm{SP} - (\mathrm{TUC} + \mathrm{TCC} + \mathrm{CS} + \mathrm{RMC} + \mathrm{VTC}^{i-k} + \mathrm{FTC}^{i-k} + \mathrm{VTC}^{k-m} + \mathrm{FTC}^{k-m}) \tag{29}$$

where SP is the profit due to sales of products. TAUC and TACC are the total utilities and annualized capital costs, respectively. CS is the storage cost of raw material and products, which is considered to be 0.059 USD/ton. RMC is the raw material cost. Finally, VTC^{i-k}, $\mathrm{VTC}^{i\text{-}k}$, $\mathrm{FTC}^{i\text{-}k}$, and $\mathrm{FTC}^{i\text{-}k}$ are the variable and fixed transportation costs for the different arcs, $i \rightarrow k$ and $k \rightarrow m$. The complete and detailed mathematical formulation of profit is given as follows:

$$\begin{aligned}\mathrm{maxProfit} = {} & \sum_{j \in P} \sum_k \sum_m \sum_t \mu_j \cdot S_{j,k,m,t}^{\mathrm{P}} - \Big(\sum_k \sum_{j \in \mathrm{RM}} \mathrm{AUC}_{j,k}^{\mathrm{RM}} \\ & + \sum_j \sum_k \sum_n \mathrm{ACC}_{j,k,n} \\ & + \sum_i \sum_{j \in \mathrm{RM}} \sum_t 0.059 A_{i,j,t}^{\mathrm{RM}} \\ & + \sum_i \sum_{j \in P} \sum_t 0.059 A_{i,j,t}^{P} \\ & + \sum_i \sum_j \sum_k \sum_t \mathrm{CBT}_j \cdot S_{i,j,k,t}^{\mathrm{RM}} \\ & + 0.0069 \sum_i \sum_k \sum_t D_{j,k,t}^{i-k} \\ & + 3.126 \sum_i \sum_j \sum_k \sum_t S_{i,j,k,t}^{\mathrm{RM}} \\ & + 0.0069 \sum_k \sum_m \sum_t D_{k,m,t}^{k-m} \\ & + 3.126 \sum_j \sum_k \sum_m \sum_t S_{j,k,m,t}^{\mathrm{P}}\Big)\end{aligned} \tag{30}$$

where $A_{i,j,t}^{\mathrm{RM}}$ and $A_{i,k,t}^{\mathrm{P}}$ are the inventory levels for biomass and products in a harvest site i or biorefinery k, respectively. μ_j represents the sales prices of products to the consumer, which are of 2500 USD/ton for furfural and 850 USD/ton for methanol.[38]

6.2. Environmental Objective Function: Eco-Indicator 99 (EI99). The environmental objective function is quantified using eco-indicador 99 (EI99), which is a methodology based on a life cycle assessment proposed by Goedkoop.[39] EI99 has proved to be a powerful tool in the environmental impact of supply chains; it has been applied successfully in several previous works.[40−42] This method quantifies the environmental impact of a specific process or activity by the evaluation of three main damage categories, which are damages to human health, damage to ecosystems, and resource depletion. Additionally, the EI99 provides three different perspectives for evaluating the environmental impact, which are based on cultural theory. These perspectives are Individualist, Egalitarian, and Hierarchist. In this work, a Hierarchist perpective is chosen to estimate eco-indicator 99, because this perspective considers a balance between short- and long-term effects in the evaluation of environmental impact. In this way, for a Hierarchist perspective, the contribution to total EI99 is given as follows: damages to human health and damage to ecosystem quality contribute 40% each, while the resource depletion contributes 20%.[39] On the basis of the above, the damage factors of these three categories in the supply chain are known, and they are directly associated with the amount of substances, transportation distance, and the process involved. The parameters used to calculate EI99 are reported in Table S11 of Supporting Information. These parameters were taken from previous literature reported by Goedkoop,[39] Russo et al.,[43] and Santibañez-Aguilar et al.[44] In the case of eco-indicator factors for processing biomass to furfural (biorefineries eco-indicator), the factor values were taken from the previous work of Contreras- Zarazua et al.,[29] dividing the EI99 value reported by the tons of raw material used. This consideration provides a linear dependence of eco-indicator 99 with respect to the amount of raw material used during the

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processing stage at biorefineries. This linear dependency is in accord with results reported in previous works.[41,45] Finally, the objective function for EII9 can be expressed as follows:

$$\min \mathrm{EI99} = \sum_{j\in \mathrm{RM}} \sum_{k} \sum_{t} \mathrm{EILW}_j \cdot \mathrm{BC}_{j,k,t}^{\mathrm{RM}} + \sum_{j\in \mathrm{RM}} \sum_{k} \sum_{t} \mathrm{EIBR}_k \cdot \mathrm{BC}_{j,k,t}^{\mathrm{RM}} + \sum_{j\in \mathrm{RM}} \sum_{k} \sum_{m} \sum_{t} \mathrm{EITHR}_j \cdot D_{j,k,t}^{i-k} S_{i,j,k,t}^{\mathrm{RM}} + \sum_{j\in P} \sum_{k} \sum_{m} \sum_{t} \mathrm{EITRM}_j \cdot D_{k,m,t}^{k-m} \sum_{m} S_{j,k,m,t}^{P} \quad (31)$$

where EILW_j is the eco-indicator factor due to use of lignocellulosic wastes (raw materials). EIBR_k is the indicator factor due to conversion of lignocellulosic wastes j to furfural at biorefinery k. EITHR_j is the eco-indicator factor for the transportation of lignocellulosic waste from harvest to refineries. EITHR_j is the eco-indicator factor for the transportation of products from refineries to markets.

6.3. Social Objective Function: Jobs Generated. The incorporation of a social objective gives a more integral vision of the effects on the local economy caused by implementation of a supply chain for furfural production. Additionally, the incorporation of this objective provides a social perspective and how the SC can benefit the society by the generation of jobs. The jobs generated during the supply chain are calculated using the Jobs and Economic Development Impact method (JEDI) developed by NREL.[30] This is a multiplier input−output model, where a multiplier is a simple relationship between systematic changes caused in a region by economic activities and the initial state of the region.[45,46] This methodology provides an estimation of the total impact (jobs) caused by the implementation of a project from an initial change in the economic output. In this way, three different kinds of jobs are identified by the method, which are as follows:

Direct: Jobs created on site of the project. This category implies all the jobs created during the construction and operation of a project.

Indirect: Jobs created outside the site of the project. In this category are included transportation jobs, manufacturers, suppliers, etc.

Induced: These jobs are created owing to the economic impact caused by the project.

In this work, the required multipliers were derived from the IMPLAN model, National Renewable Energy Laboratory, and information provided by different institutions of the Mexican government.[30,35,47] The social objective is quantified and measured by all the jobs generated in the supply chain; mathematically, it is expressed using the following equation:

$$\begin{aligned}\max \mathrm{Jobs} = &\sum_{i} \sum_{j\in \mathrm{RM}} \sum_{k} \sum_{t} \mathrm{JHS}_i^{\mathrm{Direct}} \cdot \mathrm{CBT}_j \cdot S_{i,j,k,t}^{\mathrm{RM}} + \sum_{i} \sum_{j\in \mathrm{RM}} \sum_{k} \sum_{t} \mathrm{JHS}_i^{\mathrm{Indirect}} \cdot \mathrm{CBT}_j \cdot S_{i,j,k,t}^{\mathrm{RM}} \\ &\sum_{i} \sum_{j\in \mathrm{RM}} \sum_{k} \sum_{t} \mathrm{JHS}_i^{\mathrm{Induced}} \cdot \mathrm{CBT}_j \cdot S_{i,j,k,t}^{\mathrm{RM}} + \sum_{j\in \mathrm{RM}} \sum_{k} \sum_{n} \mathrm{JCR}_k^{\mathrm{Direct}} \cdot \mathrm{CC}_{j,k,n}^{\mathrm{RM}} \\ &+ \sum_{j\in \mathrm{RM}} \sum_{k} \sum_{n} \mathrm{JCR}_k^{\mathrm{Indirect}} \cdot \mathrm{CC}_{j,k,n}^{\mathrm{RM}} + \sum_{j\in \mathrm{RM}} \sum_{k} \sum_{n} \mathrm{JCR}_k^{\mathrm{Induced}} \cdot \mathrm{CC}_{j,k,n}^{\mathrm{RM}} + \\ &\sum_{k} \sum_{j\in \mathrm{RM}} \mathrm{JOR}_k^{\mathrm{Direct}} \cdot \mathrm{UC}_{j,k}^{\mathrm{RM}} + \sum_{k} \sum_{j\in \mathrm{RM}} \mathrm{JOR}_k^{\mathrm{Indirect}} \cdot \mathrm{UC}_{j,k}^{\mathrm{RM}} + \sum_{k} \sum_{j\in \mathrm{RM}} \mathrm{JOR}_k^{\mathrm{Induced}} \cdot \mathrm{UC}_{j,k}^{\mathrm{RM}} \\ &+ 0.856 \sum_{i} \sum_{j\in \mathrm{RM}} \sum_{k} \sum_{t} \mathrm{JT}^{\mathrm{Direct}} y_{i,j,k} D_{j,k,t}^{i-k} + 0.856 \sum_{i} \sum_{k} \sum_{t} \mathrm{JT}^{\mathrm{Indirect}} \cdot y_{i,j,k} D_{j,k,t}^{i-k} + 0.856 \sum_{i} \sum_{k} \sum_{t} \mathrm{JT}^{\mathrm{Induced}} \cdot y_{i,j,k} D_{j,k,t}^{i-k} \\ &+ 3.126 \sum_{i} \sum_{j} \sum_{k} \sum_{t} \mathrm{JT}^{\mathrm{Direct}} \cdot S_{i,j,k,t}^{\mathrm{RM}} + 3.126 \sum_{i} \sum_{j} \sum_{k} \sum_{t} \mathrm{JT}^{\mathrm{Indirect}} \cdot S_{i,j,k,t}^{\mathrm{RM}} + 3.126 \sum_{i} \sum_{j} \sum_{k} \sum_{t} \mathrm{JT}^{\mathrm{Induced}} \cdot S_{i,j,k,t}^{\mathrm{RM}} \\ &+ 0.856 \sum_{k} \sum_{j\in P} \sum_{m} \sum_{t} JT^{\mathrm{Direct}} U_{j,k,m} D_{k,m,t}^{k-m} + 0.856 \sum_{k} \sum_{j\in P} \sum_{m} \sum_{t} JT^{\mathrm{Indirect}} U_{j,k,m} D_{k,m,t}^{k-m} + 0.856 \sum_{k} \sum_{j\in P} \sum_{m} \sum_{t} \mathrm{JT}^{\mathrm{Induced}} U_{j,k,m} D_{k,m,t}^{k-m} \\ &+ 3.126 \sum_{j} \sum_{k} \sum_{m} \sum_{t} \mathrm{JT}^{\mathrm{Direct}} \cdot S_{j,k,m,t}^{\mathrm{P}} + 3.126 \sum_{j} \sum_{k} \sum_{m} \sum_{t} \mathrm{JT}^{\mathrm{Indirect}} \cdot S_{j,k,m,t}^{\mathrm{P}} + +3.126 \sum_{j} \sum_{k} \sum_{m} \sum_{t} \mathrm{JT}^{\mathrm{Induced}} \cdot S_{j,k,m,t}^{\mathrm{P}}\end{aligned} \quad (37)$$

where $\mathrm{JHS}_i^{\mathrm{Direct}}$, $\mathrm{JHS}_i^{\mathrm{Indirect}}$, and $\mathrm{JHS}_i^{\mathrm{Induced}}$ are the coefficients (jobs/million USD) for direct, indirect, an induced jobs created at harvest site i, respectively. $\mathrm{JCR}_k^{\mathrm{Direct}}$, $\mathrm{JCR}_k^{\mathrm{Indirect}}$, and $\mathrm{JCR}_k^{\mathrm{Induced}}$ are the coefficients of jobs created during the construction of biorefinery k. $\mathrm{JOR}_k^{\mathrm{Direct}}$, $\mathrm{JOR}_k^{\mathrm{Indirect}}$, and $\mathrm{JOR}_k^{\mathrm{Induced}}$ represent the jobs generated during the operative time of biorefinery k (jobs/million USD). Finally, $\mathrm{JT}^{\mathrm{Direct}}$,

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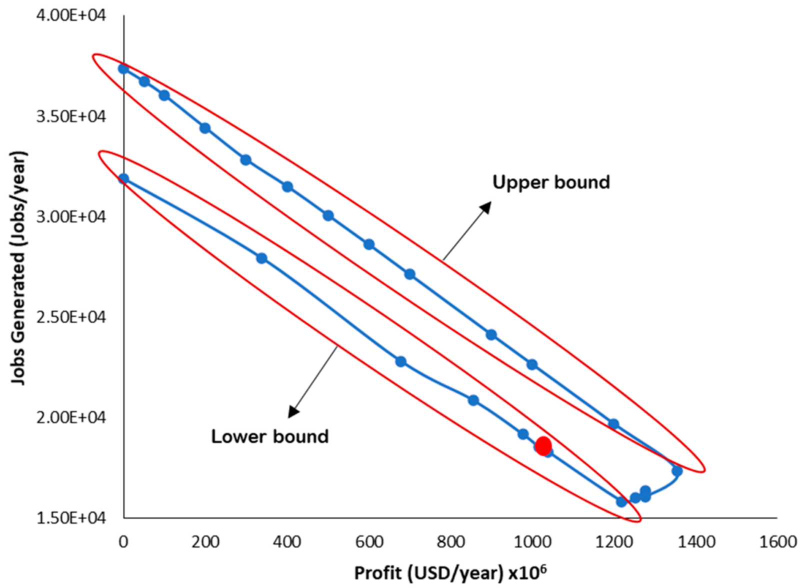

Figure 4. Pareto front social benefit vs profitability.

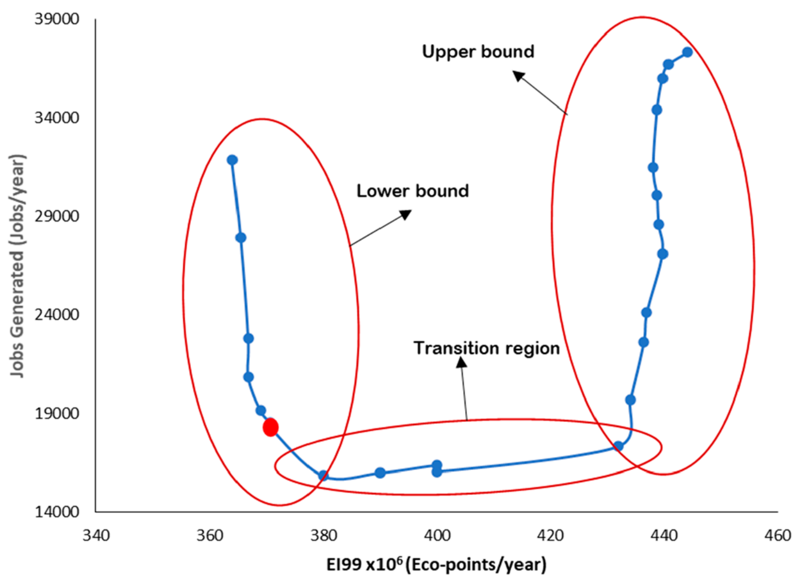

Figure 5. Pareto front social benefit vs environmental impact.

$JT^{Indirect}$, and $JT^{induced}$ are the jobs created during the transportation activities.

Finally, for solving the multiobjective supply chain, the ε-constrained method was used. It consists of solving the MILP for the individual objectives without considering the others, in order to achieve the limits; then using these limits the multiobjective problem is solved for each objective using the other objectives as constraints. More details about this technique are provided by Mavrotas.[48]

7. RESULTS

This section provides an analysis of the supply chain results. The model proposed was formulated as a Mixed Integer Linear Program (MILP), which was solved in Gams. The model consists of 194 207 equations, 16 284 binary variables, and 282 316 continuous variables. This model was solved using a computer with an AMD Ryzen 5-1600 @ 3.2 GHz and 16 GB of RAM @ 2400 MHz, each Pareto point required an average computational time of 600 s. The solver used was CPLEX with a relative gap of 1%.

Figure 4 shows the Pareto front Jobs vs Profit obtained during the optimization procedure. In this case, two sections defined by two remarkable lines are identified. The shape of this chart can be explained based on the constraints considered in this work. Please note that eq 9 constrained the model between a lower and upper bound for the demand. In this case, the lower bound is the demand required and the upper bound corresponds to the demand plus an excess of 10%. In this case, the bottom line corresponds to different supply chain solutions operating in the lower bound, whereas the top line corresponds to supply chain solutions working in the upper bound. The average difference between the lower and upper bounded solutions is about 11%, which is expected because the difference between bounds is 10%. In addition, it is appreciating a competitive behavior for these two objectives.

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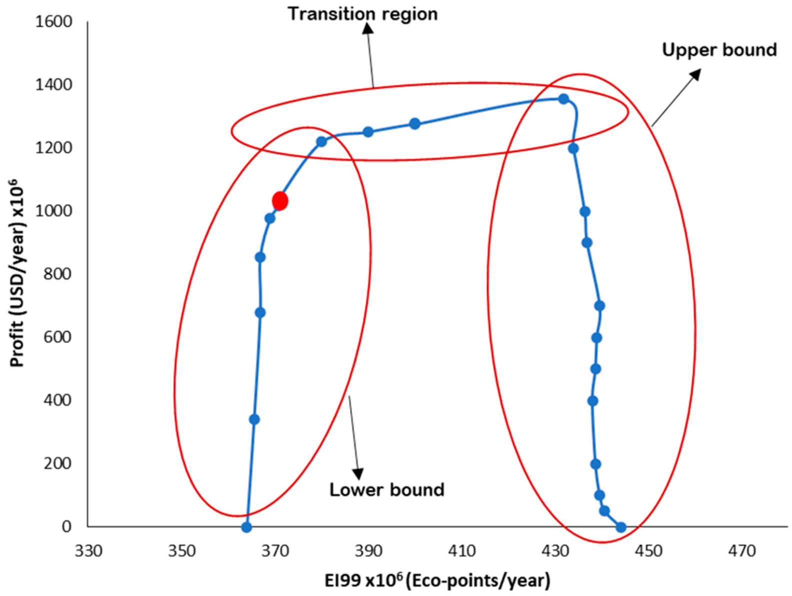

Figure 6. Pareto front profitability vs environmental impact.

The JEDI method is based on a multiplier input−output model, which implies that this index depends strongly on monetary expenditure (monetary investment). This method estimates the jobs generated considering the investments or expenditures required in the supply chain by different economic activities, e.g., installation and operation of biorefineries, transportation, use of biomass, storage, etc. Therefore, when more economic activities are implied in the SC, the investment and expenses will increase, which means that more jobs are needed. For this reason, according to the JEDI methodology, when the expenditure or investment increases, the number of jobs also increases.[30,45] Consequently, the Pareto solutions (points) with more jobs generated are characterized by an important increment in the number of biorefineries installed, an increment in plant capacities, longer transportations distances, and increments on products and biomass inventory levels in order to justify the economic activities and expenses to generate more jobs. In addition, more expensive biomasses such as sorghum or sugar cane bagasse are preferred to increase the jobs generated, since their more expensive costs are associated with more labor, which increases the number of jobs, but at the same time, it reduces the profitability. In contrast, solutions that benefit the profitability are characterized by shorter transportation arcs, lesser inventory levels, and a lesser number of biorefineries installed; this solution increases the profitability but reduces the number of jobs. The solutions that trend to improve the profitability are characterized by a greater use of wheat straw, because the processing of this raw material is the cheapest, in contraposition with other raw materials.

Figure 5 illustrates the Pareto front jobs generated vs EI99; once again two sections are clearly appreciated (upper and lower bounds section). Nevertheless, in this case, the presence of a transition region from the lower bound to upper bound is more obvious. Equation 9 constrained the sales in a continuous interval between the upper and lower bounds. For this reason, the transition region shows a change from the lower bounded solutions toward upper bounded solutions in a continuous interval. The solutions located in the transition region correspond to the extreme Pareto solutions for the intermediate sales values contained between the upper and lower bounds. The behavior of Figure 5 can be explained based on the previous case of Figure 4. By comparing both the transition and the lower bound regions, a competition van be seen between the number of jobs and EI99. Despite the small decrease in the E99, a trend to increase the ecoindicator is observed for these two regions. This tendency will be better appreciated in Figure 6. The changes in the environmental impact in these regions are small, because the solutions trend close to the lower bound. However, Figure 5 follows the same tendency with respect to Figure 4. A decrease in the number of jobs is associated with an increase of profitability, hence, an increase of the environmental impact. EI99 is more influenced by the biorefinery size than other activities of the supply chain. This affirmation is easily corroborated analyzing the eco-indicator parameters shown in Table S11 of the Supporting Information. In this case, the reduction of jobs generated is related with a lower number of biorefineries; however the remaining biorefineries must have greater capacities in order to supply the demand of furfural and methanol, which affects the environmental impact. In addition, when the product sales begin increasing toward the upper bound, the increments in the EI99 are more obvious. Finally, when the upper sales limit is reached, the optimization determines that, to increase the generation of jobs, it is necessary to increase the inventories of furfural, which means a larger amount of biomass processed, impacting in this way on EI99; in this case, both objectives follow the same tendency.

Figure 6 shows the Pareto front Profit vs EI99. Similar to the other cases, three regions are observed. In this case, the profitability and the EI99 follow the same tendency up to the upper bound for sales reached; beyond that point profitability and environmental impact cannot improve simultaneously. This behavior is associated with the number of jobs. Please note in Figure 4 how the profitability decreases with the number of jobs. When the maximum sales are reached, the profitability is maximized. Beyond this point, the profit can only decrease when the number of jobs and environmental

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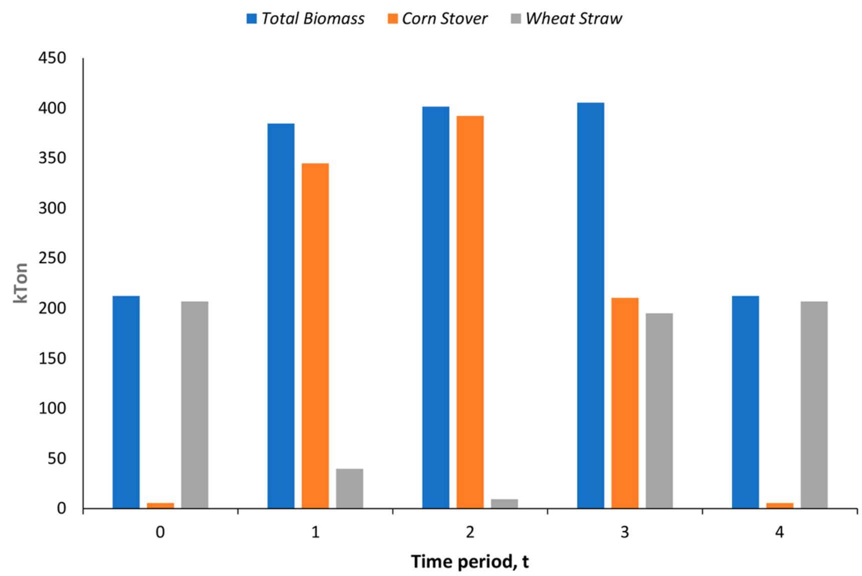

Figure 7. Biomass inventory levels for a one-year time horizon.

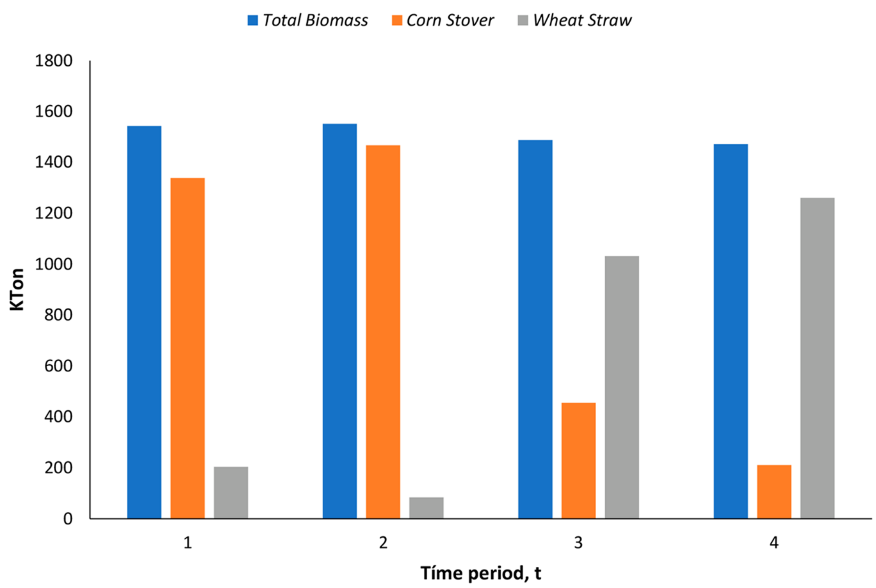

Figure 8. Biomass shipments from harvest to refineries for a one-year time horizon.

impact increase. After the point at max profitability, the EI99 increases in small intervals because the activities required to generate more jobs are close to their respective limits.

This work considers with equal importance the three objectives (economical, environmental, and social); for this reason, it is very important to select a solution with the best balance among social, economic, and environmental aspects. Once the Pareto front is obtained, the selection of an optimal solution can be carried out using the utopian point methodology. The utopian point is an ideal solution, which minimizes or maximizes a set of two or more objectives. When three or more objectives are considered and the shape of their Pareto fronts is complex, the solution selected is usually located such that the multiple objectives have a balance among them, which is usually located in the middle of the Pareto charts.[49,50] With this in mind, please note the presence of a red point in Figures 4−6; this point represents the solution chosen as the best supply chain solution, owing to it having the best trade-off among the different objectives. This point is located close to the middle of the Pareto charts in order to avoid an excessive degradation of the indexes considered in this work. In this solution, the SC has about 75% of the maximum profitability, the EI99 is close to its lower limit, and the jobs generated are around 19 500 jobs/year, which represents almost 50% of the maximum possible jobs. The red points correspond to 1056 million USD/year, 19 300 jobs generated/year, and 370 million eco-points/year. Therefore, the SC results described below correspond with this point. The biomass inventory levels for each period are reported in Figure 7. In this work, the period of time 1 corresponds to spring, 2 to summer, 3 and 4 to autumn and winter, respectively. The results indicate that only corn stover and wheat straw are feasible biomasses for producing furfural owing to a lower processing cost than sorghum bagasse and sugar cane bagasse.

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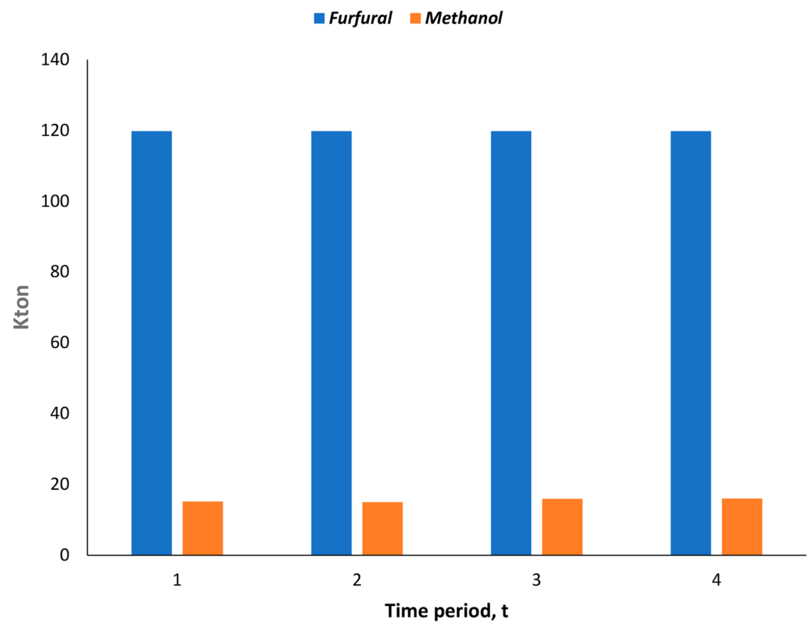

Figure 9. Product shipments from refineries to markets for a one-year time horizon.

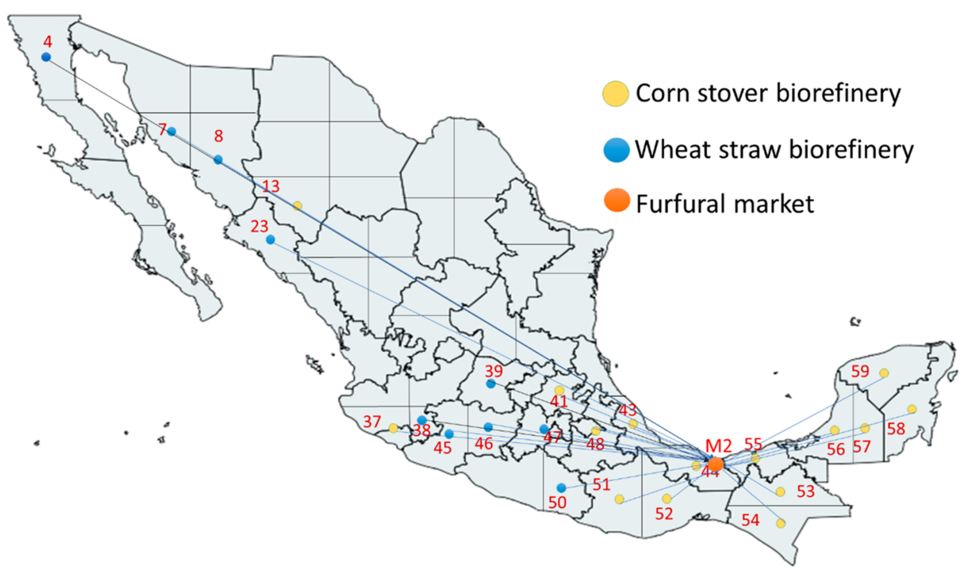

Figure 10. Optimal furfural supply chain for market 2.

In addition, it is clear that the corn stover is the base biomass to produce furfural, thus the wheat straw has some availability problems during the period $t = 1$ and $t = 2$ (spring and summer; see Supporting Information) due to its poor availability during these seasons. It is for this reason that enormous amounts of corn stover must be stored in order to keep a constant furfural production.

Figure 8 shows the biomass shipments considering each time period. The results show a clear relationship between the biomass availability and the shipments. During spring and summer ($t = 1$, $t = 2$), when the wheat straw availability is poor the shipments are predominantly base corn stover. In contrast, during autumn and winter ($t = 3$, $t = 4$), the biomass shipments are mainly wheat straw. These shipments also indicate that most of the corn stover based biorefineries will be active during seasons in which corn stover is abundant; the same behavior occurs with wheat straw. In addition, Figure 9 shows the furfural and methanol shipments to the markets. Note that the cyclic inventory proposed during the mathematical modeling achieves a continuous and stable supply of furfural and methanol throughout the year, overcoming in this way, the seasonality challenges of biomass. Furthermore, the results indicate that the products' storage is not necessary, hence, all the methanol and furfural produced in each season is directly sent to markets. Therefore, it can be concluded that only a suitable scheduling for biomass storage is required to obtain a stable product supply.

The complete set of biorefineries required to supply the furfural and methanol demand is shown in Figures S4−S9 of the Supporting Information. The corn stover biorefineries are characterized by an average plant size of 850 ton/year of furfural, whereas the average plant size for wheat straw biorefineries is about 4500 tons/y of furfural (see Table S12). This difference in sizes could be generated by the availability of

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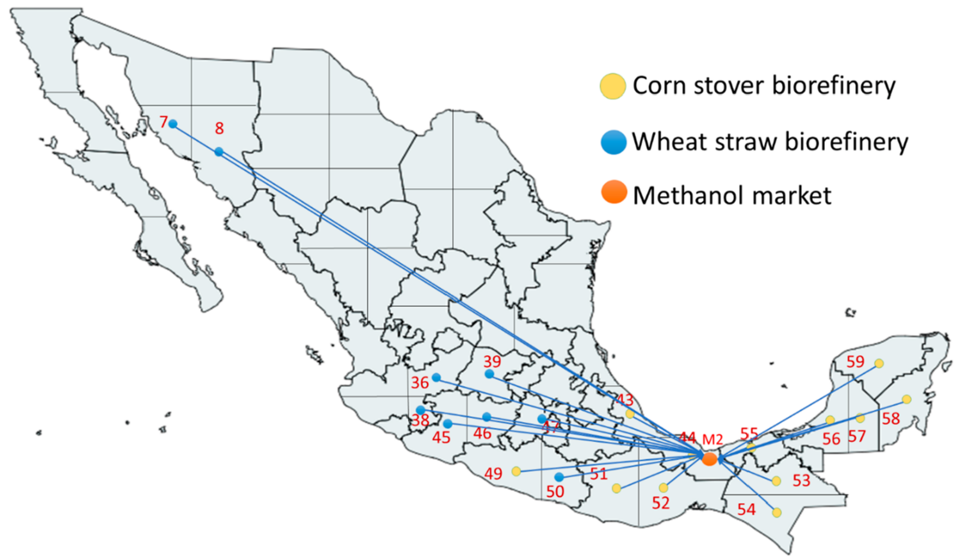

Figure 11. Optimal methanol supply chain for market 2.

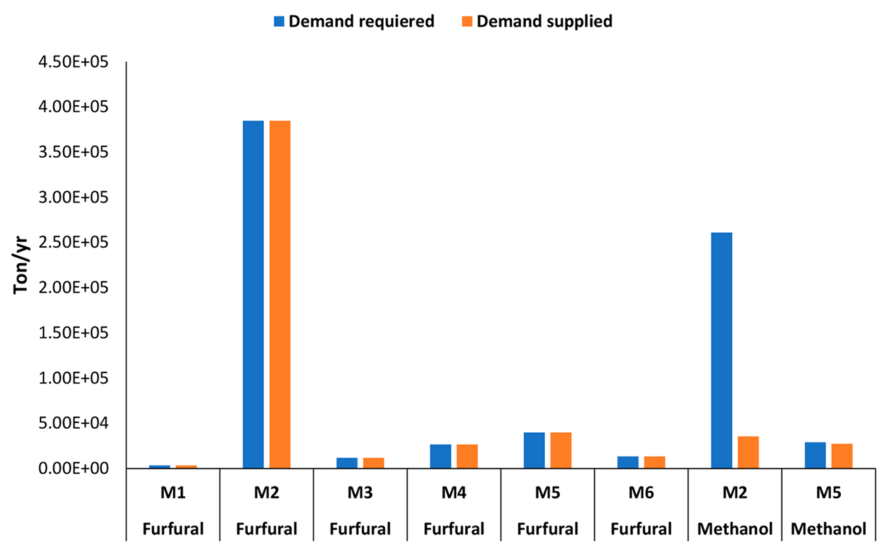

Figure 12. Demand of products supplied by the supply chain.

biomass. The corn stover is more abundant, and smaller plants are required in contrast to wheat straw biorefineries. On the other hand, the wheat straw biorefineries require greater sizes in order to process all the biomass generated during autumn and winter, which can be easily corroborated by analyzing the maps for wheat straw availability and the plants installed (see Figures S1 and S3). This decentralized furfural production is quite similar to China's case. In this country, there are about 200 furfural plants with an average production of 1000 ton/y distributed in all the territory with the aim to supply a demand of 210 kton/year; hence, the solution proposed for this model is realistic.[51]

Finally, the supply chain solution for market M2 was chosen as the representative case; since it is the largest market. Market M2 represents around 80% of Mexico's total demand of furfural, whereas its methanol demand represents 90% of the total methanol demand in Mexico. The optimal solutions to supply furfural and methanol to market M2 are shown in Figure 10 and Figure 11, respectively. The results indicate that 12 wheat straw biorefineries are required; their annual capacities are about 3229 tons of furfural per year up to 51 000 tons furfural per year (see Table S12). On the basis of Figure 10, please note that 10 wheat straw biorefineries are supplying furfural to market M2; also note that the methanol supply chain is quite similar (see Figure 11). Despite the wheat straw being the second more expensive raw material, its higher conversion to furfural and methanol in contrast to other raw materials makes the biorefineries efficient and cheap enough to ship methanol and furfural from far regions to the M2 market. On the other hand, the results shows that 45 corn stover biorefineries are required; these biorefineries have capacities of about 850 tons of furfural per year up to 25 000 tons of furfural per year. Please note that the corn stover biorefineries tend to be closer to market M2 in contrast to wheat straw biorefineries. The reason is quite simple; according to the data provided by Contreras- Zarazúa et al.,[29] the corn stover biorefineries are significantly more expensive than a wheat straw biorefinery, thus the corn stover biorefineries are located closer to market

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M2 in order to reduce their transportation costs and compensate in this way for their more expensive production costs. Finally, Figure 12 shows the supplied demand of furfural and methanol considering all markets. It is important to emphasize that the supply chain is capable of covering all of the furfural demand required by Mexico. On the other hand, the methanol demand exceeds the amount of methanol produced by all biorefineries; however, the supply chain is capable of covering around 62 867 tons of methanol per year, which represents the 21.67% of the total methanol demand of Mexico. Furthermore, almost all of the demand of market M5 is covered; thus based on these results it can be concluded that the coproduction of furfural and methanol is feasible.

8. CONCLUSIONS

Lignocellulosic wastes have important potential as raw material in the production of biochemicals. They can play an important role in the transition toward a more sustainable society. In order to achieve this transition, the oil-based commodities must be replaced by renewable biochemicals. However, the major barrier preventing the transition to these eco-friendly chemicals is the biomass production variability, which jeopardizes meeting the demand. This work proposed a supply chain model to produce furfural considering a cyclic availability of biomass; also the sale of methanol is an important coproduct of furfural production that was considered. The scale of SC was set on an industrial scale in order to produce the furfural required to replace the terephthalic acid importation in Mexico, whereas the methanol produced is used to satisfy part of the methanol demand. Economic, environmental, and social objectives were selected for measuring the solution of the supply chain. These indexes were chosen in order to provide a more sustainable solution.

The results indicate that the production of furfural and methanol from lignocellulosic residues to replace current commodities in Mexico is feasible. The production of furfural and methanol can reach important profits up to 1250 million USD/year. However, the SC solution with the best trade-off among different objectives consists of a profitability of 1056 million USD/year, 19 300 jobs generated/year, and 370 million eco-points/year. In addition, the results show that corn stover and wheat straw are the best lignocellulosic wastes to produce furfural owing to their lowest processing cost and environmental impact. Sorghum bagasse and sugar cane bagasse are not selected as raw materials to produce furfural and methanol, because they have remarkably lower conversions to products, which notably increases the production costs in contrast to corn stover and wheat straw. Furthermore, the results show that the multiperiod cyclic inventory achieves a continuous furfural and methanol production, overcoming in this way the prejudices associated with the technical feasibility of biochemical use to replace current commodities. The supply chain model proposed a distributed furfural production scheme, where 57 furfural plants are installed and located in different places. According to the results,12 of these 57 plants are refineries that work with wheat straw as a raw material; these biorefineries have production capacities of about 3229 tons of furfural per year up to 51 000 tons of furfural per year. On the other hand, the results indicate that the 45 remaining refineries will work with corn stover as a raw material with capacities of about 850 tons of furfural per year up to 25 000 tons of furfural per year. Finally, the results indicate that the supply chain proposed has the capability of covering the complete demand of furfural and 21.67% of the total methanol demand of Mexico. On the basis of the results obtained, it is concluded that a supply chain for furfural production is feasible.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c01847.

Biomasses availability; equations transportation distances, coordinates data, information piecewise linear approximation, information supply chain solution; information plants installed; information plant capacities (PDF)

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Notes

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■ NOMENCLATURE

$i \in I$ = Harvest sites
$j \in J$ = Compounds
$k \in K$ = Biorefinery sites
$m \in M$ = Markets
$t \in T$ = Time periods
$n \in N$ = Piecewise segments

Subsets

J^{RM} = Raw materials
J^{P} = Products (furfural, methanol)

Parameters

$\varphi_{i,j,t}$ = Biomass availability for biomass j at the harvest side i during the period t
$\alpha_{i,j,t}$ = Biomass lost factor due to biomass degradation (10%)
$b^{L}_{i,j,t}$ = Lower bound biomass required of a harvest in a specific period
$b^{U}_{i,j,t}$ = Upper bound biomass required of a harvest in a specific period

$\eta_{i,j'}^{RM}$ = Conversion from biomass j to products j'
γ^U = Upper bound for shipment biorefinery to market (sales)
γ^L = Lower bound for shipment biorefinery to market (sales)
β^L = Lower bound for biomass consumed at biorefinery
β^U = Upper bound for biomass consumed at biorefinery
ε^U = Yearly upper bound of shipments biorefinery to market
$m_{j,n}$ = Slope ($m_{j,n}$) parameters for piecewise function
$a_{j,n}$ = Intercept ($a_{j,n}$) parameters for piecewise function
d_j = Slope (d_j) parameters for utilities cost
c_j = Intercept (c_j) parameters for utilities cost
CBT = Cost per ton of raw material
$EILW_j$ = Eco-indicator factor due to use of lignocellulosic wastes
$EIBR_k$ = Eco-indicator factor due to conversion of lignocellulosic wastes
$EITHR_j$ = Eco-indicator factor for the transportation of lignocellulosic waste from harvest to refineries
EITRM = Eco-indicator factor for transportation of products from refineries to markets
JHS_i^{Direct} = Coefficients (jobs/million USD) for direct jobs created at harvest site i
$JHS_i^{Indirect}$ = Coefficients (jobs/million USD) for indirect jobs created at harvest site i
$JHS_i^{Indcued}$ = Coefficients (jobs/million USD) for induced jobs created at harvest site i
JCR_k^{Direct} = Coefficients of direct jobs created during the construction of biorefinery k
$JCR_k^{Indirect}$ = Coefficients of indirect jobs created during the construction of biorefinery k
$JCR_k^{Induced}$ = Coefficients of induced jobs created during the construction of biorefinery k
JOR_k^{Direct} = Coefficients of direct jobs generated during the operative time of biorefinery k
$JOR_k^{Indirect}$ = Coefficients of indirect jobs generated during the operative time of biorefinery k
$JOR_k^{Induced}$ = Coefficients of induced jobs generated during the operative time of biorefinery
JT^{Direct} = Coefficients of direct jobs generated during the transportation activities
$JT^{Indirect}$ = Coefficients of indirect jobs generated during the transportation activities
$JT^{Induced}$ = Coefficients of induced jobs generated during the transportation activities

Variables

$S_{i,j,k,t}^{RM}$ = Amount of biomass j shipped along the arc $i \rightarrow k$ during the period t
$b_{i,j,t}^{RM}$ = Biomass required of a harvest in a specific period
$A_{i,j,t}^{RM}$ = Biomass inventory at harvest side i for biomass j during the period t
$A_{i,j,t\text{-}1}^{RM}$ = Biomass inventory at harvest side i for biomass j during the period $t - 1$
$A_{j,k,t}^{P}$ = Product inventory at biorefinery k during the period t
$A_{i,k,t\text{-}1}^{P}$ = Product inventory at biorefinery k during the period $t - 1$
$S_{j,k,m,t}^{P}$ = Amount of furfural shipped along the arc $k \rightarrow m$ during the period t
$PP_{j,k,t}^{P}$ = Furfural produced at biorefinery k at the time t
$BC_{j,k,t}^{RM}$ = Biomass j consumed at biorefinery k in the period t
$D_{j,k,t}^{i\text{-}k}$ = Distance along the arc $i \rightarrow k$ for biomass j at time t
$D_{k,m,t}^{k\text{-}m}$ = Distance along the arc $k \rightarrow m$ for product j (furfural) at time t
$V_{j,k,n}^{RM}$ = Piecewise function variable for the interval n
$ACC_{j,k,n}^{RM}$ = Piecewise costs (installation cost) for the interval n (USD/year)
VTC^{i-k} = Variable transportation costs along the arc $i \rightarrow k$
FTC^{i-k} = Fixed transport costs along the arc $i \rightarrow k$
FTC^{i-k} = Variable transportation costs along the arc $k \rightarrow m$
FTC^{k-m} = Fixed transport costs along the arc $k \rightarrow m$
CBT_j = Cost of raw materials
RMC = Total raw materials costs
TACC = Total annualized capital cost (USD/year)
$AUC_{j,k}^{RM}$ = Utilities cost for biorefinery k and biomass j (USD/year)
TAUC = Total annualized utility costs (USD/year)

Binary Variables

$y_{i,j,k}$ = Binary variable 1 if the arc $i \rightarrow k$ (harvest side biorefinery) is selected to biomass j
$U_{j,k,m}$ = Binary variable 1 if the arc $k \rightarrow m$ (harvest side biorefinery) is selected to furfural
$W_{j,k}$ = Binary variable 1 if a biorefinery is installed at the site k for the biomass j
$\tau_{j,k,n}$ = Binary variable for piecewise approximation 1 if a segment of piewese is selected

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