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BIOREFINERY - ETHANOL AS A RAW MATERIAL

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Abstract: The availability of ethanol in Brazil is indisputable and tends to grow mainly due to the use of corn as a raw material, and also due to technological developments that allow the use of sugarcane straw and excess bagasse. With the migration of some combustion engine vehicles to electric vehicles, we will soon be facing a scenario that favors the search for new uses for ethanol. The use of corn as a raw material and increased production means lower costs for ethanol. In addition, the lower greenhouse gas emissions from products that replace naphtha with ethanol will allow companies to obtain carbon credits, further improving their profit margins. This is a very promising scenario for setting up biorefineries in Brazil using ethanol as a raw material. Between the 1960s and the early 1990s, several companies in Brazil successfully used ethanol as a raw material, replacing naphtha to produce, among other things, basic products for the petrochemical chain, such as 1.3 butadiene and ethylene. There is still isolated production of ethylene via ethanol. In this article, we analyze the feasibility of an ethanol plant associated with a biorefinery using ethanol as a raw material to simultaneously produce the same oil derivatives currently obtained via naphtha. The economic advantages are shown, as well as the reduction in CO emissions$_2$ and the possibility of alternative biodegradable products.

Keywords: Ethanol, Naphtha, Polymers, Refinery, Environment

INTRODUCTION

The word refinery is usually applied to the processing of oil used as a raw material. Crude oil is not used in the way it is extracted; it needs to be refined, which is a set of physical and chemical processes aimed at obtaining what are known as oil derivatives. These oil derivatives are basically fuels (gasoline, diesel oil, kerosene, fuel oil, heavy waste, LPG), lubricating oils and naphtha. Fuels are used to generate various forms of energy, and naphtha to produce the raw materials for petrochemical products. Fuels account for around 70%, with naphtha accounting for between 3 and 15%. The first-generation derivatives are obtained from naphtha, with ethylene and butadiene being two of the most important for the petrochemical chain. Ethylene is used to produce plastics and butadiene to produce elastomers known as synthetic rubbers. As oil is made up of hydrocarbons, when naphtha is processed it releases CO_2 and generates products that are not biodegradable.

The term biorefinery encompasses the facilities and processes through which renewable raw materials and their residues are transformed into chemical products to be used as biofuels. Biomass has a strategic position for the sustainability of our planet because it represents a major source of renewable raw materials. The term alcohol chemistry refers to the use of ethanol as a raw material for the manufacture of various chemical products in an isolated or integrated manner.

In this article, the author aims to show the competitiveness of ethanol use in a biorefinery that is designed in an integrated way, similar to a petrochemical plant. To this end, he will use as a methodology papers published in congresses, seminars, magazines, master's dissertations, statistical yearbooks, books, as well as data from the experience acquired during the period in which he worked in the alcohol and petrochemical industries.

HISTORY OF ETHANOL AS A RAW MATERIAL

In the 1920s, Brazil even had an alcohol industry, which was practically abandoned when petrochemicals were consolidated in the 1990s. In the 1970s, trade agreements between the major producing countries sharply increased oil prices, reaching a level equivalent to today's 80 U$/barrel. In order to minimize the impact of imports, Brazil encouraged research into the substitution of oil derivatives and most industries implemented research and development programs, supported by various research centers. Pilot plants were designed in various industries to develop technologies for using ethanol as a raw material. In 1975, the National Alcohol Program (PROALCOOL) was created, as reported by SILVA, O on pages 65 to 74 of the book Ethanol a revolução verde e amarela, 2008, which was discontinued in the 1990s for political reasons. Table 1 shows some of the industries that have used ethanol as a raw material in Brazil.

NAPHTHA AND ETHANOL AVAILABILITY IN BRAZIL

NAPHTHA

As shown in figure 1, based on the data in tables 2.37 and 2.55, pages 109 and 123, of the Brazilian Statistical Yearbook of Petroleum, Natural Gas and Biofuels - ANP, Brazil is not self-sufficient in naphtha, depending on imports to meet the demand for petrochemical derivatives. In 2023, for example, Brazil imported 61% of the naphtha it consumed.

ETHANOL

Unlike naphtha, Brazil does not depend on imports to meet its domestic ethanol consumption. Figure 2 shows the evolution of anhydrous and hydrous ethanol production in Brazil between 2013 and 2022.

Ethanol can be produced via sugar cane or corn. There are mills that produce both sugar and ethanol, and independent distilleries that only produce ethanol. Production via corn only produces ethanol.

According to CONAB - Companhia Nacional de Abastecimento (National Supply Company), available at htpps://agenciagov.ebc.com.br, the area planted with sugarcane for the 2023/2024 harvest is 8.29 million hectares, which represents just 12.5% of the total area cultivated in Brazil. Sugarcane produces between 5,600 and 6,800 liters of ethanol/ha. With technological developments in new varieties of sugarcane and new technologies for hydrolysis of sugarcane straw, productivity is expected to increase by around 50% . A corn plantation produces around 2,442 liters of ethanol per hectare. Table 2 shows the current average yields.

	Liters of Ethanol / Ton of raw material	Tons of raw material/ha	Liters of Ethanol/ ha
Sugarcane			
Autonomous distillery	89	80	7.120
Plant	70	80	5.600
Corn	407	6	2.442

Table 2 - Current yield averages

Source: Author's work based on data from UNEM (National Corn Ethanol Union).

ETHANOL SPECIFICATION FOR USE AS A RAW MATERIAL

Ethanol is produced as anhydrous (99% by weight) or hydrated (94% by weight). The ethanol received in a biorefinery may have a lower alcohol content than hydrous, because in the production process for ethylene, steam is added to the feed and ethanol is recycled in other processes. The main concern with the ethanol specification is impurities that could affect the performance of the catalysts used.

Company	Location	Products	Period	Applications
COPERBO	Pernambuco	Butadiene Acetaldehyde Ethylene	1964 a 1971 1983 a 1993 1988 a 1992	Polymers Acetic acid Vinyl acetate
ALCOHOL	Pernambuco	Acetic acid, vinyl acetate	1986 a 1993 1986 a 2008	Polyvinyl acetate (PVA).
Salgema, Trikem	Alagoas	Ethylene	1981 a 1992	Dichloroethane, Polyethylene
Braskem	RGS	Ethylene	Since 2010	Polyethylene
Elekeiroz	Pernambuco	Octanol	1970 a 1980	Solvents
Rhodia	São Paulo	Acetic acid, solvents	1980 a 1996	Polyvinyl acetate (PVA), solvents
Union Carbide	São Paulo	Ethylene	1970 a 1980	Polyethylene

Table 1 - Ethanol as a raw material in Brazil

Source: author's surveys

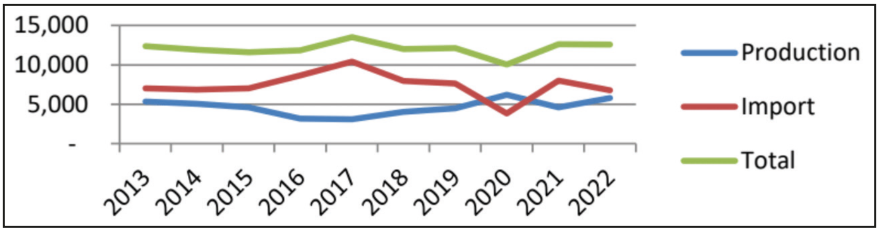

Figure 1 - Naphtha Production and Imports in Brazil (10^3 m^3) 2013 - 2022

Source: Author's work with tables 2.37 and 2.55, pages 109 and 123, ANP Yearbook 2023

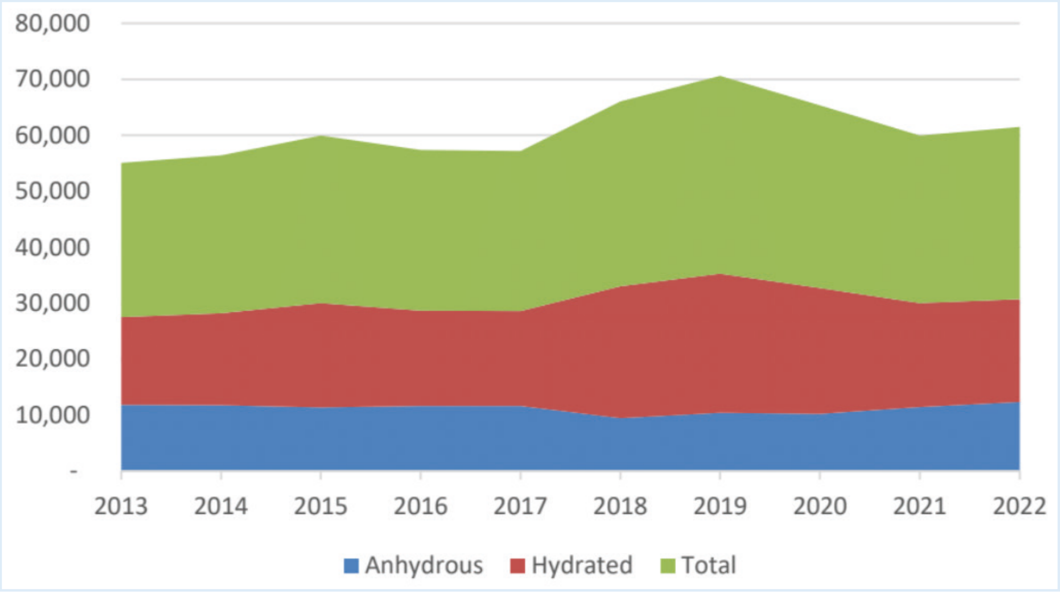

Figure 2 - Ethanol production in Brazil (10^3 m3) 2013 - 2022

Source: ANP Yearbook 2023, page 181, graph 4.2

TECHNOLOGIES

ETHYLENE PRODUCTION VIA ETHANOL

Ethylene can be obtained from ethanol by catalytic dehydration as shown in equation (1)

$C H_{26} O \rightarrow C H_{24} + H_2 O$ (1) ethanol ethylene water

The catalyst is activated alumina and the reaction is endothermic with temperature control of around 360° C and low pressure. Low temperatures favor the formation of heavier compounds, such as the formation of ethyl ether, as shown in equation (2).

$2\ C\ H_{26}\ O \rightarrow (C\ H\ )_{252}\ O + H2O$ (2) ethanol ethyl ether water

Temperatures above 360° C favor the formation of light compounds such as methanol and CO2, as well as carbon deposits on the catalyst. Temperatures below 360° C favor the formation of heavy compounds such as ethyl ether. Two technologies are currently known: fixed bed and fluidized bed. Fixed bed technology has always been used in Brazil and is already in the public domain. Fluidized bed technology has never been used in Brazil and is the result of a development by Lummus Technical Center, according to an article published by TSAO U. et al in Hydrocarbon Process magazine, February 1978, pages 133 to 136. According to the authors, the advantages of this process are lower investment costs, because a single reactor will produce the equivalent of five fixed bed reactors. It also has lower production costs due to the higher yield obtained by better temperature control. Both technologies require around 2 liters of hydrated ethanol per kg of ethylene. With fixed bed technology there are two processes, isothermal and adiabatic. The difference is that in the isothermal process the reactor is kept warm by means of a thermal fluid, while in the adiabatic process the ethanol is heated outside the reactor, in a furnace using natural gas or another type of fuel.

BUTADIENE PRODUCTION

Butadiene is a hydrocarbon with four carbon atoms and two double bonds. These bonds can be located on the primary carbon (1), the secondary carbon (2) or the tertiary carbon (3). Butadiene 1,3 (double bonds at carbons 1 and 3) is the monomer that produces synthetic rubbers when polymerized. In this article we'll call butadiene 1,3 simply butadiene.

During World Wars I and II, the United States built plants to produce butadiene via ethanol, given the difficulties in importing oil. When the war ended, these plants were shut down and an agreement between the United States and Brazil made it possible to buy an existing plant in Kentrucky - Louisiana to produce butadiene in the municipality of Cabo de Santo Agostinho - PE, giving rise to COPERBO - Companhia Pernambucana de Borracha Sintética. Butadiene is the main monomer in the production of homopolymers and copolymers, which are called synthetic rubbers.

Technologies

The best-known technology for producing butadiene via ethanol was developed by Union Carbide using fixed-bed reactors with two stages. In the first stage, acetaldehyde is formed by dehydrogenation and in the second, butadiene is formed by dehydration of ethanol plus acetaldehyde. Equations (3) and (4) show the main reactions.

$C\ H_{26}\ O \rightarrow C\ H_{24}\ O + H_2$ (3) ethanol acetaldehyde hydrogen

$C\ H_{26}\ O + C\ H_{24}\ O \rightarrow C\ H_{46} + 2H_2\ O$ (4) ethanol acetaldehyde butadiene water

These reactions are endothermic with temperatures between 330 and 360° C and low pressure, similar to the reactions involved in producing ethylene. In addition to the formation of hydrogen, other by-products are also formed, such as ethyl ether (see equation 2), ethyl acetate, butyl acetate and others. The catalyst used by COPERBO in the acetaldehyde production stage was a chromium-copper alloy supported on silica gel, and for the butadiene production stage it was tantalum oxide also supported on silica gel. The yield is around 4 liters of hydrated ethanol per kg of butadiene.

ETHANOL AS A RAW MATERIAL

As the matrix in figure 3 shows, ethanol can produce various products with the same or similar properties to petrochemical products, sharing the entire infrastructure in an integrated manner similar to the petrochemical chain.

ADVANTAGES OF USING ETHANOL AS A RAW MATERIAL

DECENTRALIZATION

A biorefinery installed close to ethanol production units, especially in the west and centre-south regions, will decentralize the production chain, creating new jobs and consequently reducing the export of products to the interior of the country. In addition, the capacity of a biorefinery using ethanol as a raw material could be suited to local demands, because unlike the route via naphtha, the technologies for ethylene and butadiene via ethanol allow for low-capacity production. COPERBO in Pernambuco, for example, had a 25,000 t/year unit for butadiene and 35,000 t/year for ethylene. Braskem in Rio Grande do Sul has a 200,000 t/year ethylene unit.

LOWER CO_2

BOTO, R.S. in the article Ethanol as a Raw Material, Reducing CO2 Emissions / Biodegradable Products, published at the Rio Oil Gas 2022 Congress, shows, based on Simapro software version 9.3.03, that naphtha releases 0.249 $kgCO_2$ Eq/kg-naphtha. In ethanol production via sugar cane in a best case scenario (ethanol from a mill in the south of Brazil, with simultaneous sugar production, sale of CO_2 from the fermentation vats, sale of electricity generated from excess sugar cane bagasse, use of vinasse as fertilizer and mechanized sugar cane harvesting) the release is 0.0548 $kgCO_2$ Eq/kg-ethanol or 0.109 $kgCO_2$ Eq/kg-ethanol if these assumptions are not taken into account. For corn ethanol there is still no consensus on the value of CO_2 Eq/kg-ethanol emitted, but preliminary analyses indicate that it is between the values for ethanol produced in an Autonomous Distillery and that produced by cracking naphtha, as shown in figure 4.

BETTER QUALITY PRODUCTS

According to BÔTO, R. S. in the article Innovation with Hybrid Technologies Naphtha / Ethanol - Cases, e-book Modern Environmental Science and Engineering, v. 6, n. 5, pg. 84-110. New York, USA DOI 10.34188/bjaerv4n2-055, some by-products in ethylene and butadiene produced via ethanol, often considered impurities, can add quality to the final product. Of course, the types of impurities that benefit the process must be suitable for the final product.

POSSIBILITY OF BIODEGRADABLE PRODUCTS

According to BOTO R.S. in his master's thesis Ethanol and Other Sugarcane Derivatives as Raw Materials in the Plastic Polymer Industry UFBA, 2014, CDD 670.42, 2014, pages 31 and 32, biodegradability, among other factors, is associated with the electronegativity between the chemical elements in the molecules. Without taking into account symmetry and the degree of coverage of shared orbitals in covalent bonds, the greater the difference in electronegativity between the atoms, the lower the binding energy between them, and the weaker the binding energy between the atoms, the greater the possibility of biodegra-

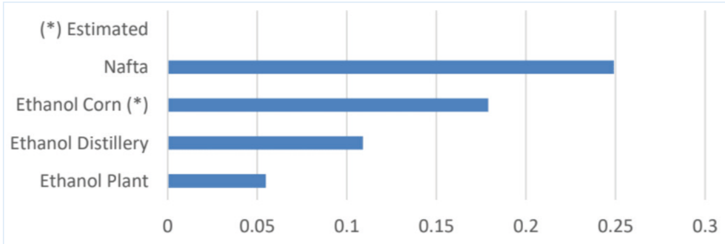

Figure 4 - CO_2 Eq/kg-raw material - Simapro software version 9.3.03

Source: Author's work

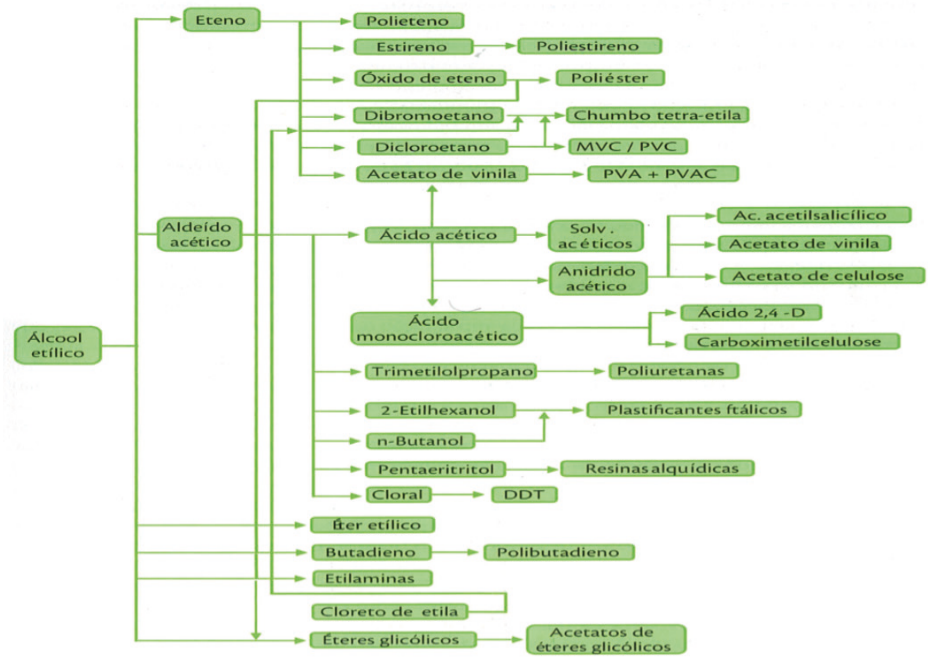

Figure 3 - Alcohol-chemical matrix

Source: Green Chemistry in Brazil 2010-2030, page 119

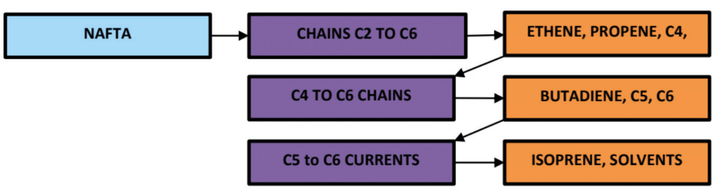

Figure 5 - Naphtha cracking products

Source: Author's work

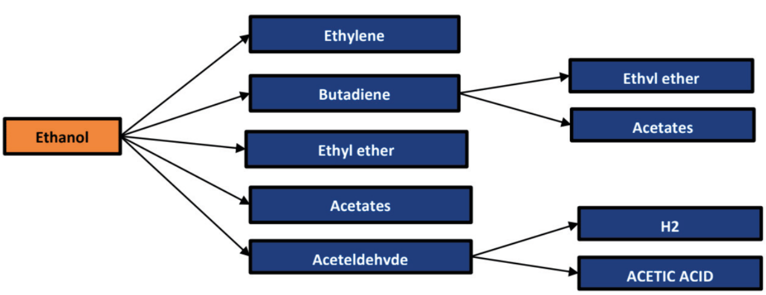

Figure 6 - Ethanol products as raw materials (examples)

Source: Author's work

dation. Based on WINTER Organic Chemistry for Dummies, 2011, page 28, table 3 shows the electronegativities of the elements Carbon (C), Hydrogen (H) and Oxygen (O). Electronegativity is a periodic property of chemical elements which indicates the tendency each one has to attract electrons in a chemical bond. They are indicated in dimensionless form, according to Linus Pauling's concepts.

Element	C	H	O
Electronegativity	2,5	2,1	3,5

Table 3 - Electronegativities of Carbon, Hydrogen and Oxygen

Source: Author's work

As can be seen, the difference in Carbon--Oxygen electronegativity (2.5 - 3.5 = 1.0) is greater than the difference in Carbon-Hydrogen electronegativity (2.5 - 2.1 = 0.4), which we can interpret as the Carbon-Oxygen bond being weaker than the Carbon-Hydrogen bond. ARUTCHELVI, et al, in the article Biodegradation of Polyethylene and Polypropypene, published in the Indian Journal of Biotechnology**.** v.7, p 9-22, 2008, showed experiments on the biodegradability of plastics, concluding that biodegradability is facilitated when there are carbonyl (C=O) and hydroxyl (C-OH) bonds in the molecules. Products derived from naphtha only have carbon-hydrogen bonds, while ethanol, in addition to carbon-hydrogen bonds, also has hydroxyl bonds (C-OH), which can also be converted into carbonyl (C=O). Proof of this influence on the biodegradation process needs to be further investigated, but it is an indication that the development of technologies using ethanol as a raw material could result in biodegradable products.

CONTRIBUTION TO THE BRAZILIAN TRADE BALANCE

According to the Brazilian Statistical Yearbook of Petroleum, Natural Gas and Biofuels - ANP 2023, page 133, the import of naphtha into Brazil has always generated expenditure. In 2022, for example, the cost was 3.7 billion dollars. In other words, replacing imported naphtha would contribute to a better performance of our trade balance.

ECONOMIC EVALUATION OF THE USE OF ETHANOL AS A RAW MATERIAL

The economic evaluation of ethanol as a raw material has been done by comparing ethane produced via naphtha with ethane produced via ethanol. When naphtha is cracked, other products are obtained in addition to ethylene, the transformation yield of which is around 25 to 30%, as shown in figure 5. To calculate the cost of ethylene, all the costs inherent in cracking are apportioned between ethylene and the other products.

For the cost of ethylene via ethanol, the costs are allocated only to ethylene, because the yield is around 97%. However, ethanol can generate several other products in parallel with ethylene, as shown in figure 3 and examples in figure 6. Therefore, the evaluation needs to consider all the products and items related to production, and not just the isolated production of ethylene. Table 4 shows the list of items to be considered.

Item	Ethanol via sugar cane	Ethanol via corn
Sale of products from the ethanol matrix	Yes	Yes
Sale of CO_2 from the fermentation vats	Yes	Not applicable
Sell energy with excess sugarcane bagasse	Yes	Not applicable
Valorization of vinasse as fertilizer	Yes	Not applicable
Selling carbon credits	Yes	Yes
Sale of solid waste (DDG)	Not applicable	Yes
Increased productivity in sugarcane fields	Yes	Not applicable
Ethanol price w/ 2nd generation, influence of corn	Yes	Yes

Table 4 - Items to be considered in the economic evaluation of ethanol as a raw material

Source: Author's work

Considering a 1 (one) million ton/year ethylene plant, Mateus Van Hombeeck in his master's thesis Comparison between the Naphtha and Ethanol Routes for Ethylene Production - Analysis of Costs and CO Emissions$_2$, UFRJ/COPPE 2019, page 85, emphasizes the viability of ethanol compared to naphtha, considering the incorporation of carbon credits, as already exists in several countries. We would point out that in Brazil the regulation of carbon credits is already in the process of being regulated.

FINAL CONSIDERATIONS

Brazil has a privileged climate for ethanol production. It also has a history of using ethanol as a raw material and sufficient technological knowledge of alcohol-chemical processes to use ethanol as a raw material in a biorefinery to replace naphtha. The advantages described in item 6 are relevant and signal opportunities for diversifying Brazilian agribusiness.

On the other hand, the implementation of biorefineries will motivate universities and research centers to promote technological innovations for new catalysts and truly biodegradable products.

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