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Integrated Biorefinery from Corn Waste Biomass: A Case Study in the North of Colombia

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Abstract : This work proposes a conceptual design of a biorefinery developed in Aspen Plus software from corn residues to produce bioethanol and succinic acid as an strategy to assist in the management of solid waste, while strengthening the economic and energy sector in the Bolivar department and establishing valid scientific basis for future studies. The stages of the process were established for the production of 4,332 kg/h and 1,252 kg/h succinic acid and ethanolfrom87,810 t of corn waste per year. The plant, without energy integration showed an IRR of 33 %. A heat integration analysis was performed to determine the potential energy reduction. As a result, a heat exchange network was proposed. After integration, 99% and 64% of heating and cooling utilities were reduced.

Key words: Integrated Biorefinery, Corn Waste Biomass, North of Colombia.

Introduction

Over the years there has been an increasing interest in developing technologies for energy production from renewable sources. In this way, lignocellulosic biomass, which are mainly composed of cellulose, hemicellulose and lignin[1], generates a great interest since biofuels and derived products can be obtained through biological processes with applications in several industries[2].

In Colombia, there was approximately 51 million hectares of land dedicated for agricultural production of which the 77% was used for livestock activities. In the north region of Colombiain2014, more than90,000 hectares of corn were cultivated producing around146,000 and 206,590t for corn and waste respectively[3]. All the waste biomass resources give an opportunity to propose alternatives that offer solution to waste management and contribute to the renewable industry, taking into account economic and environmental parameters[4].

In the department of Bolívar, located on the North region of Colombia, the National Government and agroindustry companies have an interest in stimulate the development of traditional corn, so a plan is needed to integrally use waste to produce fuels from lignocellulosic biomass. Thus, in this research paper we present the conceptual design of a biorefinery from agro-industrial waste from corn, in order to strengthen the production chains of department of Bolívar and provide alternatives for integrated waste management by obtaining succinic acid and ethanol.

A biorefinery is defined as an installation that transforms biomass, through unit operations and biological reactions, into biofuels, energy and chemical products[5]. In this way, a biorefinery is analogous to the oil refineries that produce a multiple variety of products from oil. The industrial biorefineries represent a strategy for the use of biomass and the creation of a new activities based on it[6].

Bioethanol has been widely used as fuel or economic and environmental enhancer of gasoline[7]. In recent years, the alternative of production of second-generation biofuels has rised since these renewable energy is abundant with a production of approximately 200 Gtper year[8].

Additionally the process integration methodologies applied to biorefineries allows the development of more environmentally-friendly and sustainable processes taking into design alternatives to reduce resource consumption[9].

According to the Ministry of Agriculture and Rural Development of Colombia[10], the regions of higher corn production were from the center to the south of the department of Bolivar, specifically rural areas; therefore, this region were considered as possible location of the biorefinery in order to reduce costs of transport and supply of raw material.

Process Description

A calculation basis of 87,810 t/h of corn residues was considered as raw material.

Since properties for cellulose, hemicellulose and lignin, were not available in Aspen Plus Software, these components were created using properties estimated by the National Renewable Energy Laboratory (NREL)[11]. The thermodynamic model selected was NRTL according to Carlson (1996).

The transformation of raw materials is the initial process of the biorefinery, using pretreatment to obtain pentose (xylose) and increase the digestibility of the components via acid dilution[12-13]. Subsequently, the liquids and solids were separated from the pre-treatment outflow. The solid stream was treated in the enzymatic hydrolysis process, to produce glucose, which was later fermented using C. glutamicum as biocatalyst to obtain succinic and acetic acid. The liquid stream was prepared and sent to fermentation to produce bioethanol using *Zymonona mobilis* as catalyst. The process streams from each fermentation stage were sent to purification trains to obtain high purity products[14].

Corn waste was pretreated with diluted acid, to convert the hemicellulose fraction in soluble sugars, as xylose, arabinose, mannose, and galactose[15]. Glucan in the hemicellulose fraction and a portion of cellulose were converted into glucose[16]. The reaction in the acid pretreatment was simulated using a stoichiometric reactor, with a temperature of 190 °C and 13 atm of pressure. Other conditions of acid pretreatment reaction implied treat the biomass with excess of water, maintaining a 22% of solids mass concentration with a conversion fraction of 0.9 for hemicellulose to xylose, 0.07 cellulose to glucose and solubilization of a small fraction of lignin[17].

The enzymatic hydrolysis was simulated using a stoichiometric reactor, with a conversion fraction of 0.9, 30 °C of temperature and 1 atm of pressure. For the fermentation of glucose to succinic acid and acetic acid Recombinant *C. Glutamicum* was used as biocatalyst due to its efficiency and selectivity in the formation of highly concentrated succinic acid. A concentration of 146 g of biocatalyst/L is used, under anaerobic conditions and in the presence of carbon dioxide[14].

The ethanol purification was carried out in a separation train; the first process was an absorption, which separated the carbon dioxide and a portion of water from the fermented stream. A subsequent distillations towers were used to get the ethanol to the azeotropic point[18]. Molecular sieves were simulated to achieve a concentration of 99.7% of ethanol. With the data obtained from the simulation, an economic analysis was used to determine feasibility of the biorefinery without energy integration. Project evaluation criteria such as IRR and VPN were used, with a return period of 20-year, and a gradient of 2.54% for increased of raw materials cost, equivalent to average annual inflation in Colombia for 2014[19-20].

To estimate the energy integration potential for the biorefinery, the process was analyzed using pinch analysis methodology, to find energy integration alternatives for the process design. The graphical and algebraic methods were used to determine the pinch point and the potential energy savings of the biorefinery[21]. Through the pinch point the minimum number of heat exchangers needed to get the energy integration was estimated.

With the design of HEN (Heat exchange network), a total capital cost estimation of the process was used to compare the integrated and base case.

Results

The biorefinery simulation was performed using data reported in the literature to set yields and properties of the substances. The corn waste biomass stream was pretreated with acid in a reactor at 190 ° C temperature and 13 atm pressure14. This process was simulated with a concentration of 6% w/w of sulfuric acid[22] to maintain the yields of the reactions, the percentage of solids was 22%. Figure 1 shows the simulated pretreatment scheme.

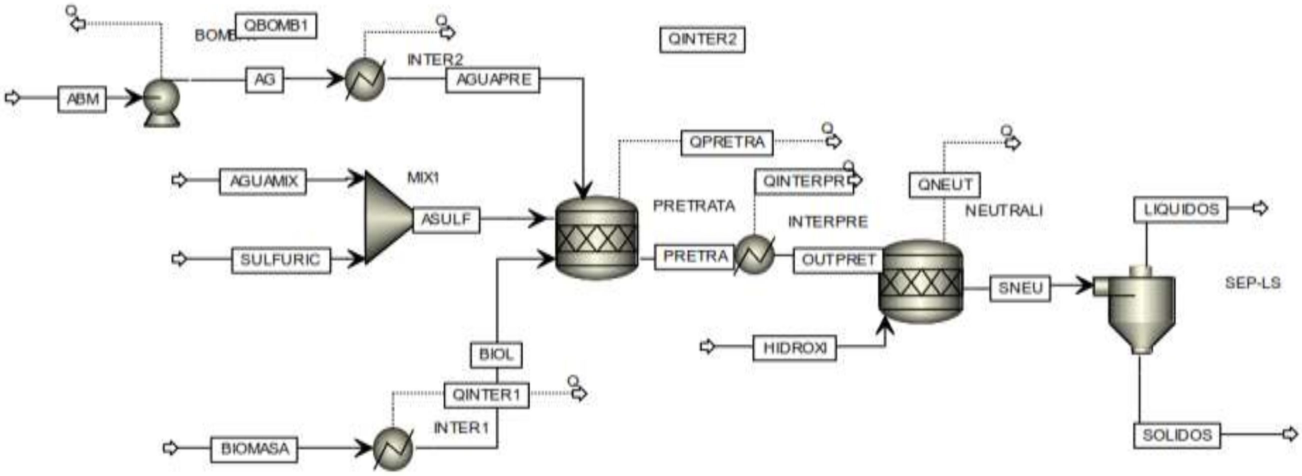

Figure 1.Simulated pretreatment scheme.

The output stream went to solid-liquid separation, since each stream has its independent process of fermentation. The solid's stream was sent to hydrolysis, where it was cooled to 33 °C and the pressure were reduced to 1 atm. In this stage, the cellulose, by the action of cellulose, reacts to form six-carbons sugars as glucose. Luo[14] reported a performance up to 90%, for a concentration of cellulase in a proportion of 0.006 kg/kg of solids, and 5 kg of water/kg of solids. The simulation for enzymatic hydrolysis shows a yield of 3,941.2 kg/h for glucose. The Figure 2 shows the simulated hydrolysis process.

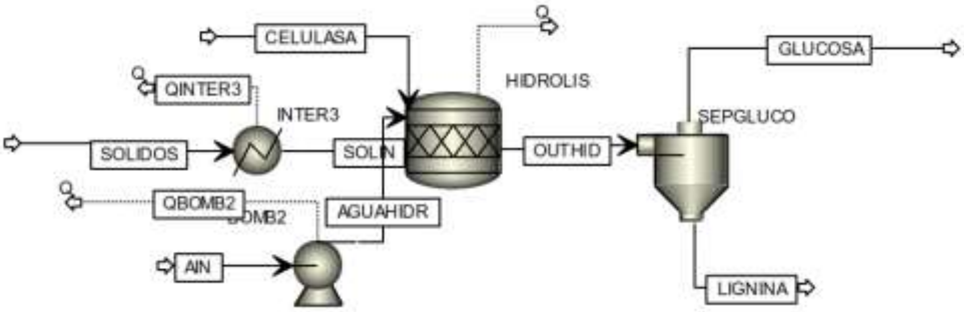

Figure 2.Simulated hydrolysis scheme.

After the enzymatic hydrolysis, the stream was sent to delignification. In this stage, no soluble solids and lignin are separated from glucose. The fermentation was simulated in a reactor at 30 °C and 1 atm of pressure. In this stage, were produced both succinic and acetic acids. The biocatalyst C.Glutamicunwas used with high concentration (0.15 kg/kg of glucose) under anaerobic conditions. The yields for this reaction are

70% to succinic acid and 10% for acetic acid[23]. The biocatalyst was separated and sent back to the reactor, in order to reduce the need for this raw material and reduce costs. The residual glucose is separated and re-circulated to the process to improve the production of acids. The output stream is sent to purification train[14,16].For the acid purification, distillation towers followed by an evaporator were used. For these stages, the succinic acid is purified up to 99.75% w/w (Figure 3).

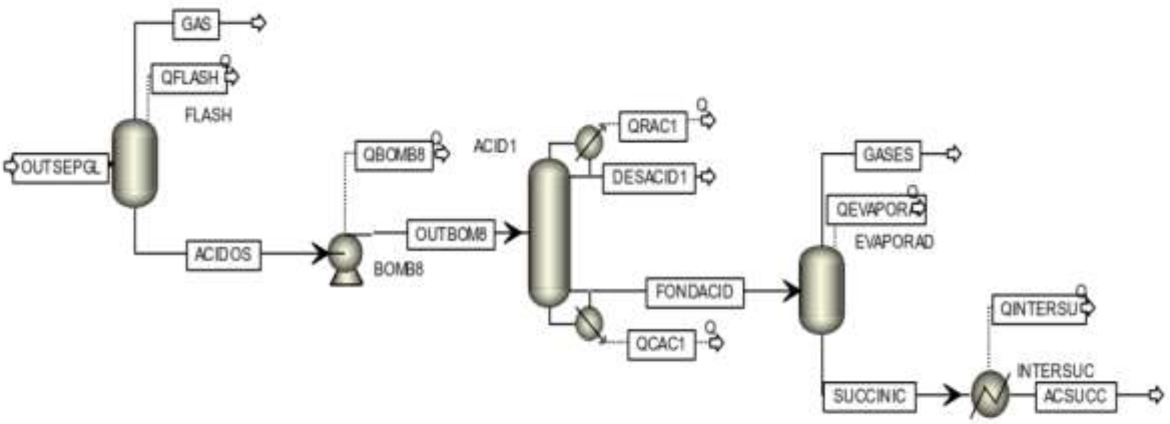

Figure 3.Simulated succinic acid purification scheme.

The liquid stream, mainly contains xylose, is headed to alcoholic fermenter reactors.This stream was purified, separating the substances like lignin, non-soluble materials, furfural, among others, to be able to enter the fermentation process. Fermentation was performed using *Zymomonamobilis*as biocatalyst, at 30 °C and 1atm pressure. For the reaction, yields up to 95% for ethanol production, maintaining a concentration of 6% by mass of microorganism and 50% w/w of water[24]. Ethanol exited at low concentration, close to 3% w/w. The purification of ethanol was carried out in a consecutive series of operations, that in the first instance, the ethanol was distilled to the azeotrope. Molecular sieves were simulated in the process to reach up to 99.5% w/w of ethanol[18]; the processes described above are presented in Figures 4 and 5.

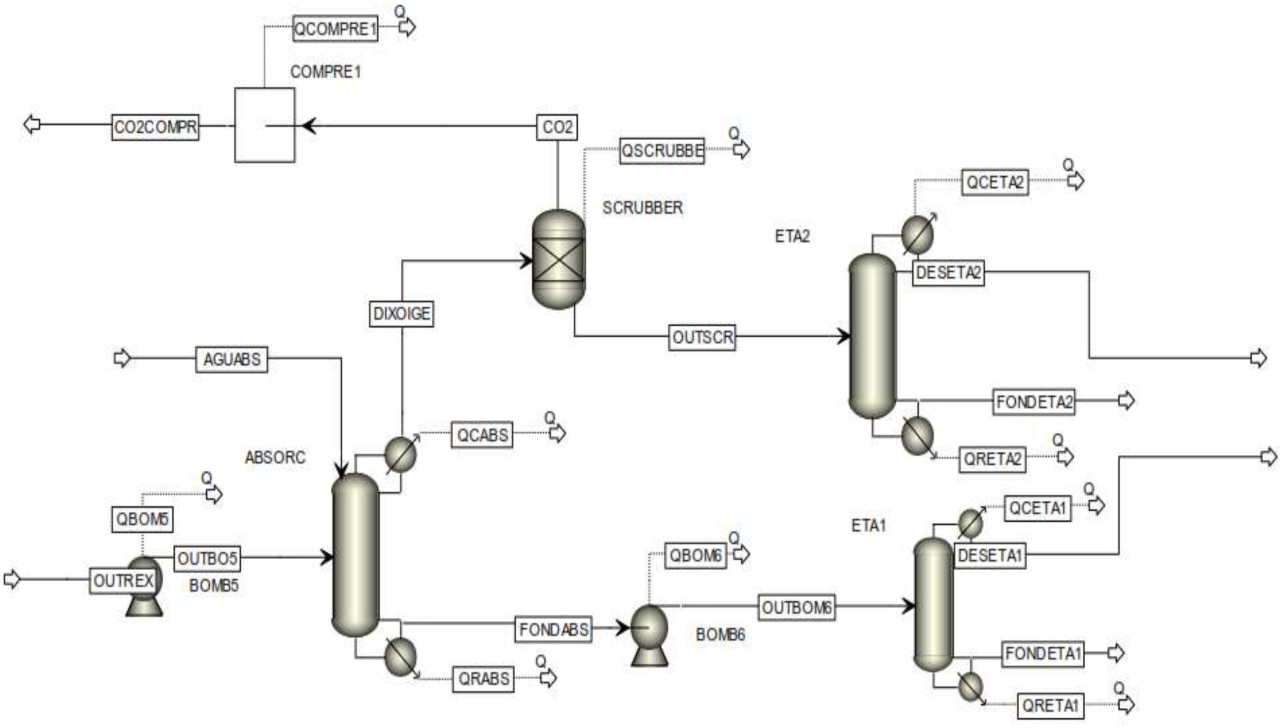

Figure 4.Simulated ethanol purification scheme.

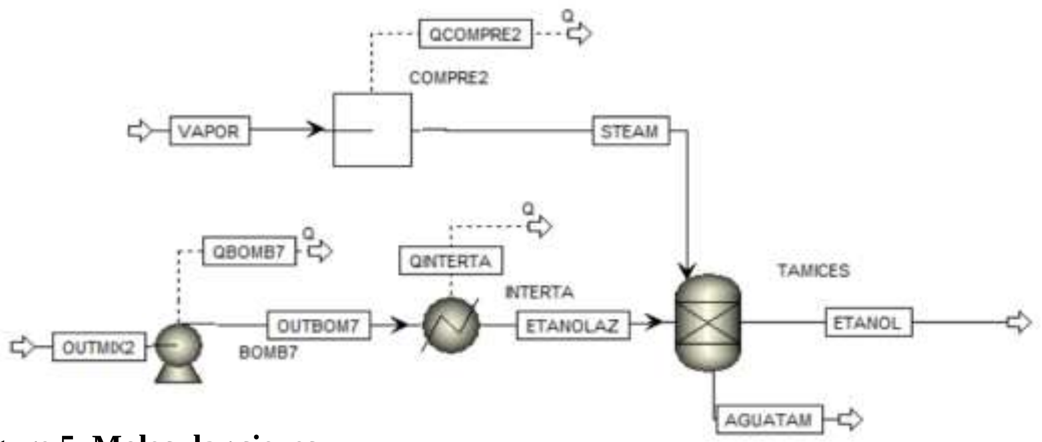

Figure 5. Molecular sieves.

The base case of analysis was simulated without purification of acetic acid. Based on the described process, were obtained 1,252.36 kg/h of alcohol at about 99.5%.

Economic Analysis

The economic analysis considered the price of reagents, raw materials and products, involved in the process (Table 1).

Table 1.Prices of products and raw materials.

Substances	Price (USD/kg)
Biomass	0.0819
H_2O	0.003678
CO_2	0.12
$NaOH$	0.37
H_2SO_4	0.094
Ethanol	0.976
Succinic Acid	1.1
Acetic Acid	0.836

The prices of biocatalysts were calculated based on the production, at a rate of $0.35 per liter of biofuels[25].Thompson & Tyner[26] reported an international reference value for corn residues (stubble and stalk), although they mention that it can vary according to each farm. The ICIS, Chemical Industrial Service, reports updated prices of chemicals in the international market, such as sodium hydroxide, sulfuric and acetic acid. The values reported by ICIS were taken as reference costs for the reagents and products mentioned above. The ethanol price is reported by the National Federation of Biofuels of Colombia.

The base and modified cases were compared to establish the potential benefits of their production. For these calculations, Net Present Value analysis was applied, with an interest rate of 25% annual cash flow, and the IRR as economic criteria to compare which scenario will be the base case proposed by the project. It was assumed that the life of the biorefinery is 20 years and that the gradient to raise prices of products and reagents goes from average inflation in Colombia for 2013-2015, which was 4.2% effective annually. The estimation shows that the production of ethanol and succinic acid, have a greater economic viability, a NPV of $10,598,127 and IRR of 33%, than the scenario for acetic acid production, which shows a NPV of $-17,613,688 and IRR of 15%. The IRR obtained by the base scenario is in line with the average range of IRR for similar process, located between 21% and 36% annual cash[14].

Energy integration

A conceptual design of corn waste biorefinery applying process integration methodology was proposed to obtain a reduction for industrial services for heating and cooling. Table 2 show the energy data obtained in the system for streams that had to be cooled or heated by process requirements.

Table 2.Thermal streams of process.

Number	**Stream**	T_s	T_t	mC_P	ΔH
Hot Streams					
1	Pretrata	190	30	142.56	22,806.40
2	Succinic	230	25	9.67	1,982.35
3	Outbom 7	68	60	4.07	32.56
4	Etanol	33	25	3.06	24.51
Cool Streams					
5	AguaHidro	25	33	135.86	-1,086.86
6	Solidos	30	33	27.79	-83.38
7	Outsep	30	90	163.19	-9,791.46
8	Fondacip	127	230	13.62	-1,403.1
9	Outbo5	59	80	198.10	-3,970.93

A temperature interval diagram was performed for the process. From heat flows of each interval, the cascade diagram was constructed, by this method it is possible to determine the quantity optimum energy, either to supply or withdraw through industrial services[27]. The pinch analysis was performed, obtained minimum requirements for cooling and heating, about 8,668.85 MJ/h and 158.10 MJ/h, respectively. The pinch point was located at temperature of 190 °C.

Table 3 summarizes a comparison between the requirements of the industrial services for the integrated and not integrated case.

Table 3.Energy potential integration.

Item	Cooling utility (MJ/ h)	Heating utility (MJ/ h)
Base case	24845.82	16335.78
Integrated case	8668.85	158.10
Integration potential	65.11 %	99.03 %

The pinch point and energy potential analysis allowed to determinate the minimum number of heat exchangers that guarantee an efficient transfer for utilities, and the design of the heat exchange network (HEN). The heat exchange network is presented in figure 6.

For thecase without integration, the energy and water consumption was significantly higher than integrated case, which reduce the potential economic benefits and shows the need for energy integration. The HEN proposed uses 11 heat exchangers, will achieve the integration potential found for the pinch analysis of this system.

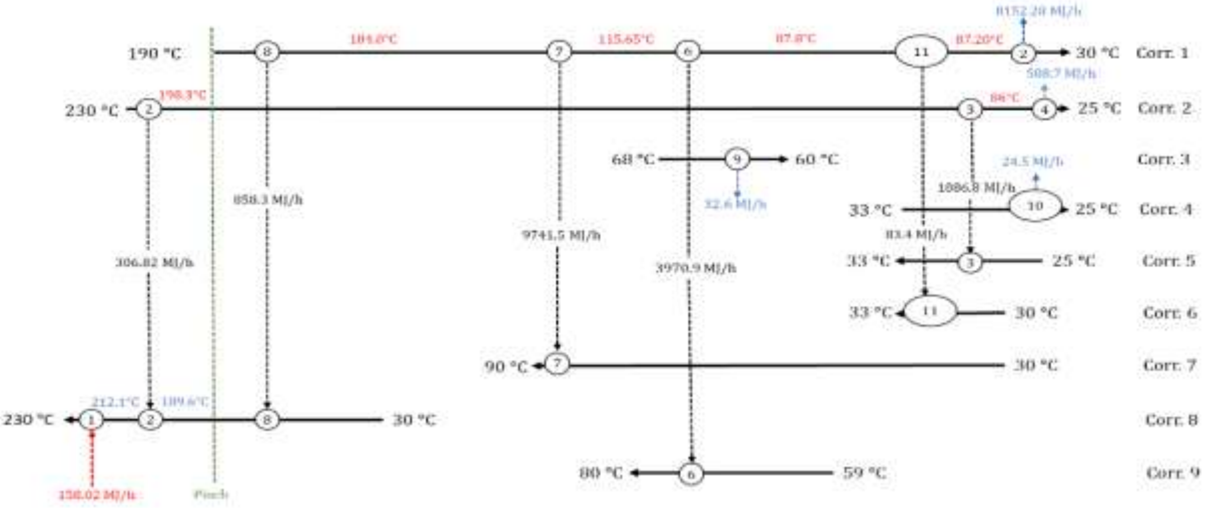

Figure 6.Heat Exchange Network.

Conclusions

The process design and simulation, together with the operations and process lines, benefits the establishment of succinic acid as the main product of biorefinery, and ethanol as by-product, with an economic viability supported by an IRR of 33%, and 10,598,127 USD for NPV,with an interestrate of 25% effective annually. Additionally, the non-viability of acetic acid production as a by-product was demonstrated, due to the high cost in the purification stages.

Through the application of energy integration, was determined the energy requirements for heat exchangers for industrial services, that was 16,335.78 MJ/h and a potential reduction of 99.03% for heating, and 24,845.81 MJ/h with potential reduction of 65.10%, for cooling. Due to this, it is recommended to implement the process integration of this design of biorefinery.

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References

1. Ward, M., Arzuaga, J., Ojeda, K., Sánchez, E. Production of biogás from acid and alkaline pretreated cocoa podhusk (Theobroma cacao L.). International Journal of ChemTech Research 2016, 9(11):252–60.
2. Shanmugam, S., Balasubramaniyan, B., Jayaraman, J., Ramanujam, P., Gurunathan, B. Simultaneous saccharification and fermentation of bioethanol from softwood moringa oleífera using thermo-tolerant yeast kluyveromycesmarxianus MTCC 1388. International Journal ChemTech Research. 2014;6(12):5118–24.
3. Agronet. Estadisticas. Ministerio de Agricultura -Departamento de Bolívar 2014.
4. Santibañez, J., González, J., Ponce, J., Serna, M., El-Halwagi, M. Optimalplanning of a biomass conversión system considerin geconomic and environmental aspects. Industrial & Engineering Chemical Research. 2011;50(14):8558–70.
5. De Jong, E., Gosselink, R. Lignocellulose-Based Chemical Products. Bioenergy Research: Advances and Applications. Elsevier; 2014. 277-313 p. Available from: http://dx.doi.org/10.1016/B978-0-444-59561-4.00017-6
6. Hellsmark, H., Mossberg, J., Söderholm, P., Frishammar, J. Innovation system strengths and weaknesses in progressing sustainable technology: The case of Swedish biorefinery development. Journal of Cleaner Production. 2016; 131:702–15.

7. Buruiana, C., Vizireanu, C., Garrote, G., Parajó, J. Optimization of cornstover biorefinery for coproduction of oligomers and second generation bioethanol using non-isothermal autohydrolysis. Industrial Crops and Products. 2014; 54:32–9. Available from: http://dx.doi.org/10.1016/j.indcrop.2014.01.003
8. Castro, C., Beltrán, L., Ortiz, J. Producción de biodiesel y bioetanol: ¿una alternativa sustentable a la crisis energética?. Ra Ximhai. 2012; 8:101–15.
9. Álvarez, X., Fortes, M., Aguilar, R. Diseño de una red de intercambio de calor utilizando la metodología supertargeting del punto de pliegue. 2007; 7:23–40.
10. Ministerio de Agricultura y Desarrollo Rural. Plan País Maíz. Cadenas productivas. Bogota; 2011.
11. Wooley, R., Putsche, V. Development of an ASPEN PLUS Physical Property Database for Biofuels Components. Victoria. 1996; (April):1–38.
12. Agbor V., Cicek, N., Sparling, R., Berlin, A., Levin, D. Biomass pretreatment: Fundamentals toward application. Biotechnology Advances. 2011;29(6):675–85. Available from: http://dx.doi.org/10.1016/j.biotechadv.2011.05.005
13. Cherian, E., Dharmendira, M., Baskar, G. Cellulosic bioetanol production by sequential fermentation using agricultural waste. International Journal ChemTech Research. 2014;6(14):5653–60.
14. Luo L, van der Voet E, Huppes G. Biorefining of lignocellulosic feed stock - Technical, economic and environmental considerations. Bioresources Technology. 2010;101(13):5023–32.
15. Singh, D., Trivedi, R. Acid and alkaline pretreatment of lignocellulosic biomass to produce ethanol as biofuel. International Journal ChemTech Research. 2013;5(2):727–34.
16. Zondervan, E., Nawaz, M., De Haan, A., Woodley, J., Gani, R. Optimaldesign of a multi-product biorefinery system. Computer and Chemical Engineering. 2011;35(9):1752–66.
17. Wooley, R., Ruth, M., Sheehan, J., Majdeski, H., Galvez, A. Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis Current and Futuristic Scenarios Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current D. Contract. 1999;(July):132. Available from: http://devafdc.nrel.gov/pdfs/3957.pdf
18. Kang, Q., Huybrechts, J., Van Der Bruggen, B., Baeyens, J., Tan, T., Dewil, R. Hydrophilic membrane storeplace molecular sieves in de watering the bio-ethanol/wáter azeotropic mixture. Separation and Purification Technology. 2014; 136:144–9.
19. Mohammady, N., Hawash, S., El-Khatib, K., El-Galad, M., El Diwani, G. Biodiesel production from Chlorella Sp: Process Design and Preliminary Economic Evaluation. International Journal ChemTech Research. 2015;8(9):297–304.
20. Baca, G. Fundamentos de Ingeniería Económica. Fourth Edition. Bogota: Fondo educativo panamericano., 2007.
21. El-Halwagi, M. Process Integration. Process System Engineering, Vol. 7., 2006.
22. López, T., Rathi, P., Ramírez, E., Sales, M. Factors affecting the acid pretreatment of lignocellulosic biomass: Batch and continuous process. European Symposium Computer Aided ChemicalEngineering. 2010;979–84.
23. Olajuyin, A., Yang, M., Liu, Y., Mu, T., Tian, J., Adaramoye, O. Efficient production of succinic acid from Palmaria palmata hydrolysate by metabolically engineered Escherichia coli. Bioresources Technology., 2016; 214:653–9.
24. Zhang, X., Yu, H., Huang, H., Liu, Y. Evaluation of biological pretreatment with whiterot fungi for the enzymatic hydrolysis of bambooculms. International Biodeterioratio & Biodegrad. 2007;60(3):159–64.
25. Klein, D., Oleskowicz, P., Simmons, B., Blanch, H. The challenge of enzymecost in the production of lignocellulosic biofuels. Biotechnology Bioengineering. 2012;109(4):1083–7.
26. Thompson, J., Tyner, W. Corn Stover for BioenergyProduction: Cost Estimates and Farmer Supply Response. Renewable Energy. 2010;1–7. Available from: https://www.extension.purdue.edu/extmedia/EC/RE-3-W.pdf
27. El-Halwagi, M. Sustainable Design Through Process Integration: Fundamentals and Applicationsto Industrial Pollution Prevention, Resource Conservation, and Profitability Enhancement. 2012.

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