

UNIVERSIDAD SAN FRANCISCO DE QUITO USFQ

Colegio Politécnico

Diseño de biorrefinería para la producción de MTBE y ETBE a partir de residuos orgánicos: evaluación técnica, económica y ambiental comparativa

Biorefinery design to produce MTBE and ETBE from organic wastes: comparative technical, economic and environmental evaluation.

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Ingeniería Ambiental

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HOJA DE CALIFICACIÓN DE TRABAJO DEFIN DE CARRERA

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RESUMEN

La dependencia de combustibles fósiles en el Ecuador, junto con la necesidad de mejorar la calidad ambiental y diversificar la matriz energética, motivó el desarrollo de este proyecto. El estudio consistió en el diseño, modelado y evaluación comparativa de dos biorrefinerías para la producción de MTBE y ETBE a partir de residuos de caña de azúcar. Se utilizaron simulaciones de procesos en Aspen Plus® V14, análisis tecno económicos y estimaciones de huella de carbono para evaluar la viabilidad técnica, económica y ambiental de cada alternativa.

Los resultados demostraron que ambas biorrefinerías son técnica y económicamente viables, aunque el MTBE presenta un precio de mezcla más competitivo, mientras que el ETBE ofrece una menor huella de carbono. Este trabajo aporta evidencia sólida sobre el potencial de los biocombustibles avanzados derivados de residuos como estrategia de transición energética en Ecuador. A futuro, su implementación podría contribuir significativamente a la mitigación del cambio climático, a la sostenibilidad energética y a la valorización de residuos agroindustriales. Se recomienda continuar con estudios de integración energética renovable y de optimización de coproductos para maximizar el impacto ambiental y económico positivo.

Palabras clave: Cambio climático, Gases de efecto invernadero, Huella de carbono, Sostenibilidad, Química verde, Biocombustibles avanzados, Biorrefinería, MTBE, ETBE, Gas de síntesis.

ABSTRACT

The dependence on fossil fuels in Ecuador, combined with the need to improve environmental quality and diversify the energy matrix, motivated the development of this project.

The study involved the design, modeling, and comparative evaluation of two biorefineries to produce MTBE and ETBE from sugarcane residues. Aspen Plus® process simulations, technoeconomic analyses, and carbon footprint estimations were used to assess the technical, economic, and environmental feasibility of each alternative.

Results showed that both biorefineries are technically and economically viable, with MTBE offering a more competitive fuel blend price, while ETBE presents a lower carbon footprint. This work provides strong evidence of the potential of advanced biofuels derived from waste as a transition strategy for Ecuador's energy sector. Future implementation could significantly contribute to climate change mitigation, energy sustainability, and agricultural waste valorization. Further studies are recommended on renewable energy integration and co-product optimization to maximize positive environmental and economic impacts.

Key words: Climate change, Greenhouse gases, Carbon footprint, Sustainability, Green chemistry, Advanced biofuels, Biorefinery, MTBE, ETBE, Synthesis gas.

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INTRODUCTION

Dependence on fossil fuels in the automotive sector in the Ecuadorian highlands represents a significant environmental and energy challenge. This problem is due to the sustained growth of the vehicle fleet, accelerated urbanization, and the limited adoption of sustainable alternatives in the national energy matrix. As a result, greenhouse gas (GHG) emissions, ecosystem degradation and air quality deterioration have intensified, especially in densely populated urban areas (Agyekum et al., 2025; Kazemi Shariat Panahi et al., 2020). The need for viable technological solutions that can at least partially replace the use of conventional gasoline is becoming increasingly urgent.

The growth of the vehicle fleet has reinforced dependence on oil, increasing GHG emissions and exacerbating climate change (Adnan, 2025). Although biofuels have been developed as alternatives, their adoption remains limited due to economic barriers, lack of incentives, and technological constraints (Ahorsu et al., 2018; Sheldon & Yusup, 2019; Srivastava et al., 2015). Diversification of energy sources is therefore essential for a sustainable energy transition (Ahorsu et al., 2018).

Although fossil fuels have physicochemical properties that favor their combustion, they generate pollutants such as NO_x, CO₂ and particulate matter, directly affecting public health (Devi et al., 2021; Kazemi Shariat Panahi et al., 2020). In addition, intensive oil extraction causes degradation of ecosystems and pollutes water bodies (Tse et al., 2021) highlighting the need to implement solutions that reduce pressure on non-renewable resources (Wei et al., 2017).

In this context, advanced biofuels such as methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE) are strategic alternatives. Both compounds, when used as oxygenated additives in gasoline, improve their octane rating and reduce pollutant emissions such as CO, NO_x

and aromatic compounds (Quevedo-Amador et al., 2024). Their production from lignocellulosic biomass - in this case, sugarcane residues - does not compete with food crops and allows the valorization of agricultural waste, promoting a circular bioeconomy model (Ahorsu et al., 2018).

This work proposes separate designs of two biorefineries: one to produce MTBE and the other for ETBE, both using agricultural residues as feedstock. The main objective is to compare both routes from three key scopes: technical performance, economic feasibility and environmental impact. The comparison is made considering their use as oxygenated additives in blends with Extra gasoline, under conditions applicable to the Ecuadorian context.

The relevance of this study is framed in the Ecuadorian energy context, where more than 60% of gasoline is imported, which implies a structural vulnerability of the country (Instituto de Investigación Geológico y Energético et al., 2024). In addition, current blends such as EcoPaís - 95% Extra and 5% Ethanol blend - cannot be used in high altitude areas such as Quito, due to the volatility of ethanol, which limits its applicability (Najafi et al., 2023). In contrast, MTBE and ETBE are more stable and suitable for the entire national territory.

As mentioned, this project aims to achieve three specific objectives, starting with the technical modeling of biorefineries (Objective 1), followed by the comparative techno-economic analysis (Objective 2) and, finally, the inventory of greenhouse gas emissions (Objective 3).

2. DEVELOPMENT OF THE TOPIC

2.1 Objective 1: Design and technically model two independent biorefineries to produce MTBE and ETBE from organic wastes in Ecuador, through simulations in AspenPlus® V.14, evaluating yields, mass and energy balances, and product purity.

2.1.1 Methodology

Activity 1. Selection of raw material for MTBE and ETBE production.

Feedstock selection is a critical aspect of biofuel production, as it directly influences process efficiency, production costs and environmental sustainability. In the case of MTBE and ETBE, the choice of biomass affects both the availability of precursor chemicals and the energy yield of the final product. This study compares sugarcane and African palm as potential sources of biomass in Ecuador, considering their availability, chemical composition, calorific value, and efficiency in the conversion processes. The evaluation of these criteria will allow determining the most suitable feedstock to produce both biofuels, considering an approach that encompasses technical, economic and environmental feasibility (Najafi et al., 2023; Pongchaiphol et al., 2022; Qureshi et al., 2019).

Raw material availability in Ecuador

Sugar Cane

- Cultivated area: 79,580 ha in 2023
- Annual production: 6.3 million tons.
- Main producing regions: Guayas (80.1%), Cañar (11.2%), Los Ríos (3.0%).
- Year-on-year variation: Reduction of 33.5% in area and 19.2% in production.
- Harvests per year: 1 to 2.
- Waste generated: Bagasse and sugarcane straw ($\sim 12 \frac{t}{h}$).

(Ipiales & Cuichán, 2024)

African Palm

- Cultivated area: 137,678 ha in 2023.
- Annual production: 2.0 million tons.

- Main producing regions: Esmeraldas (35.5%), Los Ríos (32.9%), Sucumbíos (12.1%).
- Year-on-year variation: Decrease of 2.6% in area and 10.7% in production.
- Crops per year: 2 to 3 (more stable than sugarcane). - Residues generated: Palm fiber, hulls and empty bunches ($\sim 10 \text{ t}$).

h

(Ipiales & Cuichán, 2024)

Physicochemical and Energetic Characteristics

Sugar Cane

- Chemical composition: 40-50% cellulose, 25-30% hemicellulose, 20-25% lignin (Najafi et al., 2023) - Calorific value: $17 - 19 \text{ MJ kg}^{-1}$ (dry bagasse).

kg

- Carbon footprint: Relatively low compared to palm (Qureshi et al., 2019)
- Water consumption: High, due to the constant irrigation required for its production (Pongchaiphol et al., 2022)
- Impact on biodiversity: May affect ecosystems if large areas are deforested for cultivation.

African Palm

- Chemical composition: 20-30% cellulose, 15-25% hemicellulose, 40-50% lignin (Pongchaiphol et al., 2022)
- Calorific value: $20 - 22 \text{ MJ kg}^{-1}$ (palm fiber).
- Carbon footprint: higher than that of sugarcane, due to industrial extraction and processing processes (Qureshi et al., 2019)
- Water consumption: Moderate, as many plantations depend on natural rainfall (Najafi et al., 2023)

- Biodiversity impact: High deforestation and impact on natural ecosystems.

Table 1 below shows a comparison of the key raw material parameters.

Table 1. Comparison of Key Parameters of Raw Materials

Criteria	Sugar Cane	African Palm
Cultivated area (ha)	79,580	137,678
Annual Production (t)	6.3 million	2.0 million
Crops per year	1-2	2-3
Waste generated ($\frac{t}{ha}$)	12 Bagasse and cane straw	10 Palm fiber, empty palm kernels and empty bunches
Chemical composition	40-50% cellulose, 25-30% hemicellulose, 20-25% lignin	20-30% cellulose, 15-25% hemicellulose, 40-50% lignin
Calorific Value ($\frac{MJ}{kg}$)	17-19	20-22

(Najafi et al., 2023; Pongchaiphol et al., 2022; Qureshi et al., 2019)

Comparative analysis between sugarcane and African palm has shown that feedstock selection should consider biomass availability, conversion process efficiency and environmental impact. Sugarcane has higher fermentation efficiency for ethanol production and greater availability in Ecuador, making it the preferred choice for ETBE production (Najafi et al., 2023). However, its high-water consumption and seasonal dependence may pose logistical challenges (Pongchaiphol et al., 2022). On the other hand, African palm, with its higher calorific value and production stability, is more efficient in gasification to obtain syngas, which is essential in MTBE synthesis. However, its high ecological impact limits its applicability in sustainable production models.

Since standardization of modeling and ease of comparison are key aspects in this study, it is recommended to use a single feedstock for the manufacture of both biofuels. In this context, **sugarcane** is the most viable option due to its higher availability, lower ecological impact and its flexibility in biochemical and thermochemical conversion processes. Although its gasification for MTBE production is not as efficient as that of palm, its optimization would allow minimizing this difference, ensuring a more sustainable and adaptable alternative in the long term. Consequently, it is concluded that sugarcane is the most suitable feedstock for the integrated production of MTBE and ETBE.

Activity 2. Calculation of Biomass Availability

Using the annual sugarcane production and the residues generated per hectare, the amount of available residues is calculated.

$$\frac{954,960 \text{ t}}{2 \text{ yr}} = 477,480 \frac{\text{t}}{\text{yr}}$$

The division of the available waste per year in half responds to several technical, logistical and chemical reasons. First, not all of the biomass generated is fully recoverable due to losses during harvesting, storage and transportation. Some of the material may degrade before industrial use or may not be economically viable to collect, limiting the effective amount of waste available.

In addition, a fraction of the residual biomass has other alternative uses, such as animal feed and soil improvement. Although biofuel production is a priority in this study, it is important to consider that not all the biomass available in the field can be used exclusively for this purpose without affecting other productive systems.

Another key aspect in the availability of biomass is its chemical composition, as it directly influences the fraction that can be utilized in the conversion processes. Sugarcane has an approximate content of 40-50% cellulose, 25-30% hemicellulose and 20-25% lignin. While cellulose and hemicellulose are the main precursors for bioethanol production, lignin is not easily fermented and usually requires additional processes for its energy valorization. In the context of this biorefinery, where the conversion of biomass into MTBE and ETBE involves both syngas fermentation and gasification for chemical synthesis, it is important to consider that not all biomass is directly converted into final products, but that a fraction goes to energy co-products or is lost in process inefficiencies.

Halving total waste is a conservative approach that considers these technical and economic challenges.

$$\begin{aligned}
 & 477,480 \frac{t}{yr} \times \frac{1y}{12m} \times \frac{1m}{30d} \times \frac{1d}{24h} = 55.26 \frac{t}{h} \\
 & 55.26 \frac{t}{h} \times \frac{1000kg}{1t} = 55,263.89 \frac{kg}{h}
 \end{aligned}$$

Based on the calculations performed, it is estimated that the amount of biomass available for the process is approximately 55,263.89 kg/hr. This amount represents the fraction of sugarcane residues that can be effectively collected, transported and processed, considering factors such as harvest losses, chemical composition, alternative uses and operational limitations.

This value will be used as the main input in the process simulation in AspenPlus® V.14, where the conversion of biomass into the target products will be modeled: methanol and ethanol as intermediates to finally produce MTBE and ETBE. From this feedstock availability, the process

yields, mass and energy balances, and the efficiency of the advanced biofuels production system will be evaluated.

Activity 3. General technical design

MTBE and ETBE are biofuels mainly used as oxygenated additives in gasoline, improving its octane rating and reducing pollutant emissions such as CO, NO_x and aromatic compounds. Their incorporation in gasoline blends optimizes combustion and decreases the generation of pollutants harmful to air quality (Mehrijouei et al., 2014). While MTBE is produced from methanol and isobutylene, ETBE uses ethanol and isobutylene.

To evaluate the production of these biofuels from biomass, two independent biorefineries were modeled in AspenPlus® V.14, one designed for MTBE synthesis and the other for ETBE production. Both biorefineries shared the same amount of biomass input but presented differences in their conversion pathways. The first biorefinery was designed to produce 17,205.2 kg/h of MTBE, equivalent to 150,717.55 tons/year, while the second was configured to generate 18,879 kg/h of ETBE, representing 165,380.04 tons/year.

The technical design was modeled in AspenPlus® V.14, a software widely used in the industry for simulation and optimization of chemical and energy processes (de Andrés et al., 2019). This software allowed evaluating chemical conversions, optimizing yields and analyzing overall process efficiency, ensuring a design based on accurate data and realistic conditions. Through detailed modeling, it was possible to obtain an accurate mass and energy balance, which allowed to predict more accurately the products obtained and the efficiencies of the system.

For the simulation, two thermodynamic models suitable for different stages of the process were set up. This hybrid approach was chosen because of the complexity of the system, which involves different phases, temperatures and pressures.

The NRTL (Non-Random Two-Liquid) model is an activity coefficient model developed to describe phase equilibria in non-ideal liquid mixtures, allowing prediction of molecular interactions in highly non-ideal solutions (Yi et al., 2024). It is widely used in systems where significant intermolecular forces exist, such as mixtures of ethanol and isobutylene in the production of ETBE, where the non-random distribution of molecules influences the behavior of the liquid phase. On the other hand, the Peng-Robinson model is an equation of state based on fugacity theory that describes the thermodynamic behavior of vapor and liquid phases in non-ideal hydrocarbon and gas systems (Trop et al., 2012). Its application is key in high temperature and pressure processes, such as biomass gasification and syngas production, where it allows to accurately calculate volumetric properties and phase equilibrium.

Since no single thermodynamic model can accurately predict all system properties, this combination was used to optimize simulation reliability. In industry, no one would invest valuable resources in a process based solely on assumed physical properties and phase behaviors, so this methodology allowed for reduced uncertainties and a more accurate mass and energy balance, ensuring that the simulation reflects realistic conditions for MTBE and ETBE production.

Both MTBE and ETBE production processes were modeled in AspenPlus® V.14, considering the key stages that allow the transformation of biomass into advanced biofuels. The fundamental differences between the two processes lie in the conversion of syngas: while in MTBE production the syngas is converted to methanol, in ETBE production it is converted to ethanol. Despite these differences, biorefineries share several initial stages up to syngas generation. The main stages of the MTBE production process are described below, highlighting the key elements in the box diagram.

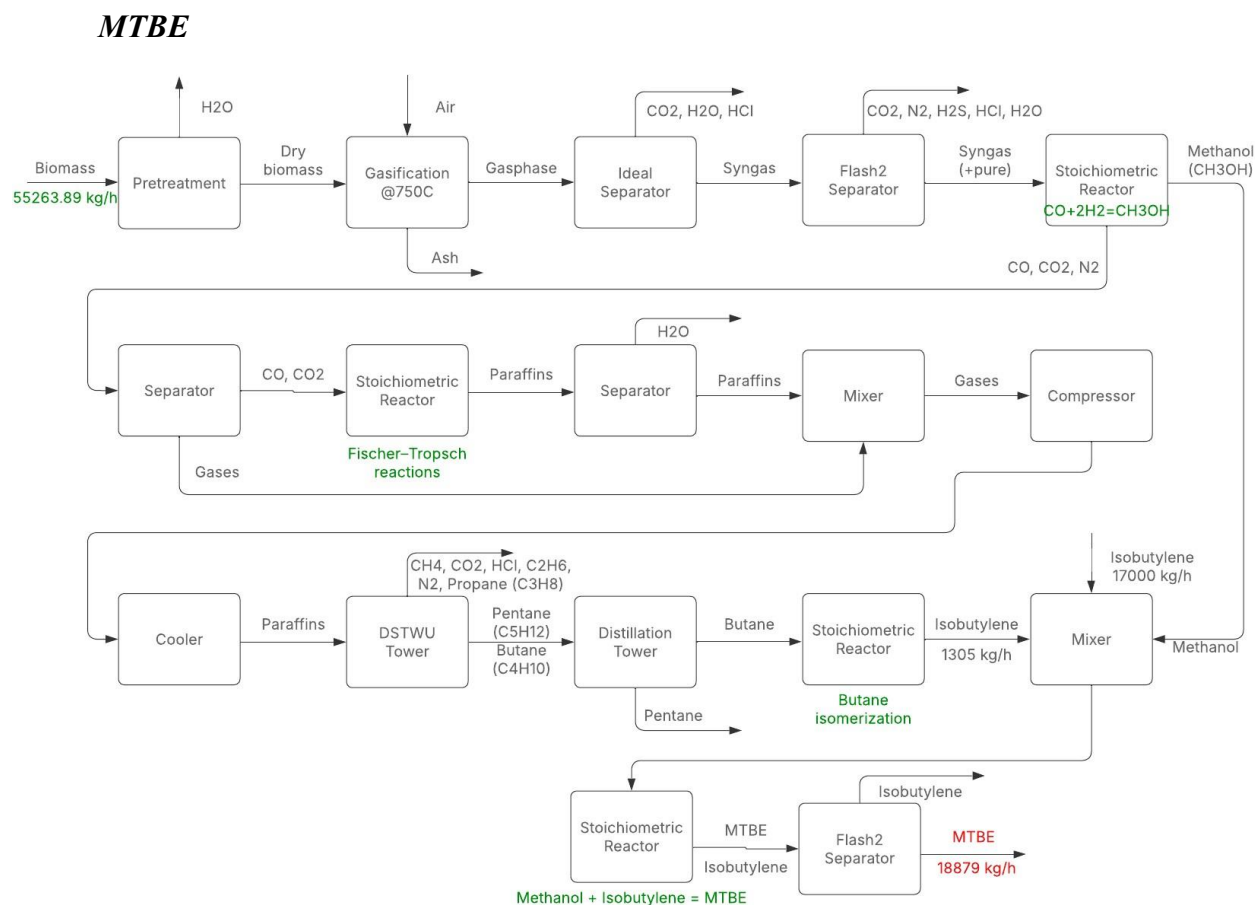


Figure 1. Box diagram to produce MTBE

The MTBE production process was structured in several key stages, which allowed the transformation of biomass into a high value-added biofuel.

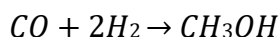
Pretreatment and gasification of biomass

The process began with the input of biomass (55,263.89 kg/h), which was subjected to pretreatment to eliminate its moisture content before being gasified. Subsequently, the dry biomass entered a gasifier operating at 750°C, where gasification was carried out with air to produce syngas (a mixture of CO, H₂, CO₂, CO₂ and other gases).

The resulting gas passed through an ideal separator, where unwanted components, such as H₂O, CO₂ and HCl, were removed, ensuring higher purity in the syngas. This step is crucial, as the composition of the syngas determines the efficiency of the following chemical reactions.

Methanol Production

The purified syngas was directed to a stoichiometric reactor, where methanol synthesis was simulated by the reaction.

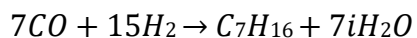
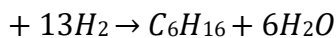
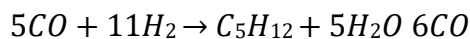
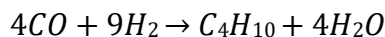
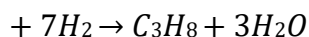
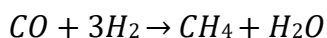


This step is essential, since methanol is the main precursor in the synthesis of MTBE.

Isobutylene Production

One of the key aspects of the process was the partial generation of isobutylene within the biorefinery, reducing dependence on external inputs. To this end, a route based on butane isomerization was implemented.

Fischer-Tropsch reactions were employed for the conversion of CO and H₂ into a mixture of kerosenes and other light hydrocarbons, which is a valuable by-product of the process.



$10CO + 21H_2 \rightarrow C_{10}H_{22} + 10H_2O$ $11CO$
 $+ 23H_2 \rightarrow C_{11}H_{24} + 11H_2O$ Through a
 distillation column, butane (C_4H_{10}) was
 separated, which was then subjected to
 isomerization to yield isobutylene
 (C_4H_8).

Although 1,305 kg/h of isobutylene was produced internally, this amount was not sufficient for the complete synthesis of MTBE, so an external flow of 17,000 kg/h of isobutylene was added. The partial generation of this compound within the plant optimizes costs and reduces dependence on fossil inputs, contributing to the viability of the process.

MTBE Synthesis and Purification

The methanol obtained in the previous stage was combined with isobutylene in a stoichiometric reactor, following the reaction.



MTBE

The resulting product passed through a Flash type separator, where the excess unreacted isobutylene was removed, ensuring a higher purity of the final MTBE. As a result, the biorefinery produced 18,879 kg/h of MTBE, which is a high-value additive in the fuel industry.

The main stages of the ETBE production process are described below, highlighting the key elements in the box diagrams.

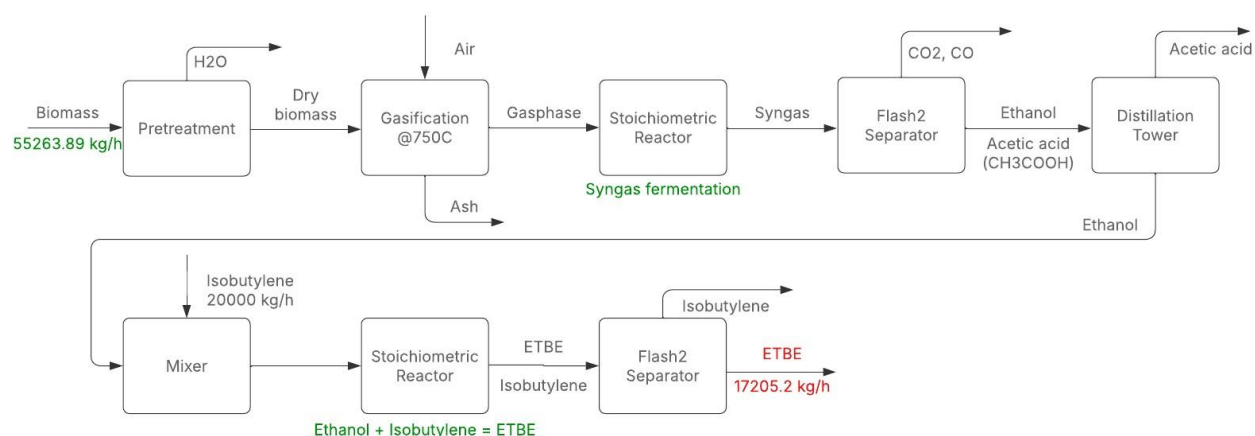
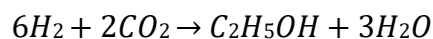
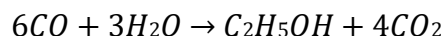
ETBE

Figure 2. Box diagram to produce ETBE

Up to the biomass gasification and syngas purification stage, the ETBE production process was similar to that of MTBE. However, instead of converting syngas to methanol, syngas fermentation was implemented in this refinery to produce ethanol.

Ethanol production from Syngas

The purified syngas was sent to a stoichiometric reactor, where ethanol production by gas fermentation was simulated.



The ethanol obtained was passed through a distillation column, where it was separated from by-products such as acetic acid, ensuring greater purity before conversion to ETBE.

One of the most innovative elements of this biorefinery was the production of ethanol without using agricultural crops, which avoids competition with food production and reduces pressure on agricultural ecosystems.

ETBE Synthesis and Purification

As in the production of MTBE, the synthesis of ETBE was carried out in a stoichiometric reactor, following the reaction.



ETBE

To complete the reaction, it was necessary to add an external flow of 20,000 kg/h of isobutylene, since this biorefinery did not implement the internal production of this compound.

Subsequently, the product passed through a Flash separator, where the excess isobutylene was removed, obtaining a final flow of 17,205.20 kg/h of ETBE.

Both biorefineries share the same biomass input and early process steps (pretreatment, gasification and syngas purification), but differ in their final conversion pathways. The aspects highlighted in green in the diagrams represent the key processes that optimized the conversion and sustainability of the system, such as syngas fermentation, internal isobutylene production and Fischer-Tropsch reactions. While the values highlighted in red indicate the final MTBE and ETBE production flows, representing the products of interest in each biorefinery.

2.1.2 Results

The simulation of MTBE production in AspenPlus® V.14 is shown below.

Activity 1. MTBE model in AspenPlus® V.14

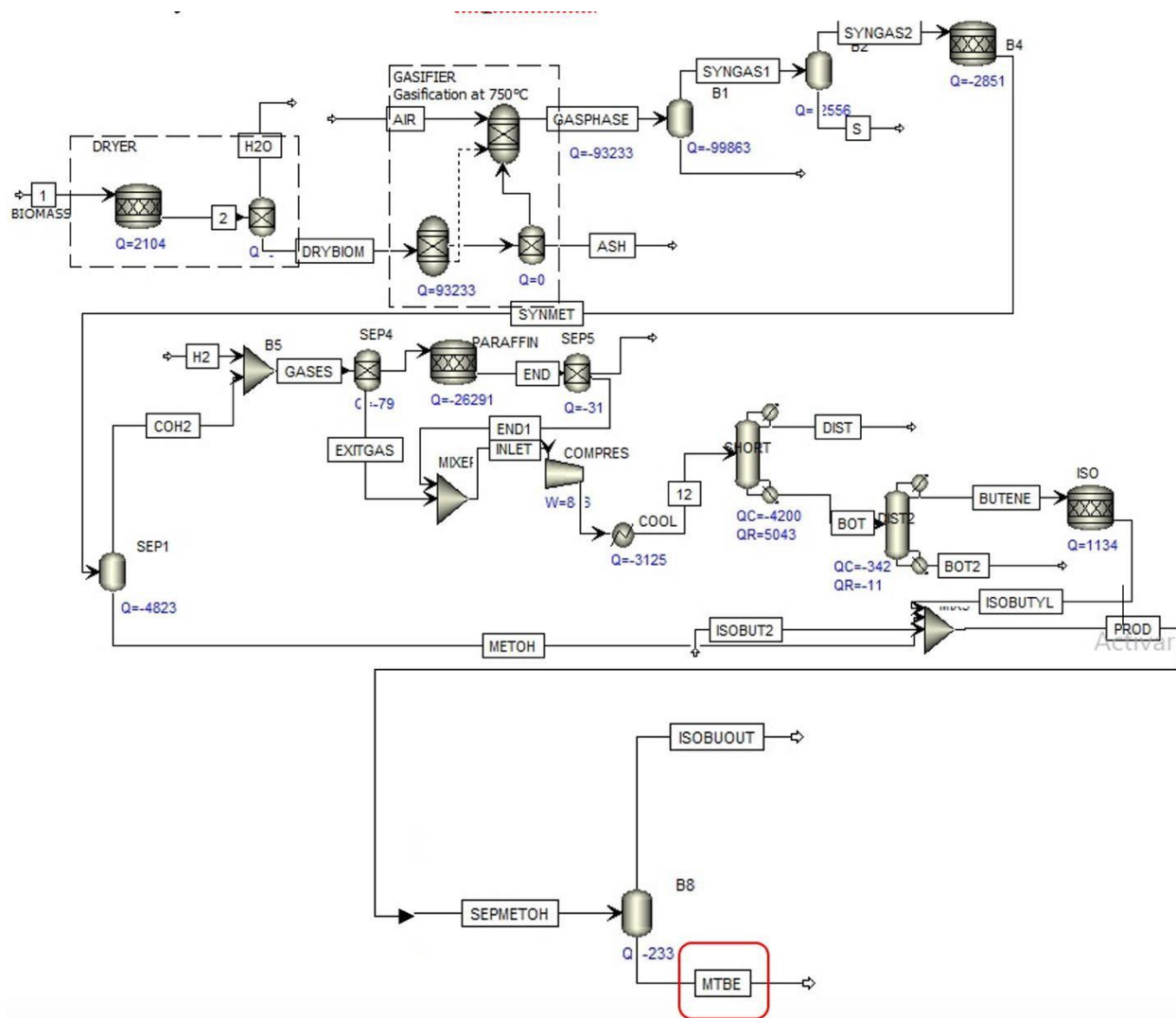


Figure 3. Model and simulation of MTBE production in AspenPlus® V.14.

The output conditions of pure MTBE are fundamental to guarantee its stability, commercial quality and compatibility with the fuel distribution infrastructure. Table 2 below shows the condition values obtained in the pure MTBE output.

Table 2. Exit conditions of pure MTBE

Temperature (C)	25.0
Pressure (bar)	1.0
Mass Vapor Fraction	0.0
Mass Liquid Fraction	1.0

Mass Solid Fraction	0.0
Mass Enthalpy (kJ/kg)	-3,442.14
Mass Density (gm/cc)	0.73
Enthalpy flow (kW)	-20,458.2

These values show that MTBE is obtained completely in liquid phase, with a density of $0.73 \frac{g}{cm^3}$, which confirms that it is in an optimal state for storage and distribution. Table 3 below shows the final composition values obtained in the flow of pure MTBE.

Table 3. Final Pure MTBE Flux Composition

	Mass flow (kg/h)	Molar fraction	Mass fraction
Methanol	1,050.2	0.11	0.049
Isobutylene	2,767.33	0.17	0.12
MTBE	1,7205.2	0.68	0.80

Although the final product still contains traces of methanol and isobutylene, its purity is 80.41% by mass, indicating a high process yield.

This design efficiently integrates biomass conversion, gasification, catalytic reactions and product separation processes, achieving the production of a biofuel with high purity and stability. The use of AspenPlus® V.14 as a simulation tool facilitated the evaluation of system performance, allowing adjustment of operating conditions to improve energy efficiency and reagent conversion.

2.1.3 MTBE Conclusions

The process designed in this biorefinery demonstrates an efficient conversion of biomass into MTBE, with a final production of $17,205.2 \frac{kg}{h}$, equivalent to an efficiency of **31.10%** in mass

with respect to the initial biomass ($55,263.9 \frac{kg}{h}$). Although this percentage might seem moderate,

the MTBE obtained has a high purity of 80.41%, which makes it a highly efficient additive to improve the quality of gasoline without requiring modifications in the fuel distribution infrastructure or in internal combustion engines.

One of the key achievements of this design is the partial production of isobutylene within the biorefinery by the isomerization of butane, which reduces the need to purchase this compound. Although the isobutylene generated was not sufficient to completely cover the reaction with methanol, having produced it locally reduced the dependence on external inputs, which is fundamental to the viability of the process. Furthermore, the production of kerosene and other light hydrocarbons in the Fischer-Tropsch reaction demonstrate that this biorefinery model not only focuses on the production of the main biofuels, but also on the efficient use of the co-products generated, which maximizes the value of the biomass processed.

This integrated and multifunctional approach not only strengthens the self-sufficiency of the process but also lays the groundwork for the economic and environmental analysis that will be developed in the following stages of the study. Evaluating the impact of co-products, their value and their potential to reduce operating costs will be key to determining the model's competitiveness against fossil fuel-based alternatives.

While the benefits are evident, large-scale implementation will depend on the availability of biomass, the stability of input supply and investment in infrastructure. In addition, it will be necessary to analyze the balance of emissions and environmental impact in the next stages of the research to assess its contribution to climate change mitigation and its competitiveness against other fuels.

The simulation of ETBE production in the AspenPlus® V.14 application is shown below.

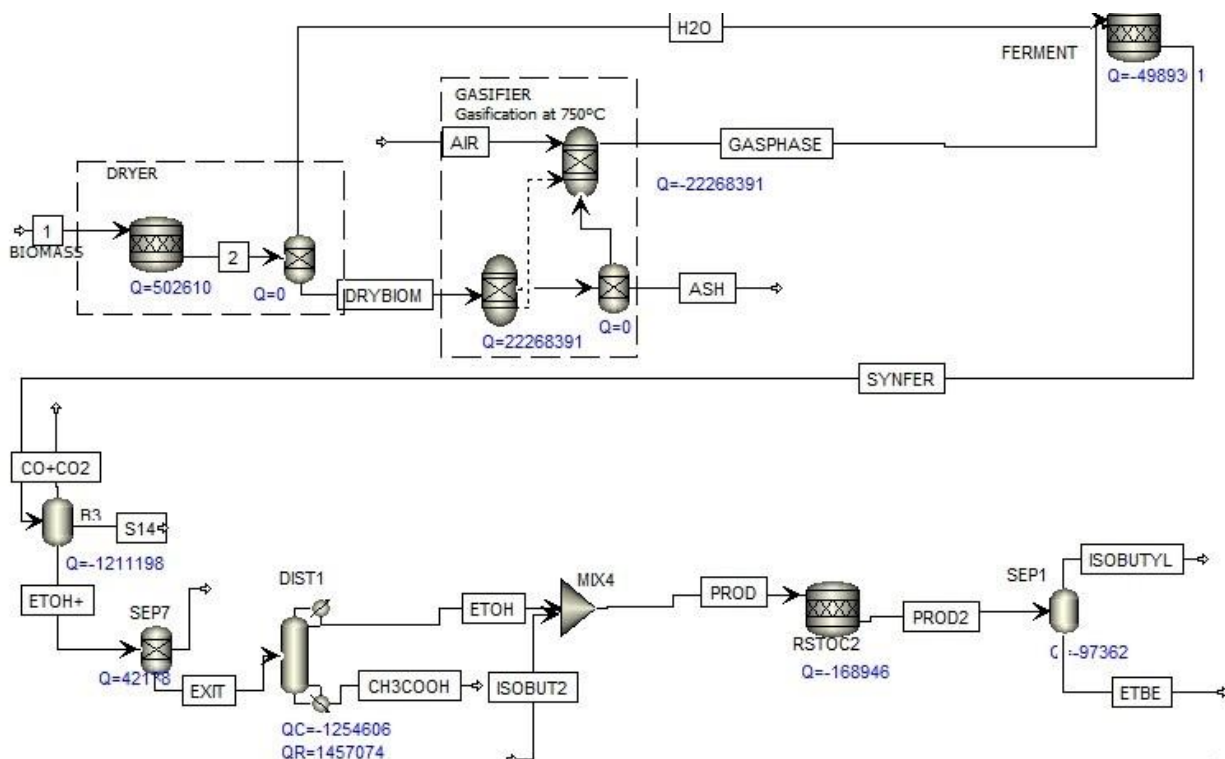


Figure 4. ETBE production model and simulation in AspenPlus® V.14.

Table 4. Exit conditions of pure ETBE

Temperature (°C)	25.00
Pressure (bar)	1.00
Mass Vapor Fraction	0.00
Mass Liquid Fraction	1.00
Mass Solid Fraction	0.00
Mass Enthalpy (kJ/kg)	-722.23
Mass Density (gm/cc)	0.71
Enthalpy flow (kW)	-5.32e+06

These values indicate that ETBE is obtained completely in liquid phase, with a density of

0.71 $\frac{g}{cm^3}$, which confirms its stability for storage and transport.

Table 5. Final Pure ETBE Flux Composition

	Flujo másico (kg/h)	Fracción molar	Fracción másica
Ethanol	2,118.6	0.14	0.079
Isobutilene	5,510.7	0.29	0.20
ETBE	18,879.0	0.56	0.71

Although the final product still contains traces of ethanol and isobutylene, its purity is 71,22% by mass, indicating a high process yield. The residual presence of ethanol and isobutylene could be reduced by additional purification steps, but process optimization in terms of conversion and energy efficiency was prioritized in this study.

2.1.4 ETBE Conclusions

ETBE production in this biorefinery reaches the value of 18,879.0 $\frac{kg}{h}$, which represents an efficiency of 34.16% by mass with respect to the initial biomass (5,263.9 $\frac{kg}{h}$). This conversion, slightly higher than that of MTBE, is largely due to the higher efficiency of the syngas fermentation process to obtain ethanol.

One of the most innovative aspects of this process is the production of ethanol from the fermentation of syngas, instead of using agricultural crops as feedstock, which represents a key advantage in terms of sustainability. In conventional ethanol production, crops such as sugarcane or corn are used, whose sugars are fermented to generate biofuels. However, this alternative generates competition with food production (Cui et al., 2022), which can increase the prices of agricultural products and put pressure on natural ecosystems.

In this case, ethanol is obtained from syngas, generated from lignocellulosic residues, avoiding the use of fertile agricultural land and maximizing the use of residual biomass. This approach not only reduces pressure on agricultural soils, but also optimizes the carbon cycle, avoiding the unnecessary release of CO₂ into the atmosphere and transforming it into a highenergy biofuel. Although the process requires the incorporation of external isobutylene of 20,000 *kg*—
the

h

integration of syngas fermentation with chemical conversion optimizes the use of available resources and improves energy independence. In addition, the chemical stability of ETBE allows it to be blended with gasoline without the phase separation problems that pure ethanol presents, which facilitates its implementation without the need to modify the fuel distribution infrastructure.

Despite its advantages, ETBE production from biomass requires specialized infrastructure for syngas handling and conversion to ethanol, which implies high initial costs and a rigorous assessment of biomass availability. These aspects will be analyzed in the following stages of the research, including a detailed study of the environmental impact and carbon balance in the production process.

2.1.5 Discussion

The results obtained show that the production of MTBE and ETBE from biomass represents two complementary approaches to the development of advanced biofuels. Both compounds have the advantage of being highly compatible with gasoline, improving its octane rating without generating phase separation problems or requiring modifications to the distribution infrastructure or internal combustion engines. Unlike pure ethanol, which in concentrations above 10-15% in blends with gasoline may require engine adjustments to avoid adverse combustion effects (Wang et al., 2022), MTBE and ETBE can be incorporated in significant proportions without

compromising engine performance or blend stability. This positions them as viable alternatives for the transition to more sustainable fuels, reducing dependence on petroleum without altering the operability of conventional vehicles.

In terms of mass efficiency, ETBE (34.16%) shows superior performance to MTBE (31.10%), largely due to the higher efficiency in converting syngas to ethanol compared to methanol production for MTBE. From a sustainability perspective, ETBE has a key advantage in using ethanol obtained from syngas fermentation, avoiding competition with agricultural crops and reducing pressure on food production. On the other hand, MTBE optimizes the internal production of isobutylene, reducing dependence on external inputs and improving the economic viability of the process.

In addition to mass efficiency, another relevant factor is the final purity of the product obtained. In this sense, MTBE reached a purity of 80.41% by mass, while ETBE had a purity of 71.22% by mass. This difference can be attributed to the nature of the synthesis and purification processes, where the conversion of methanol to MTBE in a stoichiometric reactor generates a purer product compared to the conversion of ethanol to ETBE, which has a higher fraction of residual impurities (unreacted ethanol and isobutylene). However, both biofuels reached purity levels suitable for use in gasoline blends, ensuring their efficiency and stability as oxygenated additives.

While the environmental and economic impacts of each biofuel require a more detailed assessment, this provides a solid basis for moving towards a more in-depth analysis. In conclusion, the production of MTBE and ETBE from biomass represents a viable strategy to diversify the country's energy matrix. While MTBE stands out for its integration with domestic isobutylene production, ETBE benefits from a more sustainable source of ethanol without requiring agricultural crops.

2.2 Objective 2: Evaluate the economic viability of the two biorefineries (MTBE and ETBE), through the estimation of investment costs, fixed and variable costs, cash flows, and calculation of the minimum sales price, in order to compare their competitiveness in the Ecuadorian market.

2.2.1 Methodology

Activity 1. Process simulation and mass and energy balance.

The first stage consisted of modeling the complete process in AspenPlus® V.14 software, which allowed establishing a detailed process flow, from the entry of raw materials to the production of ETBE in one simulation and MTBE in a different one. From the model, mass and energy balances were obtained for each process unit: biomass drying, gasification, fermentation for ETBE, kerosene production for MTBE, synthesis reaction, separation, and purification. These results allowed sizing the operating volumes of each equipment (reactors, mixers, separators, among others), fundamental information for subsequent capital investment calculations.

Activity 2. Estimate equipment acquisition and installation costs.

Once the required equipment was defined, the Equipment Acquisition Cost (EAC) was estimated. For this purpose, a technical database based on the publications of Guthrie (1969) and the updates of Slavsky and Klumpar (1985) was used. Each piece of equipment was compared with its equivalent in the cost table according to the type of technology and the corresponding unit of measurement (hp, ft³/min, etc.). The Unit Cost (\$) and Size Exponent fields were used to apply the scaling formula.

With the CEPCI (Chemical Engineering Plant Cost Index) values, the cost of each piece of equipment was updated to current values. Subsequently, direct investment costs were estimated by applying percentage factors on the costs of the main equipment, according to Miller's method, considering 1-Equipment not contemplated in the simulation, 2-Installation, foundations, piping,

insulation, electrical installations and instrumentation, and 3-Constructions, warehouses, utilities, catalysts, services and fees.

The Lang factor was used to estimate the total cost of installing an industrial plant. The value used was 3.50, to obtain the total direct costs, indirect investment costs, as well as contingencies of 13.00%, which resulted in a Total Capital Investment Cost.

Activity 3. Estimation of fixed operating costs

The biorefinery operation is planned for 350 days per year, with 24-hour shifts divided into 4 shifts, in order to adequately cover working days, breaks and possible unforeseen events. Based on the number and complexity of the equipment defined in the model, the human resources required to efficiently operate each version of the process were estimated: MTBE and ETBE.

To produce MTBE, the process requires a larger number of reactors and operating units, as shown in Table 6 below, in which a plant with a larger number of personnel was estimated. **Table 6. Staffing for MTBE biorefinery**

General Manager	1.0
Plant Manager	1.0
Laboratory Manager	1.0
Maintenance Supervisors	3.0
Process and Operation Engineers	24.0
Maintenance Technicians	5.0
Laboratory technicians	2.0
Plant operators	105.0
Human Resources	2.0
Catering Staff	5.0
Total	149.0

In contrast, the route for the production of ETBE involves less equipment. Table 7 below shows that it will operate with a smaller workforce.

Table 7. Staffing for the ETBE biorefinery

General Manager	1.0
Plant Manager	1.0
Laboratory Manager	1.0
Maintenance Supervisors	2.0
Process and Operation Engineers	12.0
Maintenance Technicians	3.0
Laboratory technicians	2.0
Plant operators	76.0
Human Resources	2.0
Catering Staff	4.0
Total	104.0

Salaries were estimated on an annual basis and include legal benefits and social security contributions (23.60%). These data were integrated into the basis for the fixed operating costs that will be reflected in the project's cash flow.

Activity 4. Variable cost estimation

Variable costs include all costs that fluctuate directly with the level of production and volume processed. In this project, for both MTBE and ETBE production, variable costs were determined from the quantities required by the process units modeled in AspenPlus® V.14 and the updated market prices of each input. The main inputs considered were:

- Sugar cane residue (main raw material, obtained from local distributors).
- Isobutylene as base reagents for the synthesis of the additive.
- Oxygen (O₂) and Hydrogen (H₂), used in the conversion and purification stage.
- Natural gas, used as a thermal energy source.
- Electricity, used for pumping, agitation, separation and compression.
- Maintenance and spare parts, calculated as an annual percentage of the value of the equipment installed.

The cost of each raw material was determined by multiplying the quantity required by its unit price obtained from updated sources. In all cases, consumption was normalized to an operating year of 350 days and 8,400 hours per year.

In the case of maintenance, 10.00% of the cost of equipment was considered as a general estimate to cover preventive and corrective services and minor spare parts.

In addition, the valorization of co-products was contemplated, which generates additional income that reduces the net impact of variable costs. For MTBE, the process allowed us to recover:

- Heavy kerosene waxes: sold at \$0.12/kg
- Light kerosene waxes: sold at \$0.26/kg
- Methanol: sold at \$0.52/kg
- Isobutylene: sold at \$1.20/kg

For ETBE, the process made it possible to recover

- Isobutylene: sold at \$1.20/kg
- Acetic acid: sold at \$0.60/kg
- Ethanol: sold at \$0.67/kg

Activity 5. Cash flow and calculation of Minimum Selling Price (MSP) Integrating the above data, a cash flow was constructed, considering:

- Initial investment (fixed capital).
- Annual operating costs (fixed and variable).
- Projected revenues from the sale of the final product (ETBE or MTBE) and co-products.
- Economic parameters: useful life of the project of 25 years, interest rate of 9.00%, operation and maintenance factor of 10%.

Based on the density of the final product and the projected volumes, the minimum sales price necessary to obtain a Net Present Value (NPV) equal to zero was estimated, ensuring a reasonable Internal Rate of Return (IRR) for the investment.

It should be noted that this analysis is contextualized in the reality of the Ecuadorian market: as of February 12, 2025, the price of Extra and Ecopaís gasoline is \$2.71 per gallon (El Comercio, 2025) and Super gasoline costs \$3.48 per gallon, which establishes an important competitive reference for the evaluation of the final product and its commercial viability.

2.2.2 Results

Activity 1. MTBE Biorefinery

This study evaluated the economic and technical feasibility of a biorefinery oriented to the production of MTBE from sugarcane residues. Based on process simulations, cost estimates and financial projections, the main economic indicators associated with this technological route are shown in Table 8.

Table 8. Initial investment cost for MTBE biorefinery

Concept	Cost (USD)
Direct investment cost	3,949,511.1
Indirect investment cost	2,369,706.6
Contingencies (13%)	513,436.4
Total investment cost	6,832,654.2

From the investment point of view, the project requires significant capital for its start-up. The sum of direct investment costs, those related to the acquisition and installation of the main equipment, amount to USD 3,949,511.1. To this value are added the indirect costs related to engineering, general services, instrumentation, civil works and other complementary items, for a total of USD 2,369,706.6. Finally, a 13% contingency is incorporated to cover possible unforeseen events during construction and start-up, resulting in an additional cost of USD 513,436.4. The total investment cost, therefore, amounts to USD 6,832,654.2.

Table 9 below shows the operational stage of the MTBE process. Variable costs, including raw materials such as sugar cane residue, isobutylene, oxygen, hydrogen, energy and maintenance, were estimated at USD 1.99 per kilogram of product. It is important to note that the process generates valuable co-products, including heavy and light kerosene, whose income partially offsets the costs, generating a return of approximately USD \$0.98 per kilogram of final product. The projected cash flow for the 25-year useful life reveals that the initial investment is recovered at the end of the tenth year of operation, a reasonable figure for medium-scale industrial projects. **Table 9. Variable and fixed costs MTBE biorefinery**

Concept	Value
Variable unit cost (\$/kg)	1.99
Income from co-products (\$/kg)	0.98
Fixed operating costs	\$5,396,553.31
Equivalent annual investment	\$5,550,630.03
Plant life (years)	25.0
Working days per year	350.0
Last year with negative cash flow	10.0

Fixed operating costs correspond to all those expenses that are constant over time, regardless of the level of production. These mainly include personnel payroll (salaries, social security), administrative services, fixed maintenance, insurance, environmental management and monitoring. The estimate for this project is USD 5,396,553.3 per year, considering a personnel structure distributed in rotating shifts to operate 350 days per year.

The annual equivalent investment represents the annualized value of the total project investment, calculated based on the expected useful life of the plant (25 years) and an interest rate of 9.00%. This indicator is essential to compare recurring operating expenses with the financial impact of the initial capital invested. In this case, the annual equivalent investment was estimated at USD 5,550,630.0. Table 10 below shows MTBE's Minimum Sales Price.

Table 10. MSP of MTBE

Minimum Selling Price Pure MTBE (\$/kg)	1.05
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Minimum Selling Price Pure MTBE (\$/gal)	2.90
Minimum Selling Price Blend A (70 Extra + 30 MTBE)	2.77

From a market point of view, the estimated minimum selling price for pure MTBE is USD \$2.89 per gallon. This value allows us to calculate the price of a gasoline blend containing 30% MTBE and 70.00% extra gasoline, which results in a final price of USD \$2.77 per gallon. This figure becomes relevant when compared to current prices in the Ecuadorian market: Extra gasoline has a value of USD \$2.71 per gallon, while Super gasoline reaches USD \$3.48 per gallon. The proposed blend is positioned as a competitive alternative that, without reaching the price of economic gasoline, offers an intermediate value with potential environmental benefits.

2.2.3 MTBE Conclusions

In the production of MTBE (Methyl Tertiary Butyl Ether) from sugar cane residues, the simulation in AspenPlus® V.14 allowed establishing mass and energy balances, sizing the equipment and estimating the technical and economic requirements. Based on the methodology described above, it was determined that the total investment required amounts to USD \$6,832,654.2. At the operating level, variable costs average \$1.99 USD per kilogram of MTBE, reflecting raw material expenses (sugarcane residue, isobutylene, oxygen, hydrogen), thermal and electrical energy, and maintenance proportional to production. The existence of co-products with market value, including light and heavy kerosene, methanol and recovered isobutylene, reports revenues close to USD \$0.98/kg, which partially reduces the impact of variable costs. On the other hand, the plant's fixed operating costs, based on personnel, insurance, administrative expenses and other invariable costs, amount to USD \$5,396,553.3 per year.

The financial evaluation over a 25-year horizon and an interest rate of 9% show that the investment has recovered around year 10 of operation, which is considered an acceptable period for projects of this magnitude in the industrial sector. The cash flow confirms the viability of the plant, especially when analyzing the minimum sales price (MSP) necessary to cover all costs. For pure MTBE, this price was estimated at \$2.90 USD/gal. As a result, the blend of 70.00% extra gasoline and 30.00% MTBE achieves a value of \$2.77 USD/gal, competitive in the Ecuadorian market by positioning itself below the price of Super gasoline (\$3.48 USD/gal) and slightly above Extra gasoline (\$2.71 USD/gal).

Based on the above, it is concluded that the MTBE biorefinery shows a favorable economic performance when compared to the price range of the local market. Although the volume of personnel and the amount of equipment required are higher than in other technological routes, the possibility of commercializing various co-products contributes substantially to balance the variable costs. The 10-year payback period is evidence that the proposal is feasible at the scale of production analyzed, if market assumptions and raw material supplies are maintained at similar levels to those estimated.

Activity 2. ETBE Biorefinery

This evaluation corresponds to the techno-economic analysis of a plant for the production of ETBE using sugar cane residues as raw material. Through the simulation of the process, the estimation of costs and the projection of financial indicators. Table 11 shows an integral vision of the viability of this production route.

Table 11. Initial investment cost of ETBE biorefinery

Concept	Cost (USD)
Direct investment cost	2,984,188.0
Indirect investment cost	1,790,512.8
Contingencies (13.00%)	387,944.4

Total investment cost	5,162,645.3
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The investment analysis reveals that the ETBE plant has a total capital requirement of USD \$5,162,645.3. Direct investment costs amount to USD \$2,984,188.0, with additional USD \$1,790,512.8 in indirect costs and USD \$387,944.4 for contingencies (13.00%).

During the operational phase, the unit variable cost for ETBE production is estimated at USD \$2.00 per kilogram. This value contemplates the acquisition of raw materials (sugar cane residue, ethanol, oxygen, thermal and electrical energy), in addition to proportional maintenance costs. Unlike the MTBE process, ETBE production generates fewer valuable co-products, with estimated income of only USD \$0.48 per kilogram, which directly affects the profitability margin of the process. Table 12 below shows the operating stage of the ETBE process.

Table 12. Variable and fixed costs of ETBE biorefinery

Concept	Value
Variable unit cost (\$/kg)	2.00
Income from co-products (\$/kg)	0.48
Fixed operating costs	\$ 3,714,293.3
Equivalent annual investment	\$ 5,550,630.0
Plant life (years)	25
Working days per year	350
Last year with negative cash flow	10

The cash flow analysis indicates that the initial investment is also recovered at the end of the tenth year of operation. However, the lower co-product valorization and the higher total investment cost imply that the profitability margin of the ETBE process is more limited compared to MTBE. Table 13 below shows the minimum selling price of ETBE.

Table 13. MSP of ETBE

Minimum Selling Price Pure MTBE (\$/kg)	1,54
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Minimum Selling Price Pure MTBE (\$/gal)	4,14
Minimum Selling Price Blend B (70% Extra + 30% MTBE)	3,14

From the commercial point of view, the minimum sales price for pure ETBE was calculated at USD \$1.54 per kilogram, which corresponds to USD \$4.14 per gallon. In a blend with extra gasoline in a 70/30 proportion, the final price would be USD \$3.14 per gallon, placing it between extra gasoline (USD \$2.71/gal) and Super gasoline (USD \$3.48/gal).

2.2.4 ETBE Conclusions

The ETBE production route was also based on the conversion of sugar cane residues, but with slightly different process requirements and plant configuration than MTBE. From the simulation and cost estimation, it was determined that the total initial investment for this plant amounts to USD \$5,162,645.3. Although these values imply a lower outlay than that of the MTBE plant, the variable costs reach USD \$2.00 per kilogram of ETBE, influenced by the purchase of ethanol, oxygen, thermal and electrical energy, and proportional maintenance. In addition, recoverable co-products, mainly isobutylene, acetic acid and ethanol, generate revenues of \$0.48 USD/kg, which is substantially lower than the figure obtained in the case of MTBE.

The cash flow evaluation, established in the same 25-year horizon and with the same discount rate of 9.00%, shows a recovery of the investment also around year 10. However, due to the lower valorization of co-products and the higher variable cost, the minimum sales price (MSP) of pure ETBE amounts to \$4.14 USD/gal. When formulating a blend of 70.00% extra gasoline and 30.00% ETBE, the value is \$3.14 USD/gal, intermediate between Extra and Super gasoline.

In light of these results, it is concluded that the ETBE biorefinery is characterized by lower total investment and operational complexity; however, the combination of high variable cost and less significant co-product revenues increases the minimum necessary to achieve the desired profitability.

2.2.5 Discussion

The comparison between the two biorefineries evaluated (MTBE and ETBE), developed under the same methodological framework, shows that both routes can be positioned as intermediate alternatives between the fuels currently available in the Ecuadorian market, specifically between Extra gasoline, EcoPaís (\$2.71 USD/gal) and Super gasoline (\$3.48 USD/gal). However, Figure 5 shows the differences in the minimum sales prices of both the pure additive and the blends with Extra gasoline, revealing important nuances in their technical and economic competitiveness, directly linked to their cost structure and the valorization of co-products generated in each process.

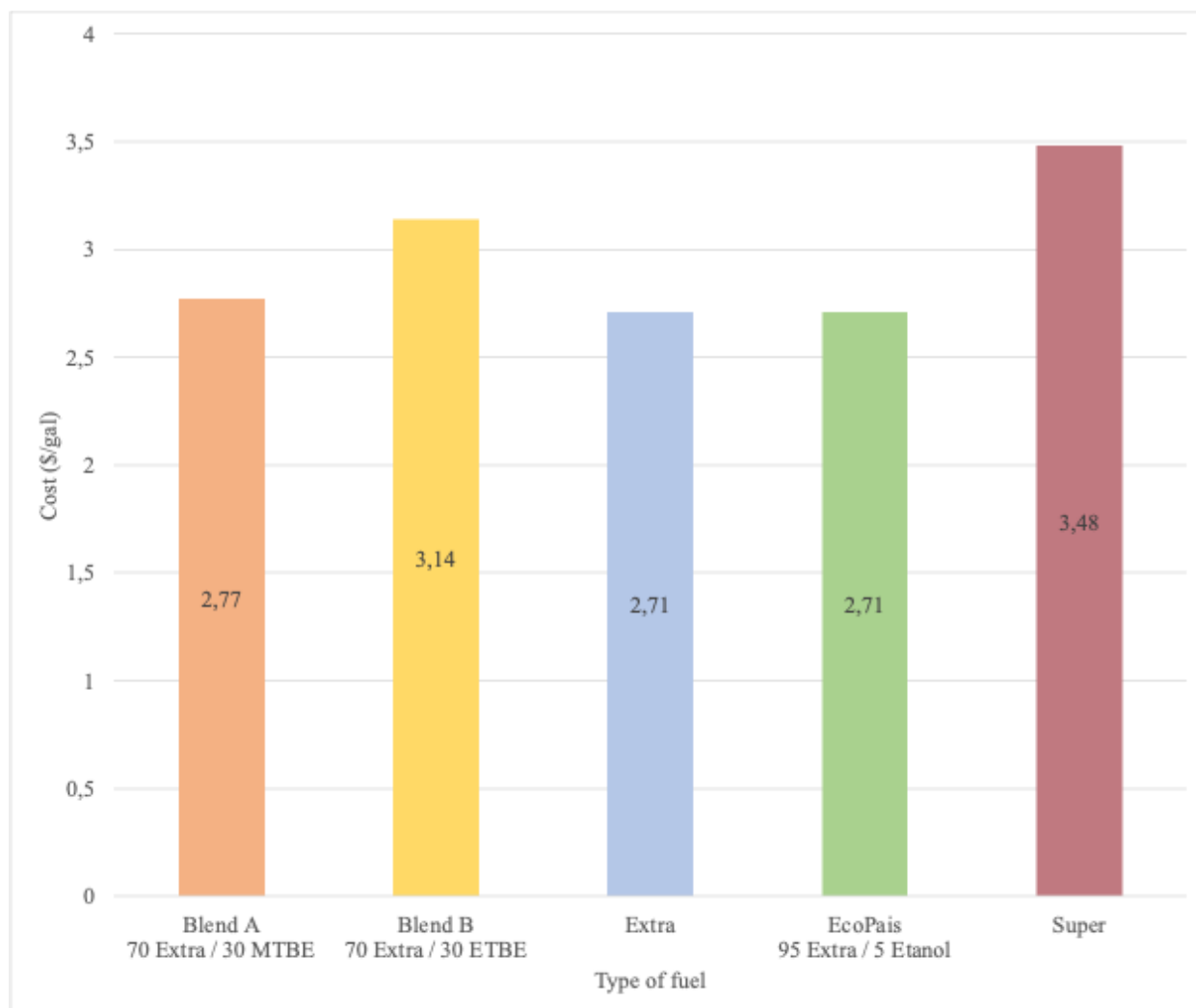


Figure 5. Comparison of the cost per gallon of the different fuels and blends evaluated.

In the case of MTBE production, the minimum selling price of the pure additive is 2.90 USD/gal (1.05 USD/kg). When formulating blend A (70.00% Extra gasoline and 30.00% MTBE), a final cost of 2.77 USD/gal is obtained, just 0.06 USD above the price of Extra and EcoPaís gasoline (2.71 USD/gal), and considerably below Super gasoline (3.48 USD/gal). This implies that, despite a higher initial investment and the need for a larger staff, this blend is a technically and economically attractive alternative. Its competitiveness is mainly due to the valorization of co-products generated during the process, such as light and heavy kerosenes, methanol and

isobutylene, which contribute an additional income of US\$0.98/kg that considerably reduces net operating costs. In addition, isobutylene is partially produced within the plant, which reduces external dependence on this key input.

In contrast, ETBE production is based on the internal generation of ethanol from syngas fermentation, which represents a strategic advantage by eliminating dependence on commercial or imported ethanol. However, the valorization of co-products in this route is more limited, reaching only 0.48 USD/kg. The minimum selling price of pure ETBE was estimated at 4.14 USD/gal (1.54 USD/kg), and when formulating blend B (70.00% Extra gasoline and 30.00% ETBE), the final price amounts to 3.14 USD/gal. This figure places it 0.43 USD above Extra and EcoPaís gasoline, and only 0.34 USD below Super. Its cost makes it a less accessible market segment for the average consumer, if there are no policies to encourage or subsidize its consumption.

An additional element to be highlighted is the comparison with EcoPaís gasoline, currently available in Ecuador as a blend of 95.00% Extra gasoline and 5.00% ethanol. Although it is promoted as a cleaner and renewable fuel, its implementation faces a geographical limitation: ethanol is highly volatile and cannot be used in cities located in the Ecuadorian Sierra region, such as Quito or Cuenca due to their altitudes. Therefore, its distribution is mainly restricted to the coastal region. In this context, both MTBE and ETBE represent more stable oxygenated alternatives, suitable for distribution and use throughout the national territory. Unlike ethanol, they do not present the same vapor pressure challenges or risk of vapor formation in high altitude conditions, which gives them an important logistical advantage.

In addition to cost analysis, it is essential to evaluate whether the proposed blends maintain or improve fuel quality in terms of performance. One of the most relevant indicators in this regard is the Research Octane Number (RON), which measures the fuel's resistance to premature

detonation inside the engine. A higher-octane number allows for better performance in high-compression engines and improves the vehicle's energy efficiency.

In Ecuador, Extra and EcoPaís gasoline are the fuels of mass use and have an average octane rating of 87.0 RON, while Super gasoline reaches between 92.0 and 95.0 RON, depending on the formulation and supplier (Mirabella, 2003).

The oxygenated additives MTBE and ETBE were designed, among other functions, to improve fuel octane. Several studies report that each 10.00% by volume of MTBE can increase between 2 and 3 units of RON, while ETBE, in the same proportion, raises octane between 1.70 and 2.70 units (Mirabella, 2003).

In this project, blends formulated with 30.00% of additive and 70.00% of Extra gasoline were evaluated. From this data, the RON of each blend is estimated using the following approximate linear relationship.

$$RON_{mix} = (\%Extra) * RON_{Extra} + (\%Additive) * RON_{Additive}$$

Since Extra gasoline has a RON of 87.0 and considering a range of RON for the additives (based on experimental data and technical literature), the final octane rating of each blend can be estimated by applying the equation for a 70/30 blend. Table 14 below shows the estimated octane number of different gasolines.

$$RON_{MTBE} = (0.70) * 87.0 + (0.30) * 115.0 = 95.40$$

$$RON_{ETBE} = (0.70) * 87.0 + (0.30) * 113.0 = 94.80$$

Table 14. Estimated octane number (RON) of different gasolines.

Gasolines	Estimated octane rating (RON)
Blend A (70.00% Extra + 30.00% MTBE)	95.40
Blend B (70.00% Extra + 30.00% ETBE)	94.80
Extra	87.00

EcoPaís	88.00
Súper	93.00

These results show that they offer a performance equivalent to that of Super gasoline, which implies that they could be used as a direct substitute for high-octane fuels without compromising engine performance. From a technical perspective, both blends A and B are far superior in quality to Extra and EcoPaís gasoline, reaching octane values above 94.00 RON, comparable to those of the highest quality gasoline in the country. Overall, these results reinforce the relevance of the techno-economic analysis developed, by demonstrating that the proposals not only maintain, but also improve the technical standard of current fuels, positioning themselves as sustainable alternatives that include both economic and environmental advantages. Figure 6 below shows the octane rating and price of different fuels.

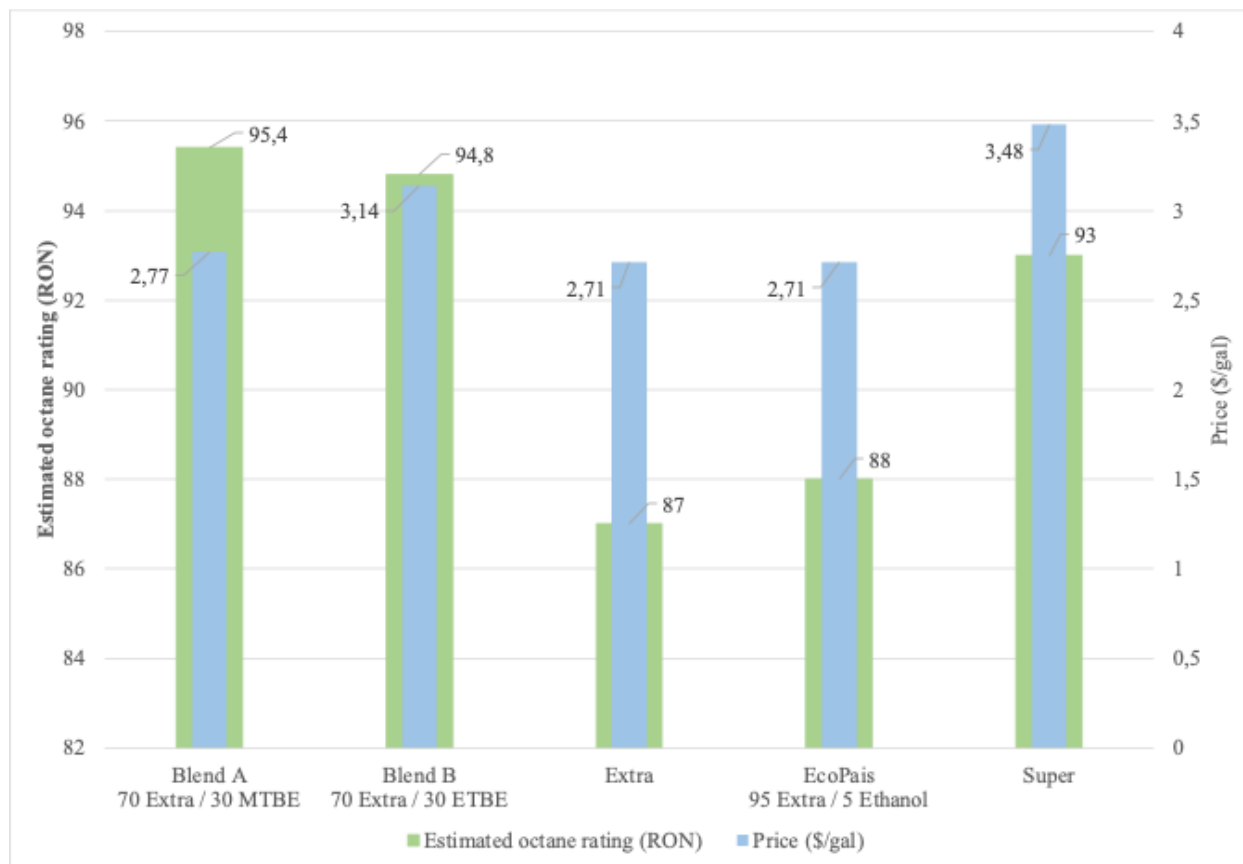


Figure 6. Octane rating and price of different fuels

The graph clearly illustrates the double advantage of blends A and B in terms of quality price. Blend A achieves the highest estimated octane rating (95.40 RON), surpassing even Super gasoline (93.00 RON), but with a price of only 2.77 USD/gal, positioning it as the most efficient option in terms of yield per dollar invested. Blend B (ETBE) also exhibits a high-octane rating (94.80 RON), higher than EcoPaís and Extra, and very close to Super, but with an intermediate price of 3.14 USD/gal. In contrast, both EcoPaís and Extra have low octane ratings (88.00 and 87.00 RON respectively), although their price is competitive their performance is limited in more demanding engines. Super gasoline, while offering good octane, has the highest price in the market (3.48 USD/gal), which makes it less accessible to many consumers. Overall, this graph visually confirms that blends A and B not only offer equal or superior performance to the highest quality

gasoline available, but do so at a lower cost, thus strengthening their proposal as sustainable, efficient and economically competitive alternatives for the Ecuadorian market.

It is crucial to highlight the role of co-products in this competitiveness. As shown in Table 15, the value of by-products has a direct impact on the final price of blends. In the case of blend A (70 Extra gasoline + 30MTBE), the final price with co-products reaches 2.77 USD/gal, while, without considering the income from co-products, the value amounts to 3.55 USD/gal. Similarly, for blend B (70 Extra + 30 ETBE), the price with co-products is 3.14 USD/gal, but without coproducts it rises to 3.50 USD/gal.

Table 15. Price of blends considering the sale of co-products generated and without considering.

Blend	With coproducts (USD/gal)	Without coproductos (USD/gal)
Blend A (70 Extra + 30 MTBE)	2.77	3.55
Blend B (70 Extra + 30 ETBE)	3.14	3.50

This difference is explained by the magnitude and valorization of the co-products. The MTBE route generates more coproducts with higher market value (heavy and light kerosene, methanol and isobutylene), which significantly offsets the variable costs of the process. On the other hand, the ETBE route, although it also generates co-products (acetic acid, ethanol and isobutylene), does so in smaller quantities and with a lower selling price. Thus, when coproduct revenues are eliminated, both blends are considerably closer: 3.55 USD/gal (MTBE) versus 3.50 USD/gal (ETBE), with a difference of only five cents. This shows that the cost advantage of MTBE is strongly conditioned to the existence of a market that efficiently values and absorbs these by-products. If market or logistical conditions prevent its commercialization, blend A would lose its economic advantage, causing it to reach the same level as blend B.

This confirms that co-products are not only a by-product of the process, but rather a key part of the biorefinery's financial model. Their proper management, valorization and sale are determining factors in maintaining the economic viability and competitiveness of oxygenated additives compared to conventional fuels.

Finally, both routes present an investment recovery horizon close to the tenth year, which suggests that, in terms of financial maturity, both options are viable in the long term. However, from an economic point of view, MTBE has better cost and final sale price indicators. The choice between one or the other technology will have to consider financial factors in conjunction with national sustainability objectives, the absorption capacity of the market for co-products, the existing industrial infrastructure and the regulatory framework in force.

2.3 Objective 3: Conduct a greenhouse gas (GHG) emissions inventory for the production and use stages of MTBE and ETBE biofuels and compare their environmental performance.

2.3.1 Methodology

Activity 1. Scope Justification

Although GHG emissions can be generated at multiple stages of a biofuel's life cycle (such as feedstock extraction, transportation, production, distribution, end use and disposal), in this study we focus exclusively on the production and use phases. This delimitation responds to two main reasons:

- Availability of accurate and modeled data: Thanks to simulations in AspenPlus® V.14, it was possible to accurately quantify the energy consumption of each stage of the process, allowing a more precise estimation of emissions in the production phase.
- Direct environmental relevance: The biofuel use stage represents the highest point of carbon release into the atmosphere. Analyzing this stage is essential to measure the environmental impact compared to the use of conventional gasoline.

Activity 2. ISO 14067-1 Standard

The methodology is based on the guidelines of ISO 14067-1, where the following formula is used to quantify emissions.

$$Emissions_{GHG} = Activity \times Emission\ Factor$$

In addition, a 20% thermal efficiency correction is considered, multiplying the energy consumption by 1.20 to reflect system losses.

Activity 3. Calculation of emissions during production

Step 1: Extract data from the AspenPlus® V.14 model

- Liquefied Petroleum Gas (LPG) consumption: sum of all positive heat fluxes ($Q > 0$)
- Electricity consumption: sum of all positive works ($W > 0$)

Step 2: Apply loss correction

Multiply each energy consumption by 1.20 (additional 20%).

Step 3: Calculation of emissions

$$Emissions_{Production} = (LPG \times 1.20 \times EF_{LPG}) + (Electricity \times 1.20 \times EF_{Electricity})$$

Emission factors used:

- FE of LPG: 0.22 kg CO₂eq/kWh (Ministerio de Energía, 2023).

- FE of electricity in Ecuador: National electricity generation factor for 2023, statistics show the following Emission Factor: 0.12 kg CO₂eq/kWh (Ministerio de Energía, 2023).

Activity 4. Calculation of emissions during use

Step 1: Calculate the total energy produced by each biofuel.

$$Total\ Energy = Mass\ produced \times Lower\ Heating\ Value_{biofuel}$$

Lower Heating Values used:

- LHV MTBE: 33,000 kJ/kg
- LHV ETBE: 36,000 kJ/kg

Step 2: Calculate Biofuel Emission Factor

$$EF_{biofuel} = \frac{Emissions_{Production}}{Total\ energy}$$

Activity 5. Calculation of mixed fuel emissions

A fuel mixture scenario was evaluated, consisting of 70.00% of extra gasoline and 30.00% of biofuel. In this context, the annual mass produced of biofuel, which represents 30.00% by weight of the total blend, is used as a starting point. From this information, both the total mass of the blended fuel and the mass of Extra gasoline needed to make up the remaining 70.00% are determined.

$$Mass_{Extra} = \frac{Mass_{biofuel}}{0.30} \times 0.70$$

With these masses determined, the total emissions of the mixture are calculated considering the energy delivered by each component (mass divided by LHV) and its respective emission factors.

$$Emissions_{Blend} = \left[\left(\frac{Mass_{biofuel}}{LHV_{biofuel}} \right) \times EF_{biofuel} \right] + \left[\left(\frac{Mass_{Extra}}{LHV_{Extra}} \right) \times EF_{Extra} \right]$$

It is assumed that the mass of MTBE is 30% of the total and the mass of Extra, which is 70%, has already been calculated.

2.3.2 Results

Activity 1. MTBE Emissions Inventory

Production

GHG emissions associated with the MTBE production phase were calculated using energy data simulated in AspenPlus® V.14.

$$Consumption_{LPG} = \sum Q = 110,070 \frac{kW}{h}$$

$$Consumption_{Electricity} = \sum w = 846 \frac{kW}{h}$$

An additional 20.00% will be applied for energy losses during production (thermal efficiency correction). For this, each energy consumption is multiplied by 1.20.

$$Emissions_{Production MTBE} = (LPG \times 1.20 \times EF_{LPG}) + (Electricity \times 1.20 \times EF_{Electricity})$$

$$Emissions_{Production MTBE}$$

$$= (110,070 \frac{kW}{h} \times 1.20 \times 0.22 \frac{kg CO_2eq}{kWh}) + (846 \frac{kW}{h} \times 1.20 \times 0.12 \frac{kg CO_2eq}{kWh}) h$$

$$Emissions_{Production MTBE} = 30,126.03 \frac{kg CO_2eq}{h}$$

$$Emissions_{Production MTBE} = 253,058,610 \frac{kg CO_2eq}{year}$$

Emission factors (EF) for LPG and for domestic electricity generation were obtained from literature.

Use

The total energy produced by MTBE is calculated, considering its hourly mass and the lower heating value (LHV) obtained from literature.

$$Total\ Energy_{MTBE} = Mass_{MTBE} \times LHV_{MTBE}$$

$$Total\ Energy_{MTBE} = 18,879\ kg/h \times 33,000\ kJ/kg$$

$$Total\ Energy_{MTBE} = 623,007,000\ kJ/h$$

$$Mass\ MTBE = 18,879\ kg/h$$

$$LHV_{MTBE} = 33,000\ kJ/kg\ \text{conversion}\ 9.17\ kWh/kg\ (\text{The Engineering Toolbox, 2003})$$

The MTBE biofuel Emission Factor is then calculated.

$$EF_{MTBE} = \frac{Emissions_{Production\ MTBE}}{Total\ Energy_{MTBE}}$$

$$EF_{MTBE} = \frac{\frac{30,126.02\ kg\ CO_2eq}{h}}{623,007,000\ kJ/h}$$

$$EF_{MTBE} = 4.84 \times 10^{-5} \frac{kg\ CO_2eq}{kJ}$$

A mixture made up of 30.00% by mass of MTBE and 70.00% of Extra gasoline was evaluated. For this purpose, the previously calculated values are used, together with the calorific value and emission factor of each component. We start from the annual mass produced of MTBE and determine the mass of Extra gasoline necessary to complete the remaining 70.00%.

$$Mass_{Extra} = \frac{Mass_{MTBE}}{0.30} \times 0.70$$

$$Mass_{Extra} = 351,674.28\ t/year$$

Both the total mass of the mixed fuel and the total mass of the mixed fuel are determined.

$$Mass_{Blend\ A} = Mass_{MTBE} + Mass_{Extra}$$

$$Mass_{Blend\ A} = 502,391.83\ t/year$$

With these masses determined, the total emissions of the mixture are calculated considering the energy delivered by each component (mass divided by LHV) and its respective emission factors.

$$Emissions_{Blend A} = \left[\left(\frac{Mass_{MTBE}}{LHV_{MTBE}} \right) * FE_{MTBE} \right] + \left[\left(\frac{Mass_{Extra}}{LHV_{Extra}} \right) * FE_{Extra} \right]$$

$$Emissions_{Blend A} = \left[\left(\frac{18,879 \text{ kg/h}}{9.17 \text{ kWh/kg}} \right) * 0.17 \frac{\text{kg CO}_2\text{eq}}{\text{kWh}} \right] + \left[\left(\frac{40,144.73 \text{ kg/h}}{12.08 \text{ kWh/kg}} \right) * 0.26 \frac{\text{kg CO}_2\text{eq}}{\text{kWh}} \right]$$

$$Emissions_{Blend A} = 1,222.44 \frac{\text{kg CO}_2\text{eq}}{\text{h}}$$

$$\text{Extra Emission Factor} = 0.26 \frac{\text{kg CO}_2\text{eq}}{\text{kWh}}$$

Lower Calorific Value of Extra= 43,500 kJ/kg conversion 12.08 kWh/kg (RACE, 2023).

2.3.3 MTBE Conclusions

Although MTBE has been promoted as a cleaner additive compared to traditional fossil fuels, the results of this study show that its production and use still imply a significant environmental footprint. Blend A (30.00% MTBE and 70.00% Extra gasoline) presented total emissions of 1,071,968 kg CO₂ equivalent per year, with an hourly rate of 1,222.44 kg CO₂eq/h. This magnitude of emissions is mainly explained by the high thermal consumption during production, which relies heavily on the use of liquefied petroleum gas (LPG), a fossil source that contributes considerably to the total greenhouse gases generated.

Although MTBE can be obtained from renewable feedstocks, the synthesis process involves operations with high energy demands, such as separation, purification and chemical reaction, which are currently supplied by fossil thermal energy and grid electricity. This shows that a biofuel does not automatically guarantee a low carbon footprint if its production chain is not energy optimized.

To mitigate these emissions, it is a priority to progressively replace LPG with renewable thermal sources such as biomass or biogas generated on-site from waste. In addition, integrating

electricity from photovoltaic or wind power systems would reduce indirect operating emissions. Other complementary strategies include improving plant energy efficiency through heat recovery, insulation of critical lines and process control automation.

Activity 2. ETBE Emissions Inventory

Production

As with MTBE, GHG emissions associated with the ETBE production phase were calculated using energy data simulated in AspenPlus® V.14.

$$Consumption_{LPG} = \sum Q = 101,615 \frac{kW}{h}$$

$$Consumption_{Electricity} = \sum w = 0$$

An additional 20.00% will be applied for energy losses during production (thermal efficiency correction) by multiplying each energy consumption by 1.20.

$$Emission_{Production ETBE} = (LPG \times 1.20 \times EF_{LPG}) + (Electricity \times 1.20 \times EF_{Electricity})$$

$$Emission_{Production ETBE} = (101,615 \frac{kW}{h} \times 1.20 \times 0,22 \frac{kg}{kW CO_2eq}) + (0 \times 1.20 \times 0.12 \frac{kg}{kW CO_2eq})$$

$$Emission_{Production ETBE} = 27,699.44 \frac{kg CO_2eq}{h}$$

Emission factors (EF) for liquefied petroleum gas (LPG) and for domestic electricity generation were obtained from literature.

Use

Subsequently, the useful energy provided by the ETBE was estimated, based on its mass produced and its lower calorific value, to determine its emission factor per unit of energy.

$$Total Energy_{ETBE} = Mass_{ETBE} \times LHV_{ETBE}$$

$$Total Energy_{ETBE} = 17,205.2 \frac{kg}{h} \times 36,000 \text{ kJ/kg}$$

$$Total\ Energy_{ETBE} = 619,387,200\ kJ/h$$

Lower Heating Value obtained from literature.

$$Mass\ ETBE = 17205.2\ kg/h$$

$$LHV_{ETBE} = 36000\ kJ/kg$$

The ETBE biofuel Emission Factor is calculated.

$$EF_{ETBE} = \frac{Emissions_{Production\ ETBE}}{Total\ Energy_{ETBE}}$$

$$EF_{ETBE} = \frac{27,699.44\ \frac{kg\ CO_2eq}{h}}{619,387,200\ kJ/h}$$

$$EF_{ETBE} = 4.47 \times 10^{-5}\ \frac{kg\ CO_2eq}{kJ}$$

As in the previous case, the 30/70 blend is simulated with Extra gasoline, obtaining the hourly emissions from the specific emission factors and the energy content of each component. It is divided from the annual mass produced of ETBE and the mass of Extra gasoline necessary to complete the remaining 70.00% is determined.

$$Mass_{Extra} = \frac{Mass_{ETBE}}{0.30} \times 0.70$$

$$Mass_{Extra} = 385,886.76\ t/year$$

The total mass of the mixed fuel is therefore determined.

$$Mass_{Blend\ B} = Mass_{ETBE} + Mass_{Extra}$$

$$Mass_{Blend\ B} = 551,266.80\ t/year$$

With these masses determined, the total emissions of the mixture are calculated considering the energy delivered by each component (mass divided by PCI) and its respective emission factor.

$$Mass_{ETBE}$$

$$Mass_{Extra}$$

$$Emission_{SBlend B} = [(\frac{\quad}{LHV_{ETBE}}) * EF_{ETBE}] + [(\frac{\quad}{LHV_{Extra}}) * EF_{Extra}]$$

$$Emission_{SBlend B}$$

$$= [(\frac{17,205.2 \text{ kg/h}}{10 \text{ kWh/kg}}) * 0.16 \text{ kg} \frac{\text{CO}_2\text{eq}}{\text{kWh}}] + [(\frac{40,144.73 \text{ kg/h}}{12.08 \text{ kWh/kg}}) * 0.26 \text{ kg} \frac{\text{CO}_2\text{eq}}{\text{kWh}}]$$

$$Emission_{SBlend B} = 1,139.84 \text{ kg CO}_2\text{eq/h}$$

2.3.4 ETBE Conclusions

Ethyl tertiary butyl ether (ETBE) shows a slightly more favorable profile than MTBE in terms of its climate impact within the context analyzed. Blend B (30.00% ETBE and 70.00% Extra gasoline) generated a total of 998,235.84 kg CO₂ equivalent per year, with an hourly rate of 1,139.84 kg CO₂eq/h, which represents a relative reduction compared to blend A. This difference is due to the fact that the ETBE production process did not require additional electricity consumption and used a smaller amount of thermal energy, which reduces the emissions associated with its manufacture. However, LPG continues to be the main source of emissions in this process, since it is the dominant energy source in the distillation and synthesis phase.

Although the ethanol used as an input for ETBE production comes from organic waste fermentation, the subsequent stages of purification, concentration and reaction with isobutene are still energy intensive.

To further reduce emissions from this process, the incorporation of biomass boilers as the main thermal source is recommended, as well as the implementation of energy integration systems to recover and reuse heat from processes such as distillation. Additionally, the optimization of fermentation, through rigorous control of parameters such as temperature, pH and substrate concentration, could reduce energy requirements per unit of ethanol produced.

2.3.5 Discussion

Activity 1. Gasoline demand in Ecuador

According to the Energy Balance Report of the Ministerio de Energía y Minas (2024), the total supply of gasoline in Ecuador in 2023 was 1,328 million gallons, of which 35.70% came from domestic production and 64.30% from imports (Instituto de Investigación Geológico y Energético et al., 2024). This excludes Ecopais.

Since MTBE and ETBE are blended with gasoline to improve its performance and reduce emissions, the production of these biofuels could contribute significantly to reducing dependence on fossil fuel imports, strengthening the country's energy security and reducing the carbon footprint of the transportation sector. In addition, the incorporation of biofuels into the gasoline blend offers an opportunity to improve urban air quality by reducing the emission of polluting compounds.

In terms of gasoline substitution, both biofuels would be used in a 30.00% blend with 70.00% conventional gasoline, which would significantly reduce the demand for crude oil. The results indicate that, under the proposed operating conditions, the biorefineries will produce the following annual volumes. Table 16 below shows the annual production of biofuels, Extra required and annual production of blends with MTBE and ETBE.

Table 16. Annual biofuel production, Extra required and annual production of A and B blends.

Product	Pure biofuel production (30%) [t/year]	Extra gasoline required (70%) [t/year]	Total mass of the blend (100%) [t/year]
MTBE (Blend A)	150,717.55	351,674.28	502,391.83
ETBE (Blend B)	165,380.04	385,886.76	551,266.80

These quantities represent the total volume of blended fuel that would be obtained from the annual production of each biorefinery. These quantities are equivalent, in volume, to 675 million

liters in the case of blend A and 702 million liters for blend B, applying specific densities for each component (MTBE: 0.73 kg/L; ETBE: 0.71 kg/L; Extra gasoline: 0.75 kg/L). In energy terms, this production would make it possible to substitute between 13.40% and 14.00% of the annual national gasoline consumption, which represents a considerable advance in the diversification of the national energy matrix.

Activity 2. Alternative scenario 100% Extra gasoline

As a reference scenario, the case was evaluated in which the fuel used corresponds exclusively to Extra gasoline, without the incorporation of oxygenated additives such as MTBE or ETBE. The objective is to estimate the emissions that would be generated if all the energy supplied by the 70/30 blends were delivered only by Extra gasoline. This alternative allows establishing a baseline of emissions associated with the use of conventional fossil fuels and serves as a reference to contrast the environmental performance of the scenario with blends.

For the comparison to be valid, it is considered that the total energy delivered by the biofuel in the 70/30 scenario will be compensated in this case only with Extra gasoline. Since each blend (blend A and blend B) has a different energy content, the average total energy delivered by both blends was used as the basis for this substitution scenario.

First, the average energy delivered by the blends is calculated.

$$\begin{aligned} \text{Mean Energy}_{\text{blends}} &= \frac{\text{Energy}_{\text{blend A}} + \text{Energy}_{\text{blend B}}}{2} \\ \text{Mean Energy}_{\text{blends}} &= \frac{623,007,000 \text{ kJ/h} + 619,387,200 \text{ kJ/h}}{2} \\ \text{Mean Energy}_{\text{blends}} &= 621,197,100 \text{ kJ/h} \end{aligned}$$

Then, the equivalent mass of Extra required to deliver the same amount of energy is determined.

$$\text{Mean Energy}_{\text{blends}}$$

$$Mass_{eq\ Extra} = \frac{621,197,100\text{ kJ/h}}{LHV_{Extra}}$$

$$Mass_{eq\ Extra} = \frac{43,500\text{ kJ/kg}}{43,500\text{ kJ/kg}}$$

$$Mass_{eq\ Extra} = 14,280.39\text{ kg/h}$$

Finally, the emissions generated by this mass of Extra gasoline.

$$Emissions_{100\%Extra} = \left[\left(\frac{Mass_{equiv\ Extra}}{LHV_{Extra}} \right) * FE_{Extra} \right]$$

$$Emissions_{100\%Extra} = \left[\left(\frac{14,280.39\text{ kg/h}}{12.08\text{ kWh/kg}} \right) 0.26 \frac{\text{kg CO}_2\text{eq}}{\text{kWh}} \right]_*$$

$$Emissions_{100\%Extra} = 307.36 \frac{\text{kg CO}_2\text{eq}}{\text{kWh}}$$

Activity 3. Comparison between both blends and the 100% Extra gasoline scenario.

The comparative evaluation of blends A (30.00% MTBE + 70.00% Extra gasoline) and B (30.00% ETBE + 70.00% Extra gasoline), compared to the exclusive use of Extra gasoline, allows us to analyze not only the absolute behavior of emissions, but also their performance per unit of useful energy supplied. This approach is key to understanding the true climate impact of each alternative in the context of transport decarbonization in Ecuador.

For a more representative comparison, the total mass of mixture consumed in each case was calculated, and the specific emissions were determined as a function of the total produced during a year. This allows simultaneous evaluation of both the absolute impact and the climate efficiency per unit of fuel. The results are presented in Table 17.

Table 17. Comparison of specific GHG emissions per ton of mixture burned.

Scenario	Production or Consumption (t/year)	Annual emissions (tCO ₂ eq/year)	Specific emissions (tCO ₂ eq/t blend).
Blend A (30 MTBE + 70 Extra)	502,391.83	10,708.57	0.0213

Blend B (30 ETBE + 70 Extra)	551,266.80	9,985.00	0.0181
100 Gasoline Extra	125,096.24*	2,692.47	0.0215**

* In this case, the mass corresponds to the amount of Extra gasoline needed per year to supply the same energy delivered by blends A and B.

** This value considers only emissions from use. If average emissions per production of Extra gasoline (11.50 kg CO₂eq/GJ) are included, the corrected value would be 0.52 t CO₂eq/t.

Figure 7 summarizes these differences visually, facilitating direct comparison between fuels.



Figure 7. Comparison of specific emissions of the different fuels.

These values clearly reflect that the blend with ETBE not only has the lowest total climate footprint but also has the best relative performance per ton of fuel delivered. This result is due to the greater efficiency of the production process, which in the case of ETBE does not include additional electricity consumption and has a lower thermal requirement than MTBE.

It is also important to note that the comparison presented here is limited by the scope of the analysis. In the case of Extra gasoline, only the use stage has been considered, while blends A and B incorporate both production and combustion emissions. This methodological asymmetry underestimates the true climate impact of fossil fuels. According to the IPCC and life cycle analysis studies, the extraction and refining stage of gasoline can generate between 8.00 and 15.00 kg CO₂eq per GJ of energy processed (IPCC, 2006), which, applied to the present case, would represent between 1,500 and 2,500 t CO₂eq/year additional (which would give a specific emission of 0.52). Incorporating this component would make blends with biofuels show an even more significant environmental advantage.

Finally, from a national strategic perspective, the adoption of blends with oxygenated biofuels (such as MTBE or ETBE) represents a technically feasible and environmentally favorable option to diversify the energy matrix of the transportation sector without requiring changes in the existing vehicle infrastructure. In the Ecuadorian context, which has a mostly renewable electricity matrix and an abundant availability of agro-industrial waste, these alternatives could be consolidated as intermediate pillars towards a more sustainable transportation system. However, their climate effectiveness will depend directly on the country's capacity to implement cleaner production processes and replace LPG with renewable thermal sources.

3. CONCLUSIONS

This integrative project developed the design, modeling and comparative evaluation of two biorefineries to produce MTBE and ETBE from sugarcane residues. It provided technical knowledge on the modeling of advanced biofuel processes, their economic analysis and

environmental impact, demonstrating that it is possible to diversify Ecuador's energy matrix through more sustainable and stable alternatives to ethanol, especially in high altitude areas.

Internationally, biofuels derived from residual biomass are consolidated as an intermediate solution for the energy transition, standing out in regions such as Europe and North America. Comparatively, in Ecuador there is still a low level of adoption of advanced biofuels due to infrastructure limitations and lack of incentives. This work shows that, with the right technology and a co-product valorization approach, it is possible to approach international energy sustainability standards

From an environmental engineering perspective, this study highlights the importance of designing solutions that integrate technical, economic and environmental analysis. The ability to propose alternatives that reduce greenhouse gas emissions is essential to meet the challenges of climate change and sustainability.

The results of the feasibility assessment corresponding to the three objectives of this work are presented below. Each conclusion synthesizes the most relevant findings obtained from the modeling, economic analysis and emissions estimation, providing an integrated view of the feasibility of the proposed alternatives.

1. Technical feasibility: Both biorefineries proved to be technically and operationally feasible, obtaining products with acceptable commercial purities (MTBE: 80.41%; ETBE: 71.22%) and improving the gasoline octane rating to levels above 94 RON.
2. Economic feasibility: MTBE production was more competitive (2.77 USD/gal blend) than ETBE (3.14 USD/gal blend), favored by a higher valorization of co-products and lower net production cost.

3. Environmental feasibility: ETBE showed a lower specific carbon footprint (0.0181 t CO₂eq/t blend) compared to MTBE (0.0213 t CO₂eq/t blend) and to the exclusive use of Extra gasoline, representing the most sustainable option.

To facilitate the comparison between the two routes studied, table 18 is presented below to clearly visualize the relative strengths and weaknesses of each alternative.

Table 18. Comparative summary of MTBE and ETBE

Indicator	MTBE (blend A)	ETBE (blend B)
Estimated octane rating (RON)	95.40*	94.80
Minimum selling price (USD/gal blend)	2.77*	3.14
Estimated initial investment (USD)	6,832,654.29	5,162,645.90*
Specific emissions (t CO ₂ eq/t mix).	0.0213	0.0181*

* The value corresponding to the most favorable scenario for each indicator evaluated is indicated.

Several important challenges were faced during the development of this project. One of the main difficulties was the limited availability of updated local information for certain critical parameters, such as input prices, infrastructure costs, emission factors and co-product market data in Ecuador. This lack of information made it necessary to resort to international sources and to make adaptations based on conservative assumptions, which could introduce a certain degree of uncertainty in the results. Another challenge was the complexity of the process simulation in Aspen Plus® V14, especially in the configuration of hybrid thermodynamic models, which required additional study of specialized technical literature.

To enrich this type of analysis in the future, it would be advisable to incorporate a full life cycle assessment, covering not only the production and use phases, but also feedstock extraction, transportation and final disposal. This would make it possible to more accurately capture the actual environmental footprint of each biofuel. In addition, it would be valuable to model energy integration scenarios that contemplate the use of renewable energies (such as internal biomass or

solar energy) in biorefineries, thus reducing dependence on fossil sources such as LPG. Another aspect to consider is the evaluation of a hybrid plant capable of producing both MTBE and ETBE in a flexible manner, optimizing resources and adapting to variations in market demand.

BIBLIOGRAPHY

- Adnan, M. A. (2025). Economic and environmental analysis of biomassbased methanol production: A comparative study with fossil-based alternative. *Biomass and Bioenergy*, 194, 107634. <https://doi.org/10.1016/j.biombioe.2025.107634>
- Agyekum, E. B., Okonkwo, P. C., & Rashid, F. L. (2025). Research on biomass energy and CO2 conversion to methanol: a combination of conventional and bibliometric review analysis. *Carbon Research*, 4(1), 4. <https://doi.org/10.1007/s44246-024-00179-0>
- Ahorsu, R., Medina, F., & Constantí, M. (2018). Significance and Challenges of Biomass as a Suitable Feedstock for Bioenergy and Biochemical Production: A Review. *Energies*, 11(12), 3366. <https://doi.org/10.3390/en11123366>
- de Andrés, J. M., Vedrenne, M., Brambilla, M., & Rodríguez, E. (2019). Modeling and model performance evaluation of sewage sludge gasification in fluidized-bed gasifiers using Aspen Plus. *Journal of the Air & Waste Management Association*, 69(1), 23–33. <https://doi.org/10.1080/10962247.2018.1500404>
- Devi, A., Niazi, A., Ramteke, M., & Upadhyayula, S. (2021). Techno-economic analysis of ethanol production from lignocellulosic biomass—a comparison of fermentation, thermo catalytic, and chemocatalytic technologies. *Bioprocess and Biosystems Engineering*, 44(6), 1093–1107. <https://doi.org/10.1007/s00449-020-02504-4>
- El Comercio. (2025, January 11). *Nuevos precios de las gasolinas extra y ecopaís rigen desde este 12 de enero.*
- Instituto de Investigación Geológico y Energético, Fontalvo Díaz, J., Ramírez Peñaherrera, P., Constante Argüello, J., Fonseca Palacios, J., & Cruz Salazar, C. (2024). *BALANCE ENERGÉTICO NACIONAL 2023*. 52–78.

- Ipiales, O., & Cuichán, M. (2024). *Encuesta de Superficie y Producción Agropecuaria Continua (ESPAC) - Boletín Técnico*.
- Kazemi Shariat Panahi, H., Dehhaghi, M., Aghbashlo, M., Karimi, K., & Tabatabaei, M. (2020). Conversion of residues from agro-food industry into bioethanol in Iran: An under-valued biofuel additive to phase out MTBE in gasoline. *Renewable Energy*, 145, 699–710. <https://doi.org/10.1016/j.renene.2019.06.081>
- Mehrjouei, M., Müller, S., & Möller, D. (2014). Decomposition kinetics of MTBE, ETBE and, TAE in water and wastewater using catalytic and photocatalytic ozonation. *Journal of Molecular Catalysis A: Chemical*, 386, 61–68. <https://doi.org/10.1016/j.molcata.2014.02.014>
- Mirabella, W. (2003). MTBE & ETBE European Key Tools to Address EU Alternative & Bio-Fuels Ambition. *Hart World Fuels Conference: Europe*.
- Najafi, H., Golrokh Sani, A., & Sobati, M. A. (2023). A comparative evaluation on the physicochemical properties of sugarcane residues for thermal conversion processes. *Industrial Crops and Products*, 202, 117112. <https://doi.org/10.1016/j.indcrop.2023.117112>
- Pongchaiphol, S., Suriyachai, N., Hararak, B., Raita, M., Laosiripojana, N., & Champreda, V. (2022). Physicochemical characteristics of organosolv lignins from different lignocellulosic agricultural wastes. *International Journal of Biological Macromolecules*, 216, 710–727. <https://doi.org/10.1016/j.ijbiomac.2022.07.007>
- Quevedo-Amador, R. A., Escalera-Velasco, B. P., Arias, A. M. R., Reynel-Ávila, H. E., Moreno-Piraján, J. C., Giraldo, L., & Bonilla-Petriciolet, A. (2024). Application of waste biomass for the production of biofuels and catalysts: a review. *Clean Technologies and Environmental Policy*, 26(4), 943–997. <https://doi.org/10.1007/s10098-023-02728-4>
- Qureshi, S. S., Nizamuddin, S., Baloch, H. A., Siddiqui, M. T. H., Mubarak, N. M., & Griffin, G. J. (2019). An overview of OPS from oil palm industry as feedstock for bio-oil production. *Biomass Conversion and Biorefinery*, 9(4), 827–841. <https://doi.org/10.1007/s13399-019-00381-w>
- Sheldon, R. A., & Yusup, S. B. (2019). Editorial Overview: Bioresources, biomass, bio-fuels & bioenergies: Biorefineries and biomass conversion: Biofuels, chemicals and bio-based materials. *Current Opinion in Green and Sustainable Chemistry*, 20, A1–A2. <https://doi.org/10.1016/j.cogsc.2019.10.001>

- Srivastava, N., Rawat, R., Singh Oberoi, H., & Ramteke, P. W. (2015). A Review on Fuel Ethanol Production From Lignocellulosic Biomass. *International Journal of Green Energy*, 12(9), 949–960. <https://doi.org/10.1080/15435075.2014.890104>
- Trop, P., Krope, J., Dobersek, D., & Goricanec, D. (2012). Simulation of Desulphurization of Synthesis Gas with Aspen Plus. *Power and Energy Systems*. <https://doi.org/10.2316/P.2012.768-065>
- Tse, T. J., Wiens, D. J., & Reaney, M. J. T. (2021). Production of Bioethanol—A Review of Factors Affecting Ethanol Yield. *Fermentation*, 7(4), 268. <https://doi.org/10.3390/fermentation7040268>
- Wang, X., Gao, J., Chen, Z., Chen, H., Zhao, Y., Huang, Y., & Chen, Z. (2022). Evaluation of hydrous ethanol as a fuel for internal combustion engines: A review. *Renewable Energy*, 194, 504–525. <https://doi.org/10.1016/j.renene.2022.05.132>
- Wei, H., Yingting, Y., Jingjing, G., Wenshi, Y., & Junhong, T. (2017). Lignocellulosic Biomass Valorization: Production of Ethanol. In *Encyclopedia of Sustainable Technologies* (pp. 601–604). Elsevier. <https://doi.org/10.1016/B978-0-12-409548-9.10239-8>
- Yi, N., Herraiz, L., Fang, M., García, S., & van der Spek, M. (2024). Open access, thermodynamically consistent, electrolyte NRTL model for piperazine, AMP, water, CO₂ systems on Aspen Plus. *Separation and Purification Technology*, 350, 127924. <https://doi.org/10.1016/j.seppur.2024.127924>

ANEXO A: TÍTULO

(Si hubiere anexos. Ver requerimientos de anexos obligatorios para trabajos de carreras relacionadas a las artes)

ANEXO B: TÍTULO

(Si hubiere anexos. Ver requerimientos de anexos obligatorios para trabajos de carreras relacionadas a las artes)

ANEXO C: TÍTULO

(Si hubiere anexos. Ver requerimientos de anexos obligatorios para trabajos de carreras relacionadas a las artes)

Se recomienda iniciar cada anexo en una nueva hoja. Se puede incluir anexos adicionales (ANEXO D: TÍTULO, ANEXO E: TÍTULO, ANEXO F: TÍTULO, etc.) de conforme la necesidad de presentación de los mismos en el trabajo. Ver requerimientos de anexos obligatorios para trabajos de carreras relacionadas a las artes.