ENVIRONMENTAL SCIENCES & PRACTICES
http://mlsjournals.com/Environmental-Science-Practices

(2024) Environmental Sciences & Practices, 2(1), 75-89.

Simulation of a process to obtain bioethanol from forestry residues from sawmills in the northern part of Costa Rica

Simulación de un proceso de obtención de bioetanol a partir de los residuos forestales de los aserraderos de la zona norte de Costa Rica

Osvaldo Antonio Chavarría Acuña
Environment, Costa Rica
(osvachavarria@gmail.com) (https://orcid.org/0000-0002-0303-7314)

Manuscript information:

Received/Recibido:21/10/22
Reviewed/Revisado: 21/12/23
Accepted/Aceptado:17/01/24

Keywords:
Sawmills, biorefinery, biomass, gasoline, ethanol.

ABSTRACT

The focus of this project is the technical evaluation of the installation of a biorefinery in Costa Rica. This includes sawmill residues from the country's north, 30 kilometers around Boca Arenal, San Carlos, and performing a mass balance from secondary sources and the DWSIM 7.5.5 chemical process simulator for ethanol production to blend with Costa Rican gasoline. The methodology makes use of a non-experimental, transactional, or transversal design. Twenty interviews were conducted for a population of 24 sawmills producing 40,447 tons of lumber per year, producing 16,414.30 kilograms of 99.8% v/v purity ethanol daily (20.84 cubic meters per day). As a result, the ethanol produced can supply 5.16% of the gasoline consumed in Costa Rica, as well as syngas residual and methanol as secondary products. The installation of a biorefinery in Costa Rica is technically feasible due to the availability of raw materials and technologies for the conversion of biomass into ethanol, and it is advantageous to consider other lignocellulosic sources such as fractions of urban waste, agricultural waste, and industrial waste, as well as other geographic regions around the country. To determine the viability of the project, a financial feasibility study for the biorefinery installation is required in other stages of project planning.

Palabras clave:
aserraderos, biorrefinería, biomasa, gasolinas, etanol.

RESUMEN

El estudio consiste en la evaluación técnica para instalar una biorrefinería en Costa Roca. **S**e cuantifican los residuos de los aserraderos ubicados en la zona norte del país, 30 kilómetros a la redonda de Boca Arenal, San Carlos, y así realizar un balance de masa a partir de fuentes secundarias y mediante el simulador de procesos químicos DWSIM versión 7.5.5, para producir etanol con el propósito de mezclar con las gasolinas consumidas en Costa Rica. La metodología consiste en un diseño no experimental, transeccional o transversal, y para una población de 24 de aserraderos, se aplicaron 20 entrevistas de donde se obtuvo que anualmente se producen 40,447 toneladas, y bajo la modalidad termoquímica, utilizando como materia prima todos los residuos de los aserraderos de la zona de estudio, se obtienen 16,414.30 kilogramos de etanol por día (20.84 metros cúbicos por día), con una pureza del 99.8 % v/v, logrando

	de esta manera abastecer mezclar con etanol el 5.16 % de las gasolinas que se consumen en Costa Rica, teniéndose como productos secundarios syngas residual y metanol. Al haber disponibilidad de materia prima y tecnologías para la conversión de biomasa en etanol, técnicamente es factible la instalación de una biorrefinería en Costa Rica, siendo favorable tomar en cuenta otras fuentes lignocelulósicas como fracciones de residuos urbanos, residuos agrícolas y residuos industriales; además de otras regiones geográficas, siendo imprescindible llevar a cabo un estudio de factibilidad financiera para la biorrefinería, para determinar la viabilidad de proyecto.

Introduction

Costa Rica has historically been highly dependent on fossil fuels in the transportation sector. From an environmental point of view, hydrocarbons represent a major problem, since combustion produces gases such as carbon dioxide, carbon monoxide, sulfur dioxide and nitrogen oxides (E-education, 2022). These gases cause the greenhouse effect, causing global warming, causing sea levels to rise and the poles to melt (National Geographic, 2022), and also cause acid rain, acidifying soils and bodies of water, altering the conditions of living beings (Castro, 2019).

In order to mitigate the impact of gasoline emissions, RECOPE (2020) (Refinadora Costarricense de Petróleo) proposed blending them with bioethanol, with the disadvantage of needing large extensions of land for sugarcane cultivation, and of being a first generation biofuel as its raw material is a source of human consumption.

By changing the raw material to residual forest biomass, it is possible to propose a model for the use of its lignocellulose, through the installation of a biorefinery, which is conceptualized in the framework of the transformation of biomass in an optimal way, to produce various products, and at the same time be self-sufficient and without being dangerous for the environment (Hingsamer and Jungmeier, 2019), therefore, a biorefinery can be defined as any plant that contemplates the necessary equipment to carry out unitary processes and operations of biomass conversion to produce food, chemicals, materials, fuels, heat and/or electricity (Ray et al., 2021).

By properly using waste as feedstock, it constitutes a second-generation biorefinery, whose raw materials come from crops, but not food, being the raw material mainly agricultural and forestry residues, so it has a great advantage over first-generation ones, as it does not compete with human consumption Chávez-Sifontes (2019).

The transformation of lignocellulosic biomass into ethanol can be carried out by biochemical conversion, where the biomass is first separated into cellulose, hemicellulose and lignin, and then the sugars are converted by enzymatic reactions. Enzymes, which can be yeast, fungi or bacteria, digest the sugar to produce, in addition to ethanol, carbon dioxide, hydrogen and other products (Dahiya, 2020).

The other way is through a thermochemical process, the controlled reaction of biomass is carried out in a solid state, which is volatilized so that, in this way, other materials can be produced either solid, liquid and gaseous, and is characterized by undergoing little or in the absence of oxygen, and regulated by pressure and temperature (IRENA, 2018).

Compared to biochemical conversion, thermochemical conversion offers greater advantages, as it contemplates a wide variety of feedstocks, including wood, as well as higher conversion and energy efficiency, and shorter reaction times (Chandraratne and Daful, 2021).

Studies have shown different results for ethanol from biomass. Technical, economic and environmental evaluations to produce bioethanol in a biorefinery from residual biomass, yielded results between 0.14 - 0.22 kg of bioethanol / kg of biomass through biological conversion (Demichelis et al., 2020).

In another variant, with a dilute sulfuric acid pretreatment, 191.96 kg of ethanol were obtained from 1000 kg of sugarcane bagasse (Dionísio et al., 2021).

This study aims to simulate the process of a biorefinery in Costa Rica to produce bioethanol so that it can be blended with gasoline to reduce the impact caused by atmospheric emissions.

Chacón (2012), studied the same area of the present project: 30 km around Boca Arenal de San Carlos, in order to determine the situation of sawmill waste in the region, with respect to the waste generated, while suggesting measures to improve the use of waste for energy purposes, determining that the study area generates about 80,000 tons of waste per year.

Therefore, as the northern region is a region with a significant amount of forest residues, it is justified to study the biomass supply in order to propose a process and a mass balance using secondary sources to produce second-generation bioethanol.

To have an idea of the benefit of obtaining ethanol under the proposed scheme, the capacity of the plant obtained was determined, to be used as a blend in the gasoline consumed in Costa Rica, replacing MTBE, which is the oxygenate that has been used in recent years, for which it was necessary to consider the consumption of gasoline, and the amount of ethanol that it is technically possible to blend with hydrocarbons.

For this purpose, we considered what was determined by López (2019), who conducted several tests at the Center for Electrochemistry and Chemical Energy (CELEQ) of the University of Costa Rica, and determined that, using blends of 10% ethanol, without MTBE or ETBE, the physicochemical properties of the gasolines are suitable for use, considering among several aspects that, no phase separation problems (ethanol - water) were found in the temperature range of study (0 ˚C - 40 ˚C).

In relation to consumption, RECOPE, which acts as the hydrocarbon marketing monopoly in Costa Rica, determined that in an average scenario for 2022, it was estimated that 1,414,320 m^3 (RECOPE, n.d.) of super and regular gasoline would be consumed, a figure that was used as a reference to determine the amount that could be blended with the ethanol in the simulation process.

The research is consistent with the National Decarbonization Plan, established by the Government of Costa Rica (2019), which among several points, promotes blending national ethanol with gasoline; in addition, it is part of the instruments of the Organization for Economic Cooperation and Development (OECD, 2020), which recommends that countries promote cleaner fuels and renewable energy sources, while promoting development in harmony with the environment and a circular economy.

The objective is to evaluate the technical feasibility of installing a biorefinery in Costa Rica for the production of ethanol from sawmill forest residues, located 30 km around Boca Arenal, San Carlos, Costa Rica, in order to blend them with gasoline.

Method

The research design was non-experimental, transectional or cross-sectional, collecting information during the course of the year 2022. It was both descriptive and action-research type, since it was developed with the intention of promoting a change in the reality regarding the use of waste, for the benefit of the environment.

The population was the number of sawmills located within a radius of 30 km around Boca Arenal de San Carlos, Costa Rica, shown in Figure 1, where it was proposed to apply a census, given the relatively small number of sawmills in the area, anticipating a lack of 20% of the population due to refusal or omission of the owners, being the variable to measure, the amount of waste (biomass) in tons from sawmills, in its different physical presentations: sawdust, burucha, firewood and wood chips, where the information was obtained through face-to-face surveys or via telephone, to the personnel of the sawmills in the northern region of Costa Rica.

The survey applied to sawmill personnel was on average weekly production, workweeks per year, most common species processed, average sawmill yield, average amount of waste, whether there is waste accumulation. In addition, and more specifically on waste, we asked about the proportion of waste between sawdust, burucha, firewood and "other", and also asked about the distribution of the use given to these: self-consumption, sale, gift and accumulation.

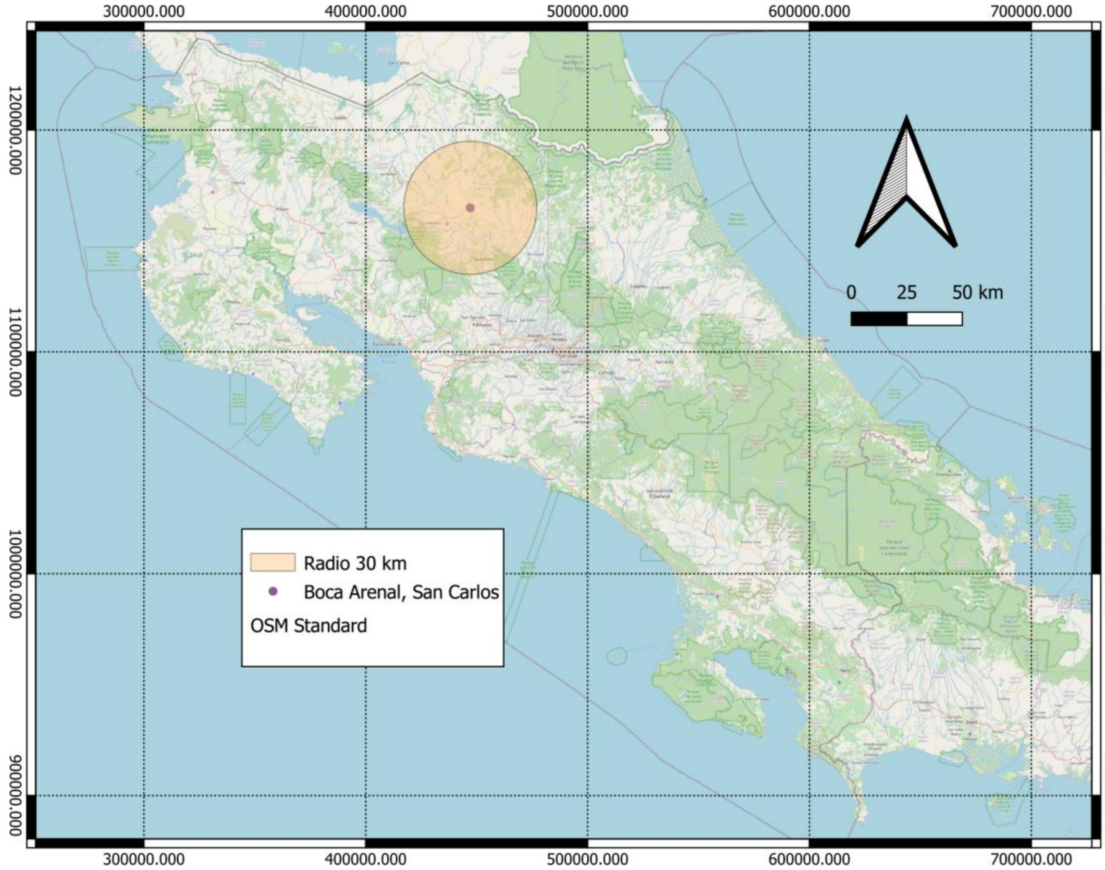
Finally, the company was asked if there is any plan or strategy for the use of waste, to what type of company it is being supplied, as well as its opinion on whether demand was being met.

To determine the sawmill population, we consulted the municipalities and the Ministry of Health of the region, and georeferenced them using QGIS software version 3.24.1, to determine which were located within the study area shown in Figure 1, whose area corresponds to a 30 km radius circle, centered in Boca Arenal, San Carlos.

Based on the current waste supply in the area, the stoichiometric thermodynamic model established by Basu (2010) was used to calculate the syngas composition after biomass gasification, and subsequently, using the DWSIM program version 7.5.5.5 and secondary sources, the processes and unit operations were determined to calculate the ethanol capacity to be produced.

Figure 1

Northern sector of Costa Rica where the research is delimited by the shaded circle, and centered in Boca Arenal de San Carlos, CRTM05 coordinates 447,131.622 longitude - 1,164,932.971 latitude



Results

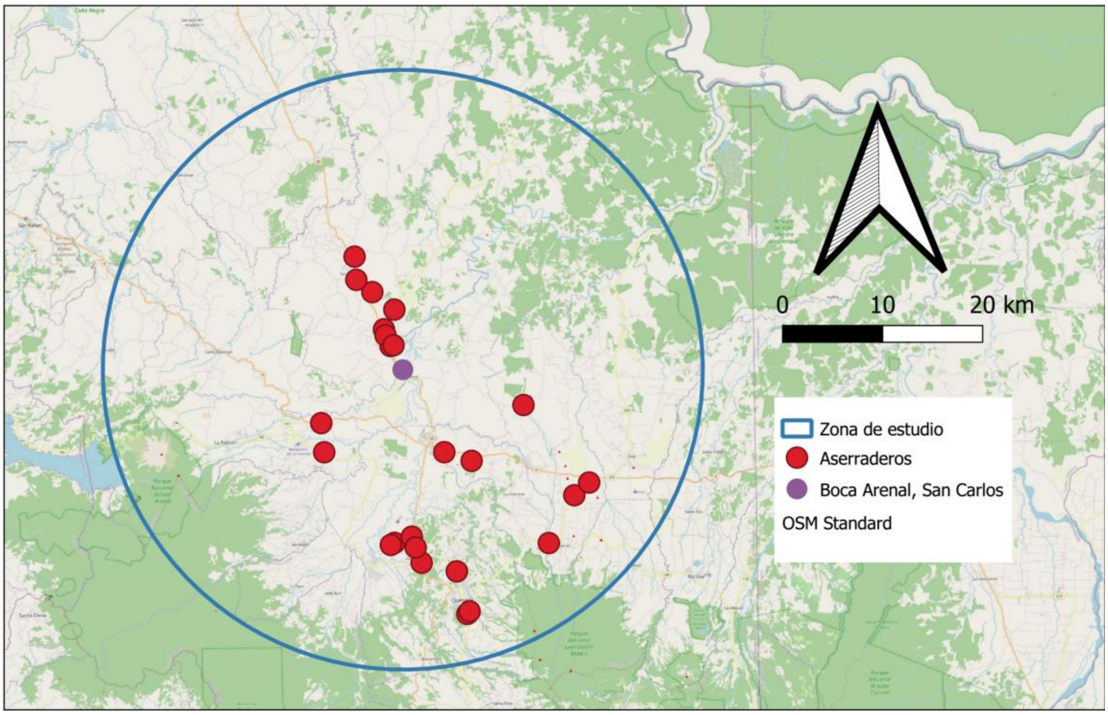
A total of 24 sawmills were located, whose location is shown in Figure 2 and the coordinates are shown in Table 1, where 100% were located in the canton of San Carlos. Information was obtained from 20 of these, obtaining that 35,338,632 PMT (Tico lumber inches) are processed annually, where 1 m^3 is equivalent to 362 PMT in roundwood, and also, 1 m3 is the same as 462 PMT in sawnwood (Barrantes and Ugalde, 2018).

The average sawlog yield was 55%, with Vochysia guatemalensis, Cordia alliodora and Vochysia ferruginea being the most common species traded, and working practically all year round. Details on the type of waste and its disposal are shown in Table 2, which shows similar proportions of waste, with the exception of burucha, and firewood being the predominant type;

and as for the disposal of waste, the vast majority (94 %) was sold, while 3 % was used for self-consumption, 2 % was accumulated in establishments, and only 1 % was given away.

Figure 2

Location of the sawmills interviewed, in CRTM05 coordinates



As for the plan or strategy for the use of waste in the sawmills, it was linked to their self-consumption (for wood drying, for example), with 35% responding that they do have a plan, while 65% indicated that they do not.

Most of the establishments have the Ticofrut company as a client for the sale of firewood, while sawdust was commonly sold to farms that had activities such as dairies and poultry farms. Other companies mentioned that purchased residues in different presentations were Cemex, Del Oro, Agrep Forestal and Agrofertilizantes Nerking.

Finally, the interviewees were asked whether, in their personal opinion, the waste is meeting the demand of the customers who buy their waste. The majority, 80% answered yes, 10% said no, while the remaining 10% said they did not know.

Table 1

Location of sawmills in coordinates CRTM05

Name of establishment	Length	Latitude
Aserradero Laraco	453852.966	1155698.201
Aserradero San Gerardo	446388.007	1170961.132
Aserradero Flor y Fauna	459132.155	1161193.906
Aserradero Atenas	445317.583	1169012.186
Aserradero Arcoiris	452176.858	1144670.679
Maderas de Sucre	453150.124	1140399.309
Aserradero Arjima	445995.262	1147634.517
Aserradero Aguas Zarcas	461427.997	1147345.077
Aserradero Muelle	451136.463	1156615.271
Aserradero Las Nieves	444217.158	1172753.887

Aserradero Bolaños	445943.236	1167326.261
Aserradero La Loma	453391.416	1140648.280
Aldequezul	447737.452	1148215.423
Aserradero Santa Rosa	442642.379	1174006.644
Aserradero Buenos Aires	445462.252	1168404.192
Tarimas Acuña y Ávila	445629.505	1147433.677
Maderas Cultivadas	442505.156	1176332.426
Tarimas del Norte	448680.262	1145593.404
Holystone Group	439129.584	1156815.792
Aserradero El Milagro	464061.439	1152082.678
HC Maderas	465565.487	1153326.342
Maderas y Molduras San Jorge	438879.674	1159737.696
Norte Madera	446240.771	1167397.932
Maderas y Molduras Acual	448102.884	1147133.559

Table 2
Breakdown of waste produced according to its classification and disposal

Type of waste	Tons per year
Sawdust	13,095
Burucha	2,587
Firewood	13,271
Chips	11,494
Use - disposition	
Self-consumption	1,183
For sale	38,066
Gift	270
Accumulation	928
Total	40,447

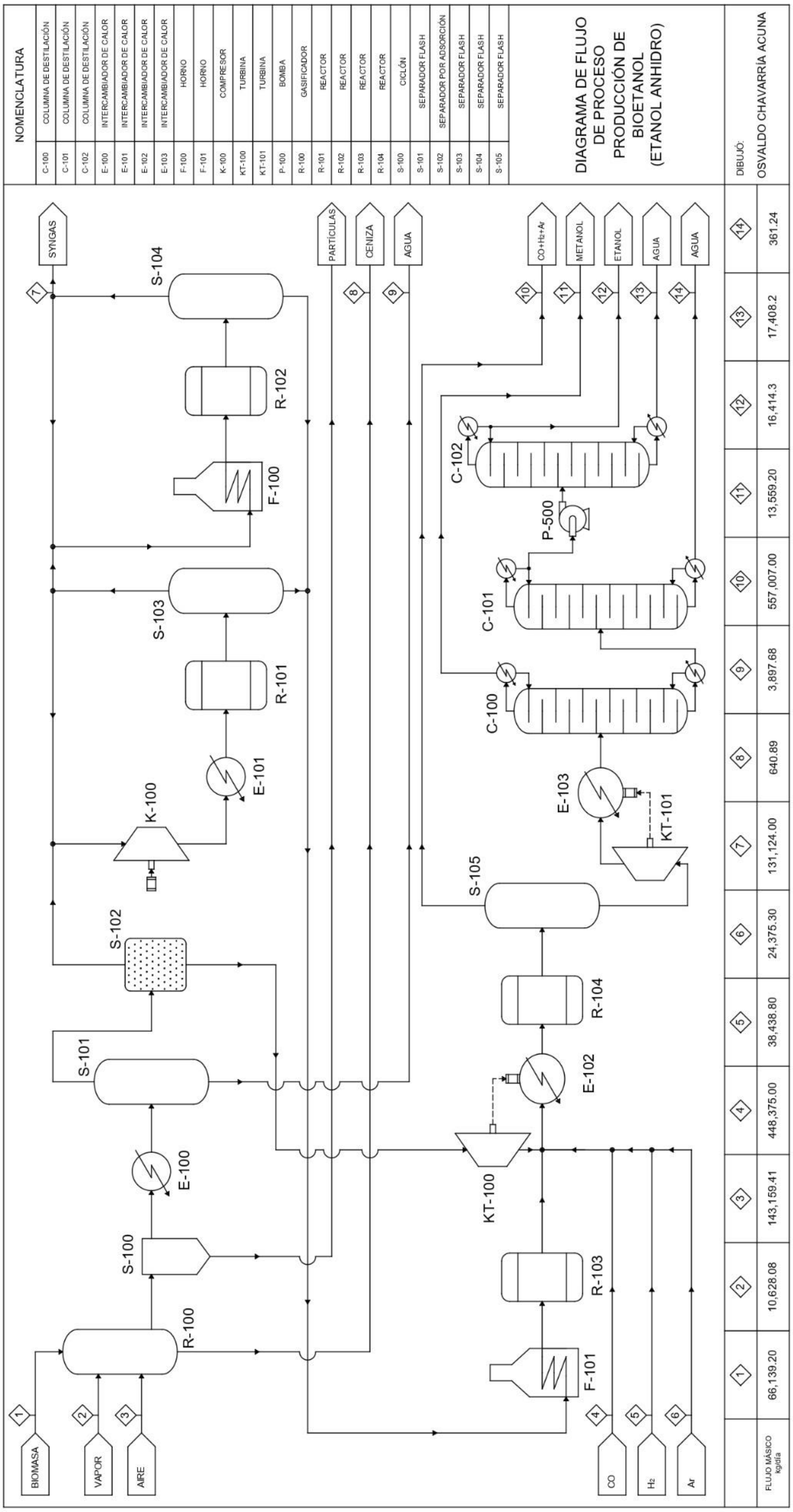
Mass Balance

In order to prepare the mass balance, the total sum of the wastes was considered: 40,447.09 ton/year, as well as moisture values: 32.0 %, 50.0 % and 32.5 %, for sawdust, firewood and burucha respectively, as obtained by Chacón (2012), cited by Chacón, Coto and Flores (2018); while 49.0 % of the wood chips, were obtained through the services of the Agronomic Research Center of the University of Costa Rica, working with an average humidity of 42.8 %.

Elemental analysis of 50.295 % C, 6.085 % H, 42.498 % O, 0.136% N, 0.018 S and 0.969 % ash was assumed, whose values are averaged from various species by Gaur and Reed (1998), cited by BEF (2022); and it was assumed that the plant would operate 350 days per year, considering some shutdowns for maintenance and holidays.

Figure 4 shows the complete process flow diagram with mass balance values.

Figure 4
Anhydrous ethanol production process flowchart



First, using the thermodynamic model in equilibrium - stoichiometric, by means of the minimization of the Gibbs free energy established by Basu (2010), we have the following chemical reaction:

$$CH_aO_bN_c + dH_2O + e(O_2 + 3.76N_2) \rightarrow n_1C + n_2H_2 + n_3CO + n_4H_2O + n_5CO_2 + n_6CH_4 + n_7N_2$$

Assuming a temperature of 1500 K and 1229.45 kg/hour of steam-air gasifying agent 50:50, in the R-100 reactor, 9,141.46 kg of syn gas/hour were obtained, with the values shown n_i Table 3. The molecular formula of the biomass resulted: $CH_{1.441512}O_{0.634299}N_{0.002319}$.

Table 3

n_i values of syngas using the stoichiometric model of Basu (2010)

Variable	Value n_i
n1: C	0.00000
n2: H_2	0.83000
n3: CO	0.83000
n4: H_2O	0.10400
n5: CO_2	0.17000
n6: CH_4	0.00000
n7: N_2	1.60400

Subsequently, the water is separated from the light gases by the S-101 flash separator. One of the drawbacks of these gases is the large proportion of CO in relation to the rest of the gases, which is why it was decided to install an S-102 separator that works with an adsorption system of activated carbon and CuCl, prepared with $CuCl_2$, considering that Gao et al. (2018) succeeded in recovering up to 92.9% of CO from syngas, obtaining close to 100% CO purity after desorption of the separated gas.

Therefore, in the present process a S-101 separator system was proposed, such as the one mentioned above, which operates in an ideal way, assuming that 90% of the CO from the syngas leaving the R-100 reactor is recovered, so that the separated CO can be used later, thus configuring the R-101 and R-102 reactors with CO/CO2 ratios close to 0.3 for both, using the kinetic model of Van den Busshe and Froment (1996).

Using the same model, but adapted to units of pressure in Pa, and reaction rate in $kmol \cdot kg^{-1} \cdot s^{-1}$, at 50 bar and 180 ˚C, a stream of 35,607.20 kg/day was obtained, with a purity of 69.2 % m/m methanol, and a purge constituting a residual of 131,124.00 kg/day, allowing the transformation of syngas into methanol through the hydrogenation of carbon dioxide, where the reverse of the gas-water exchange reaction (RWGS) is also involved (Lücking, 2017):

$$CO_2 + 3H_2 \leftrightarrow H_2O + CH_3OH$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

Then, the formation of dimethyl ether continues, which can be obtained by acid catalysis (Brunetti et al., 2020) from methanol:

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

The kinetics is modeled according to the Arrhenius equation with coefficients A_i=200034.17 and B_i=80840 (Singh, n.d.). Operating at 50 bar and 365.65 ˚C, it allows a conversion of almost 100 % of methanol, and is carried out in the R-103 reactor

Subsequently, dimethyl ether, together with carbon monoxide and hydrogen obtained from syngas, in the R-104 reactor, ethanol and methanol were obtained as main products (Li et al., 2010) as follows:

$$CO + CH_3OCH_3 \rightarrow CH_3COOCH_3$$

$$CH_3COOCH_3 + 2\ H_2 \rightarrow CH_3CH_2OH + CH_3OH$$

$$CO + 2H_2 + CH_3OCH_3 \rightarrow CH_3CH_2OH + CH_3OH$$

A selectivity of 46.16 % was obtained for methanol, 42.08 % for ethanol, while the remainder corresponds to a mixture of carbon dioxide, methyl acetate and ethyl acetate.

Finally, the ethanol was purified by means of three distillation columns, operating the first two at 1 atm (C-100 and C-101), and the third (C-1-2) at 10 bar to break the azeotropic mixture, thus obtaining anhydrous ethanol, with a purity of 99.8 % v/v, at a flow rate of 16,414.30 kg/day (20.84 m^3/day).

Amount of blending in gasoline in relation to the ethanol produced

Comparing the average scenario for 2022, of 1,414,320 m^3 determined by RECOPE (s.f.) of super and regular gasoline consumption, with the proposed plant whose capacity is 20.84 m^3/day (7,294.0 m^3/year, operating 350 days per year), means that 5.16 % of gasoline would be supplied with the ethanol produced in the plant during 2022.

Discussion and conclusions

The development of the conversion of biomass into ethanol in this study was by thermochemistry, given the advantages it offers, since it contemplates a wide variety of raw materials, including wood, in addition to greater efficiency in the conversion and energy, and shorter reaction times (Chandraratne and Daful, 2021), the same modality used by companies such as Enerkem, which has made substantial inroads in the production of products and fuels from waste (Elías, n.d.).

There are several aspects to consider when using biomass in a processing plant. One of them is the moisture content, since, during gasification, it is mainly carbon, hydrogen and oxygen, and to a lesser extent nitrogen and sulfur, that react with the gasifying agent to produce syngas, which is the start of the process to reach ethanol.

In the present project, it was determined that, of the 40,447 tons, a considerable proportion: 42.8 % corresponds to moisture, while the remaining is the biomass that enters the plant for conversion.

Under the proposed scheme, 3.32 kg syngas / kg biomass was produced; but if 22 kg/h hydrocarbon-enriched biomass is used, 41.76 kg/h can be generated, i.e., 1.9 kg syngas / kg biomass, using a non-stoichiometric gasification model between 900 ˚C - 1000 ˚C, and air as gasifying agent. (Caballero et al., 2019).

Rodriguez et al. (2010) obtained 583 kg/h of syngas from 833 kg/h of biomass (0.7 kg of syngas / kg of biomass), based on a chemical equilibrium approach, similar to the one developed in the present project, where some of the assumptions that were used in common are: the reactions are in thermodynamic equilibrium, it is carried out at atmospheric pressure, nitrogen is inert, as well as ash, so it is not involved in the chemical reactions, and the gases produced are only CO_2, CO, H_2, CH_4, N_2 and H_2O, and that in addition, the gasifying agent is a combination of steam and air. Two differences between that research and the present project were that Rodriguez et al. (2010) used 850 ˚C, and industrial sludge as a biomass source.

Therefore, the amount of syngas to be obtained differs according to the system and the conditions used. Even so, and for the purpose of designing a gasifier, it is convenient to consider some preliminary aspects. For example, if a downdraft gasifier is used, it facilitates a continuous flow of syngas, and allows processing biomass with high moisture contents, as well as being of simple design and low cost (Caballero et al., 2019).

Another aspect to take into account is the physical form of the raw material that is introduced into the reactor, because although it is true that sawdust, firewood, burucha and chips are all wood, but in different physical presentations, it should be foreseen that the reactor has the versatility to process all forms of biomass, or, alternatively, install a mechanism, either internal or external, that allows the raw material to be uniform and can even be adapted for drying it, when necessary, thus facilitating the management of the range of operating conditions of the reactor.

The amounts of steam and air used were selected to achieve maximum biomass conversion, so that there would be no unconverted carbon in the products (n_1=0), and on the other hand, the advantage of using a high temperature: 1500 K, allowed the amount of methane to be negligible in the syngas composition, and for practical purposes, CH_4 could be omitted in the next stage of the process.

Although the model used does not quantify solid particles that can be derived in the R-100 gasifier, in the flow diagram it was decided to place the S-100 cyclone downstream of the reactor, so that later, by means of the S-101 separator, the non-condensable gases (CO, CO_2, N_2, H_2) are separated from the condensable ones, of which it is mainly steam, and may contain small traces such as methanol, acetic acid, acetone and tars (Chandraratne and Dafulal), thus achieving a conditioning of the syngas for the next phase.

The next stage consists of converting the syngas into methanol, in which one of the ways to obtain it is through the hydrogenation of carbon dioxide, both gases contained in the syngas, for which the model of Van den Busshe and Froment (1996) was used, whose results are comparable with industrial processes (Luyben, 2010, Chen et al..., 2011, cited by Lüking, 2017), and furthermore, the same $Cu/ZnO/Al_2O_3$ catalyst characteristics employed by Van-Dal and Bouallou (2013) were used, which are, density: 1,775 kg_{cat}/m^3, particle diameter: 5.5 mm and porosity: 0.4.

Van-Dal and Bouallou (2013) simulated a plant to absorb CO_2, in which, they transformed it into methanol, achieving a 33 % CO_2 conversion, based on the kinetic model of Van den Busshe and Froment (1996) mentioned above, using the Aspen Plus simulator. Similarly, Nwani (n.d.), using the same kinetic expressions, but with the DWSIM simulator, also achieved a 33% CO_2conversion.

The process shown in Figure 4 works with a two-reactor system: R-101 and R-102 with double recycling, to transform syngas into methanol, in which, considering the amount of CO_2 entering and leaving the system, a conversion of 82% was obtained, which represents a considerably higher value than the simulations described in the previous paragraph.

The stream in the flowsheet, called "syngas", may well be used in a variety of ways, for example, for power generation, syngas, biofuels and waxes production through Fischer-Tropsch processes (Genia Bioenergy, 2022), or even retrofitting an additional reactor to increase methanol production, thus making it a three-reactor system instead of a two-reactor system.

Subsequently, in the R-103 reactor, the transformation of methanol to dimethyl ether is carried out, which at the outlet pressure of the methanol production section (50 bar) and the same operating temperature of 365.65 ˚C employed by Singh (n.d.), excellent conversion values of almost 100 % were obtained.

For the conversion of DME in the R-104 reactor, it is recommended to use the operating conditions studied by Li et al. (2010), to obtain ethanol: 493 K, 1.5 MPa, and a feed ratio 1/47.4/1.6/50 - DME/CO/Ar/H_2, to favor conversion to ethanol, which in the present process gave a selectivity of 46.16 % and 42.08 % for methanol and ethanol respectively, values that are very close to the 46.30 % and 42.2 % reported by Li et al. (2010).

It should be noted that the CO separated from the S-102 system was used as a reagent for the R-104 reactor, but it was insufficient to meet the 1/47.4 - DME/CO ratio indicated in the previous paragraph, which is why it was necessary to implement an additional CO stream to feed the aforementioned reactor.

Similarly with the CO stream implemented to feed the R-104 reactor, it was necessary to propose additional H_2 and Ar streams, of which CO and H_2 constitute excess reactants and Ar an inert, and which are separated in the S-105 separator, with the possibility of recirculating them to feed the R-104 reactor, or installing an additional system to produce additional methanol from the excess CO and H_2.

The final phase consists of the purification of ethanol, which is mixed with methanol, water, methyl acetate and ethyl acetate. For this purpose, three distillation columns were used.

The first column, C-100, separates mainly methanol with a purity of 96 %, the remainder being small amounts of methyl acetate and ethyl acetate, which were produced as by-products in the R-104 reactor. This stream, designated as number 11 in Figure 4, is of great importance, since it opens up possibilities for its use. One of them is to recycle it to the R-103 reactor to produce more DME, and thus more ethanol.

Another form of utilization is to purify methanol for commercialization, so that it functions as a raw material for other materials and products, which include: adhesives, paints, LCD screens, automotive manufacturing, sealants, lubricants, plastics, ethyl-propylene, polypropylene, medium-density fiberboard, plywood, in addition to the area of fuels - biofuels: biodiesel, MTBE, DME (Methanol Institute, 2022).

The bottoms of the C-100 column constitute the feed for the C-101 column, where the ethanol is partially purified. Both columns C-100 and C-101 were configured with the NRTL thermodynamic model and operate at 1 atm. The last distillation column C-102, constitutes the last step to obtain the purified ethanol, which, unlike the two previous ones, used the thermodynamics of Raoult's Law, and 10 atm of pressure to overcome the limiting azeotropic mixture formed by ethanol and water, in a similar way as Kishnani (n.d.) used to purify ethanol using a high pressure column in which he obtained ethanol at 99.8 % v/v.

Use of ethanol as an oxygenating agent

In the process of Figure 4, ethanol was also obtained at 99.8 % v/v, which falls into the category of anhydrous fuel ethanol according to the INTE E5:2017 standard (INTE, 2017), which establishes that it must have a minimum purity of 99.0 % of ethanol, so that in this way, it can be used as an oxygenate in gasoline for internal combustion engines, being able in this case, with the capacity of the biorefinery and the availability of the raw material, to supply 5.16 % of the gasoline in Costa Rica projected by RECOPE (n.d.), to be mixed with ethanol.

By way of comparison, in the city of Catalonia, when it had a population of 7,000,000 inhabitants, taking into account not only forestry waste, but also urban solid waste fractions, agricultural waste and industrial waste, 53,000 tons of (dry) waste could be produced daily, which could produce 23,000,000 liters of ethanol/day, equivalent to 66% of the demand for 34,500,000 liters/day, with a vehicle fleet of 5,500,000 units (Elías, n.d.).

With the above figures, it means that 0.43 liters of ethanol / kg of dry waste can be produced, which shows some similarity with the proposed biorefinery, since it produces 0.31 liters of ethanol / kg of dry waste. Both cases are similar in that they involve the production of second-generation biofuels, but differ in that the biorefinery considered only forestry waste, while in the case of Catalonia, forest, urban, agricultural and industrial waste was considered.

In the Costa Rican market, a project had been proposed for the Costa Rican Petroleum Refinery (RECOPE) to sell ECO95 and ECO91 gasolines, which consisted of blending gasoline with ethanol between 5% and 10% v/v (RECOPE, 2020), and thus have a different alternative to those marketed with MTBE.

To develop this project, the most viable way was to plant 14,800 hectares of sugarcane exclusively to produce ethanol, plus all the ethanol produced from molasses as a by-product of the sugar industry (RECOPE, 2020), to cover the demand until 2039.

The project was not successful, and currently gasoline with MTBE continues to be sold, and differs greatly from the proposed project, since the idea proposed by RECOPE was for a first generation biofuel.

Conclusions

Annually, in the northern zone of Costa Rica, 30 km around Boca Arenal de San Carlos, 40,447 tons of wood residues were obtained.

From the forest residues of the study area, through the simulation performed in DWSIM, and under the thermochemical modality, 16,414.30 kilograms of ethanol were obtained per day (20.84 cubic meters per day), with a purity of 99.8% v/v

The process flow diagram developed is subject to change for optimization. For example, water, being a by-product of the biorefinery, can be used to recover energy and integrated into the plant itself, or it could even be used to produce green hydrogen.

For the proposed biorefinery and taking as an example the consumption for the year 2022 and for the whole Costa Rican territory, 5.16 % of gasoline could be supplied with ethanol.

The availability of raw material is a limiting factor for the success of a project of this type, since there is no certainty of being able to cover the waste market, which constitutes the raw material for the plant, as there are competitors or even competitors that may emerge during the life of the project.

In view of this situation, the idea and opportunity arises to study not only other geographical areas to quantify forest wastes, but also to consider other lignocellulosic urban, agricultural and industrial wastes as raw material, and thus increase the biorefinery's capacity. For example, in the same northern region of Costa Rica, there are many hectares dedicated to pineapple cultivation, the waste from which is an example of raw material.

Taking into account the availability of raw material and the existence of technology to transform biomass into ethanol, we conclude that it is technically feasible to operate a biorefinery in Costa Rica, an aspect that is in line with the National Decarbonization Plan and OECD instruments.

A financial feasibility study must be carried out, for which, among other aspects, the cost of producing ethanol must be lower than purchasing it for the project to be viable.

References

Barrantes, A. y Ugalde, S. (2018). *Precios de la madera en Costa Rica para el primer semestre del 2018 y tendencias de las principales especies comercializadas.* Oficina Nacional Forestal, Costa Rica.

Basu, P. (2010). *Biomass Gasification and Pyrolysis.* Practical Design and Theory. Elsevier.

BEF (2022). *Proximate and ultimate analysis.* Biomass Energy Foundation http://drtlud.com/BEF/proximat.htm.

Brunetti, A., Migliori, M., Cozza, D., Catizzone, E., Giordano, G. y Barbieri, G. (2020). Methanol Conversion to Dimethyl Ether in Catalytic Zeolite Membrane Reactors. *ACS Sustainable Chem. Eng. 2020, 8,* 10471-10479. https://dx.doi.org/10.1021/acssuschemeng.0c02557

Caballero, A., Rojas., M., Villalobos, M., Davis., A., Roldán, C., Moya., R. y Puente, A. (2019). Simulación de gasificación de biomasa enriquecida con hidrocarburos. *Tecnología en Marcha, 32* (4), 60-68.

Castro, M. (2019). *Lluvia ácida: cómo se forma, composición, reacciones y efectos.* Lifeder. https://www.lifeder.com/causas-lluvia-acida/.

Chacón, L. (2012). *Diagnóstico de las existencias de los residuos forestales en la región Huetar Norte de Costa Rica.* Ministerio de Ambiente y Energía, Fondo Nacional de Financiamiento Forestal, Costa Rica.

Chacón, L., Coto, O. y Flores, O. (2018). *Actualización de la encuesta de biomasa como insumo para su incorporación en la matriz energética de Costa Rica.* Energía, Medio Ambiente y Desarrollo, preparado para la Secretaría de Planificación del Sub-Sector Energía (SEPSE) Costa Rica.

Chandraratne, M. y Daful, A. (2021). Recent Perspectives in Pyrolysis Research. En M. Bartoli y Giorcelli, M. (Eds.), *IntechOpen*. https://doi.org/10.5772/intechopen.95170.

Chávez-Sifontes, M. (2019). La biomasa: fuente alternativa de combustibles y compuestos químicos*. Anales de Química - RSEQ, 115 (5)*, 399–407.

Dahiya, A. (2020). *Bioenergy. Biomass to Biofuels and Waste to Energy.* Segunda Edición. Elsevier.

Demichelis, F., Laghezza, M., Chiappero, M. y Fiore, S. (2020). Technical, economic and environmental assessment of bioethanol biorefinery from waste biomass. *Journal of Cleaner Production, 277 (20).* https://doi.org/10.1016/j.jclepro.2020.124111.

Dionísio, S., Santoro, D., Bonan, C., Soares, L., Biazi, L., Rabelo, S. y Lenczak, J. (2021). Second-generation ethanol process for integral use of hemicellulosic hydrolysates from diluted sulfuric acid pretreatment of sugarcane bagasse. *Fuel, 304 (15).* https://doi.org/10.1016/j.fuel.2021.121290.

E-education (2022). *Products of Combustion*. https://www.e-education.psu.edu/egee102/node/1951.

Elías, X. (s.f.). *Residuos sólidos urbanos* [videoclase]. Programa de Máster en Ingeniería Ambiental. Universidad Europea del Atlántico. España.

Gao, F., Wang, S., Wang, W., Duan, J., Dong, J., y Chen, G. (2018). Adsorption separation of CO from syngas with CuCl@AC adsorbent by a VPSA process. *RSC Adv., 2018, 8, 39362-39370*. DOI: 10.1039/c8ra08578a

Genia Bioenergy (2022). *Syngas: el gas de síntesis o sintegás. https://geniabioenergy.com/que-es-el-syngas/*

Gobierno de Costa Rica (2019). *Plan Nacional de Descarbonización, 2018 – 2050.*

Hingsamer, M. y Jungmeier, G. Biorefineries. (2019). In C. Lago, N. Caldés y Y. Lechón (Eds.), The Role of Bioenergy in the Bioeconomy (pp. 179-222). https://doi.org/10.1016/B978-0-12-813056-8.00005-4.

INTE (2017). Norma INTE E5:2017. Combustibles - Etanol carburante anhidro (especificaciones). *Instituto de Normas Técnicas de Costa Rica.*

IRENA (2018). Solid biomass supply for heat and power: Technology brief, *International Renewable Energy Agency, Abu Dhabi.*

Kishnani, D. (s.f.). *Pressure swing distillation column for separation of Ethanol-water mixture.* [Simulación de una columna de destilación para la separación de etanol agua en DWSIM versión 7.5.5]. University of Petroleum and Energy Studies. India.

Li, X., San, X., Zhang, Y., Ichii, T., Meng, M., Tan, Y. y Tsubaki, N. (2010). Direct Synthesis of Ethanol from Dimethyl Ether and Syngas over Combined H-Mordenite and Cu/ZnO Catalysts. *ChemSus 2010,* 3, 1192-1199. DOI: 10.1002/cssc.201000109

López, I. (2019). *Análisis de las propiedades fisicoquímicas y a tolerancia al agua, de mezclas con etanol de las gasolinas utilizadas en Costa Rica.* [Tesis para obtener el grado de Licenciatura en Ingeniería Química, Universidad de Costa Rica]. http://repositorio.sibdi.ucr.ac.cr:8080/jspui/handle/123456789/16079

Lüking, L. (2017). *Methanol Production from Syngas. Process modelling and design utilising biomass gasification and integrating hydrogen supply.* [Tesis para obtener el grado de Máster en Tecnología en Energía Sostenible, Universidad Tecnológica de Delft]

Methanol Institute (2022). *Essential Methanol*. https://www.methanol.org/wp-content/uploads/2020/04/Essential-Methanol-Methanol-Institute-Infographic.pdf

National Geographic (2022). *El aumento del nivel del mar.* https://www.nationalgeographic.es/medio-ambiente/el-aumento-del-nivel-del-mar.

Nwani, A. (s.f.). *Optimization of the Methanol Synthesis by CO_2 Hydrogenation*. [Simulación para la producción de metanol a partir de syngas en DWSIM versión 7.5.5]. University of Laos. Nigeria.

OECD (2020). *Examen del proceso de adhesión de Costa Rica a la OCDE en las áreas de medio ambiente y residuos.* Informe resumido. Dirección de Medio Ambiente. Comité de Política Ambiental.

Ray, L., Pattnaik, R., Singh, P., Mishra, S., y Adhya, T. (2021). Environmental impact assessment of wastewater based biorefinery for the recovery of energy and valuable bio-based chemicals in a circular bioeconomy. In T. Bhaskar, S. Varjani, A. Pandey y E. Rene. (Eds.), *Waste Biorefinery, Elsevier,* (pp. 67-101). https://doi.org/10.1016/B978-0-12-821879-2.00003-X.

RECOPE (s.f.). *Estimaciones de demanda de gasolinas.* Departamento Investigación. Refinadora Costarricense de Petróleo.

RECOPE (2020). *Estudio de factibilidad del proyecto de mezcla de gasolina con etanol a nivel nacional.* Dirección de Planificación, Refinadora Costarricense de Petróleo.

Rodríguez, D., Zaleta, A., Olivares, A., y Torres, F. (2010). *Análisis y Diseño de un Sistema de Gasificación de Biomasa.* Memorias del XVI Congreso Internacional Anual de la SOMIM. México.

Singh, C. (s.f.). *Production of Dimethyl Ether* [Simulación para la producción de dimetil éter DWSIM versión 7.5.5], Rajasthan Technical University, Kota.

Van-Dal, E. y Bouallou, C. (2013). Design and simulation of a methanol production plant from CO_2 hydrogenation. *Journal of Cleaner Production, 57,* 2013, 38-45.

Vanden Bussche, K.M. y Froment, G.F. (1996). A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu / ZnO / Al_2O_3 Catalyst, *Journal of Catalysis 161,* 1-10.