v. 5, n. 5, 2025

Journal of
Engineering
Research

ETHANOL AS A RAW MATERIAL - REDUCING CO2 EMISSIONS / BIODEGRADABLE PRODUCTS

Acceptance date: 19/05/2025

Rivaldo Souza Bôto
MBA, MSc, PMP

Abstract: The world is increasingly demanding technological innovations aimed at reducing the emission of greenhouse gases into our planet's atmosphere and also for products that are biodegradable. Everything indicates that these demands are irreversible. The automobile industry has already set targets to stop producing combustion engines using fossil fuels. In Brazil, the same engines that run on gasoline are the ones that use hydrated ethanol. As a result, in the relatively near future, Brazil will have more production capacity than consumption, both for the anhydrous ethanol that is added to gasoline and for the hydrous ethanol used 100% as fuel. Using ethanol as a raw material is one way of solving this problem and at the same time demonstrating to the world Brazil's potential for sustainable industrial processes. Between the 1960s and the early 1990s, 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, which is still produced via ethanol. In addition, there is evidence that the use of hybrid ethanol / naphtha technologies can add quality to products, and also evidence that ethanol has the molecular structure to produce alternative biodegradable products. In this article, the author will show the feasibility of using ethanol as a raw material to help reduce CO_2 emissions.

INTRODUCTION

According to the 2021 Statistical Yearbook of the National Petroleum, Natural Gas and Biofuels Agency (ANP), page 178, 32.8 billion liters of ethanol were produced in Brazil in 2020, 10.3 billion of which were anhydrous ethanol and 20.5 hydrous ethanol. Of this volume, approximately 3 billion liters came from corn, with sugar cane being the main source of ethanol production. The southern region was the biggest producer, contributing 54.9%. For 2022 at least, these figures are expected to remain the same. With the introduction of new technologies, which are already being developed to hydrolyze the cellulose in surplus sugarcane bagasse, an increase in ethanol production in Brazil of between 30 and 50% is expected in the near future for the same area planted sugarcane. In Brazil, almost all ethanol is used as fuel. Anhydrous ethanol (99% by volume) is added to gasoline at a rate of 27% and hydrous ethanol (95% by volume) is used pure. Small quantities are used as a raw material. In the face of calls from society to reduce the use of fossil fuels, the automobile industry is calling for a reduction in gasoline consumption. Even if we consider that sugar cane could be used to produce more sugar, or that there will be an increase in the use of hydrated ethanol as a fuel, the future suggests that Brazil will have a surplus of ethanol on the market, jeopardizing the economic viability of autonomous distilleries and sugar mills.

In this article, the author will draw on bibliographical research and his operational experience of more than thirty years working in industries with petrochemical and alcohol-chemical technologies to present alternatives for using ethanol as a substitute raw material for naphtha and for developing biodegradable products from the sugar-chemical chain.

DEVELOPMENT

HISTORY OF ETHANOL AS A RAW MATERIAL

The main raw materials in the petrochemical industry are butadiene 1.3 for the production of elastomers and ethylene for the production of plastics. In the transformation into butadiene 1.3 and ethylene, ethanol needs to lose the hydroxyl radical, which ends up being discarded in the form of water, as shown in equations (2) and (3). As a result, in these

Journal of Engineering Research ISSN 2764-1317 DOI https://doi.org/10.22533/at.ed.317552529045

transformations the atomic efficiency rate is reduced by approximately 39%, which makes the alcohol-chemical route, in principle, uncompetitive compared to the petrochemical route.

The 1970s saw a sudden rise in the price of oil, which reached worrying levels for the competitiveness of the Brazilian petrochemical industry. In order to make ethanol viable as a raw material to replace naphtha, in 1975 Brazil created the National Alcohol Program (PROALCOOL), as SILVA O reports on pages 65 to 74 of the book Ethanol a revolução verde e amarela. This program established tax incentives and pricing policies, which led the Brazilian petrochemical industry to have an alcohol industry as an alternative. A price parity was established between hydrated ethanol and petrochemical ethylene. The price of a liter of ethanol at the plant, to be used as a raw material, was guaranteed by the Brazilian government at 35% of the price of a kilo of ethylene. As a result of this program, various industries and institutions began researching and implementing processes using ethanol as a raw material, as described below.

Production of 1,3 butadiene

In 1965, the Companhia Pernambucana de Borracha Sintética (COPERBO) started operating in Pernambuco, using ethanol to produce polybutadiene, an elastomer widely used in the manufacture of tires. The main chemical reactions are shown in equations (1) and (2)

$$C_2H_6O \rightarrow C_2H_4O + H_2 \quad (1)$$

ethanol acetaldehyde hydrogen

$$C_2H_6O + C_2H_4O \rightarrow C_4H_6 + 2H_2O \quad (2)$$

ethanol acetaldehyde butadiene water

In addition to hydrogen, various by-products were formed, such as ethyl ether, ethyl acetate and butyl acetate, which were not sold and were only used as fuel in the boilers. At the time, COPERBO was one of the few industries in the world to produce synthetic rubbers from ethanol.

Normally, polymer production technologies require the monomer to be of "polymer grade" purity (99% pure). COPERBO has demystified this concept, producing high-quality polymers with the monomer in "chemical grade" purity (95% purity). Some of the "impurities", such as ethyl ether, added value to the polymers for the manufacture of certain products. A pilot reactor unit was installed and fourteen more types rubber were introduced to the market. In 1971, Coperbo stopped using ethanol as a raw material and started processing petrochemical butadiene 1.3. The availability of naphtha from the raw materials plant at the Camaçarí Petrochemical Complex in Bahia, the low production capacity, the limited availability of ethanol on the market and production costs motivated this change.

Ethylene production

Ethanol can produce ethene according to the chemical reaction shown in equation (3)

$$C_2H_6O \rightarrow C_2H_4 + H_2O \quad (3)$$

ethanol ethene water

At the end of 1975, with the launch of PROALCOOL, COPERBO set up pilot plants to adapt reactors that had been deactivated in the production of 1.3 butadiene to produce ethylene using the isothermal process, the patent for which was already in the public domain. This research resulted in an ethylene production plant that operated until the mid-1980s, supplying this raw material to ALCOLQUÍMICA. At that timeCoperbo successfully developed a pilot plant based on tubular reactors to develop the technology for producing acetic acid by oxidizing the acetaldehyde produced via ethanol.

In parallel, CENPES, based on data from the COPERBO pilot plant, adapted the isothermal process and patented it under the name "Adiabatic Process for Dehydrating Ethanol". With this process, Braskem currently produces polyethylene in Rio Grande do Sul called "green plastic" with ethylene from this process.

Vinyl acetate production

In 1986, Companhia Alcoolquímica Nacional (ALCOOLQUÍMICA), initially a subsidiary of COPERBO, started operating in Pernambuco to produce vinyl acetate, according to equation (4).

$$C_2H_4O_2 + C_2H_4 \rightarrow C_4H_6O + H_2O \quad (4)$$

acetic acid ethene vinyl acetate water

Acetic acid was obtained by oxidizing acetaldehyde, according to chemical equation (4), which in turn was obtained by dehydrogenating ethanol, according to chemical equation (5).

$$C_2H_6O \rightarrow C_2H_4O + H_2 \quad (5)$$

ethanol acetaldehyde hydrogen

$$C_2H_4O + \tfrac{1}{2}\,O_2 \rightarrow C_2H_4O_2 \quad (6)$$

acetaldehyde oxygen acetic acid

Other products in the alcohol-chemical route

Between the 1960s and 1990s, in addition to COPERBO and ALCOOLQUÍMICA, several other industries such as Rhodia, Union Carbide, Elekeiroz and Salgema produced ethanol, acetaldehyde, ethylene, acetic acid, vinyl acetate, ethyl acetate, octanol, butanol, acetic anhydride, ethyl ether, dichloroethane and other products. Synthetic rubbers were obtained (polybutadiene homopolymers and SBR copolymers), PVC, acetic solvents, PVA, among others. There were several research centers set up in Brazil to develop the alcohol-chemical route. These CEPED in Bahia, IPT in São Paulo and Petrobras with CENPES. Supported and encouraged by these research centers, various industries set up pilot plants and made teams available to research and develop the alcohol-chemical route.

ETHANOL'S POTENTIAL AS A RAW MATERIAL

Figure 1, copied from page 119 of the book "Green Chemistry in Brazil 2010-2030", shows the potential of the matrix for an alcohol-chemical industry.

HYBRID TECHNOLOGIES

At COPERBO and ALCOOLQUÍMICA, the production of 1.3 butadiene and the production of ethylene, there were cases of higher quality end products being obtained when the raw materials were considered to be of chemical grade purity instead of polymer grade, according to BÔTO, R. S. Innovation with Hybrid Technologies Naphta / Ethanol - Cases (2020).

BIODEGRADABLE PRODUCTS

Metabolism - In the organisms of living beings, substances are constantly being synthesized and broken down into smaller fractions in order to maintain the cells in a dynamic state. Metabolism is the sum total of all the chemical reactions involved in maintaining the dynamic state of cells. In a metabolic process, various chemical reactions take place, resulting in the release of CO_2 and H_2O in the aerobic environment. A large part of the reactions in the bodies of living beings are carbonylated, and it is to be expected that substances that already have hydroxyl radicals or carbonyl radicals in their molecules are more likely to be metabolized in an aerobic environment than those that only have carbon-hydrogen bonds. Research indicates that the presence of the carbonyl radical in the plastic molecule is fundamental to making it biodegradable, according to ARUTCHELVI, et al. in the article Biodegradation of Polye-

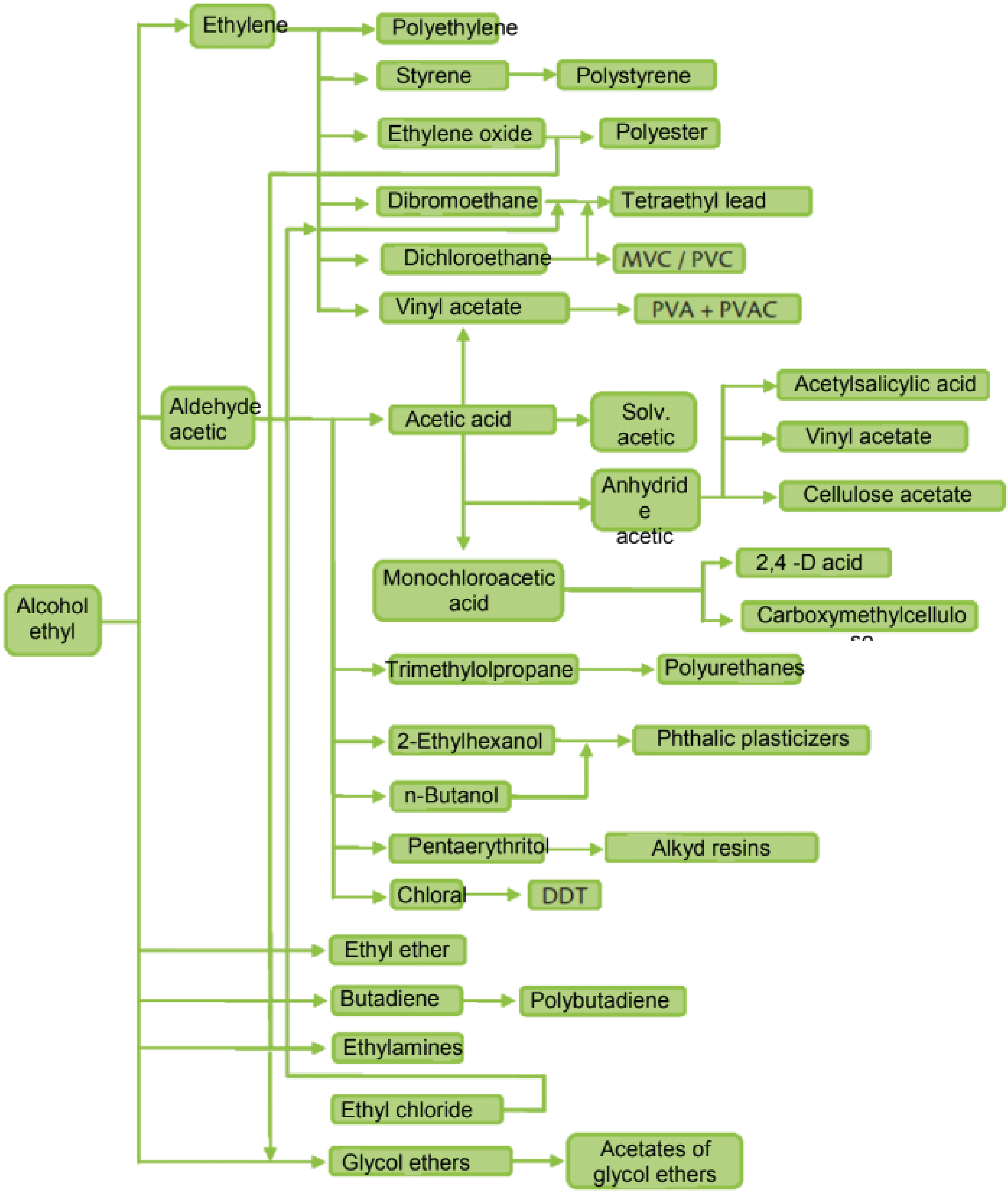

Figure 1 - Alcohol industry matrix

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

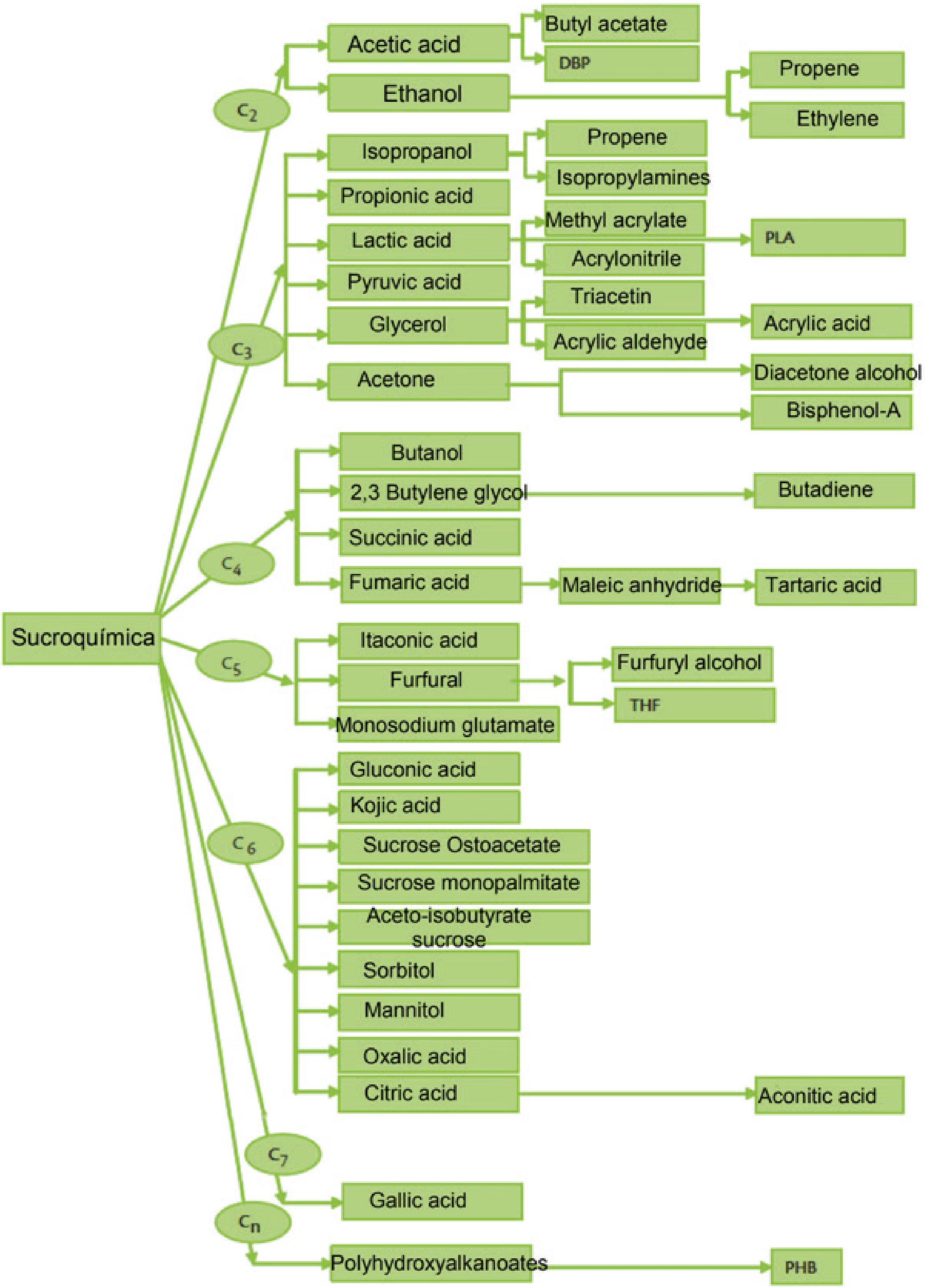

Figure 2 - Tree of products that can be obtained from sugar cane

Source: Green Chemistry in Brazil 2010-2030, pg.

thylene and Polypropypene published in the Indian Journal of Biotechnology, pages 9 to 22, in 2008.

The hydroxyl radical present in the ethanol molecule can be transformed into a carbonyl radical instead of being discarded as water, making the final product biodegradable. This fact opens up the possibility of research into products, mainly polymers, that are biodegradable, according to BÔTO, R. S. in his Professional Master's thesis "Ethanol and Other Sugar Cane Derivatives as Raw Materials in the Plastic Polymer Industry", at the Federal University of Bahia in 2014. From sugar cane and its derivatives there is a wide variety of polymers that can replace fossil-based products on the market. There is also the possibility of discovering new products. The BNDES Center for Strategic Studies in the book Green Chemistry in Brazil 2010-2030, page 197, describes the concept of "Biorefineries - Thermochemical Route", involving the installation and processes through which products traditionally obtained from oil can be produced from renewable biomass. Figure 2 on page 197 of the same book, copied from page 197, shows the tree of products that can be obtained from sugar cane and derivatives, including PLA and PHB, which are biodegradable polymers.

REDUCING CO_2 EMISSIONS

The use of ethanol as a raw material to produce polymers emits less CO_2 than the production of polymers using naphtha, as shown below.

Figure 3 shows a representative block diagram of the CO_2 generated in the production of the polymer with naphtha as the raw material.

Where

$(CO_2)_{1x}$ is the CO_2 released when oil is extracted and sent to the Refinery.

$(CO_2)_{2x}$ is the CO_2 released when naphtha is produced at the Refinery.

$(CO_2)_{3x}$ is the $CO_{(2)}$ released when monomer is produced at the Petrochemical Plant.

$(CO_2)_{4x}$ is the CO_2 released when polymer is produced.

Figure 4 shows a representative block diagram of the CO_2 generated in the production of the same polymer using ethanol as a raw material.

Where:

$(CO_2)_{0y}$ is the CO_2 absorbed from nature when the sugarcane is growing.

$(CO_2)_{1y}$ is the CO_2 released when the sugarcane is extracted and sent to the Distillery.

$(CO_2)_{2y}$ is the CO_2 released when ethanol is obtained at the Distillery.

$(CO_2)_{3y}$ is the CO_2 released when the monomer derived from ethanol is obtained

$(CO_2)_{4y}$ is the CO_2 released when the polymer is produced.

Based on the diagrams in Figures 3 and 4, we can the inequality (7)

$$(CO_2)_{1x} + (CO_2)_{2x} + (CO_2)_{3x} + (CO_2)_{4x} > (CO_2)_{1y} + (CO_2)_{2y} + (CO_2)_{3y} + (CO_2)_{4y} - (CO_2)_{0y} \quad (7)$$

which we will demonstrate below.

CO_2 emitted in naphtha and ethanol production

To determine the values of CO_2 emitted in the production of naphtha, which corresponds to the sum $(CO_2)_{1x}$ + $(CO_2)_{2x}$, and CO_2 emitted in the production of ethanol, which corresponds to the sum $(CO_2)_{1y}$+ $(CO_2)_{2y}$, - $(CO_2)_{0y}$ we used the mathematical model of the SimaPro software in version 9.3.0.3, the ecoinvest database and IPCC 2021 GWP100 criteria for CO_2Eq. Figures (5) and (6) show prints of the results obtained

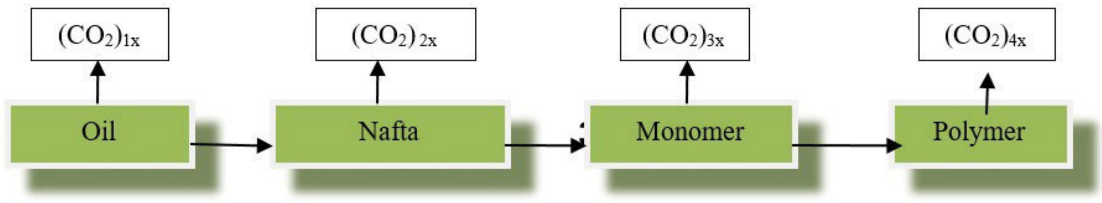

Figure 3: CO_2 cycle in polymer production via naphtha

Source: Author's work

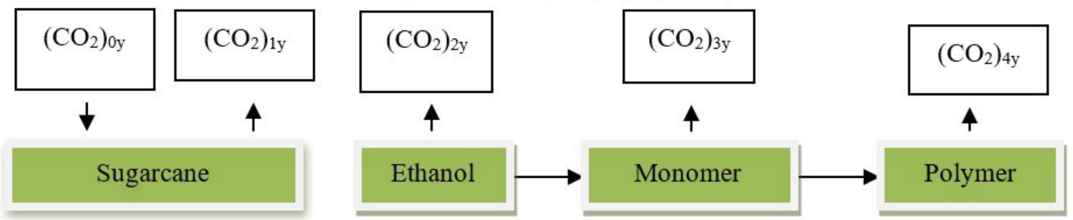

Figure 4: CO2 cycle in polymer production via ethanol

Source: Author's work

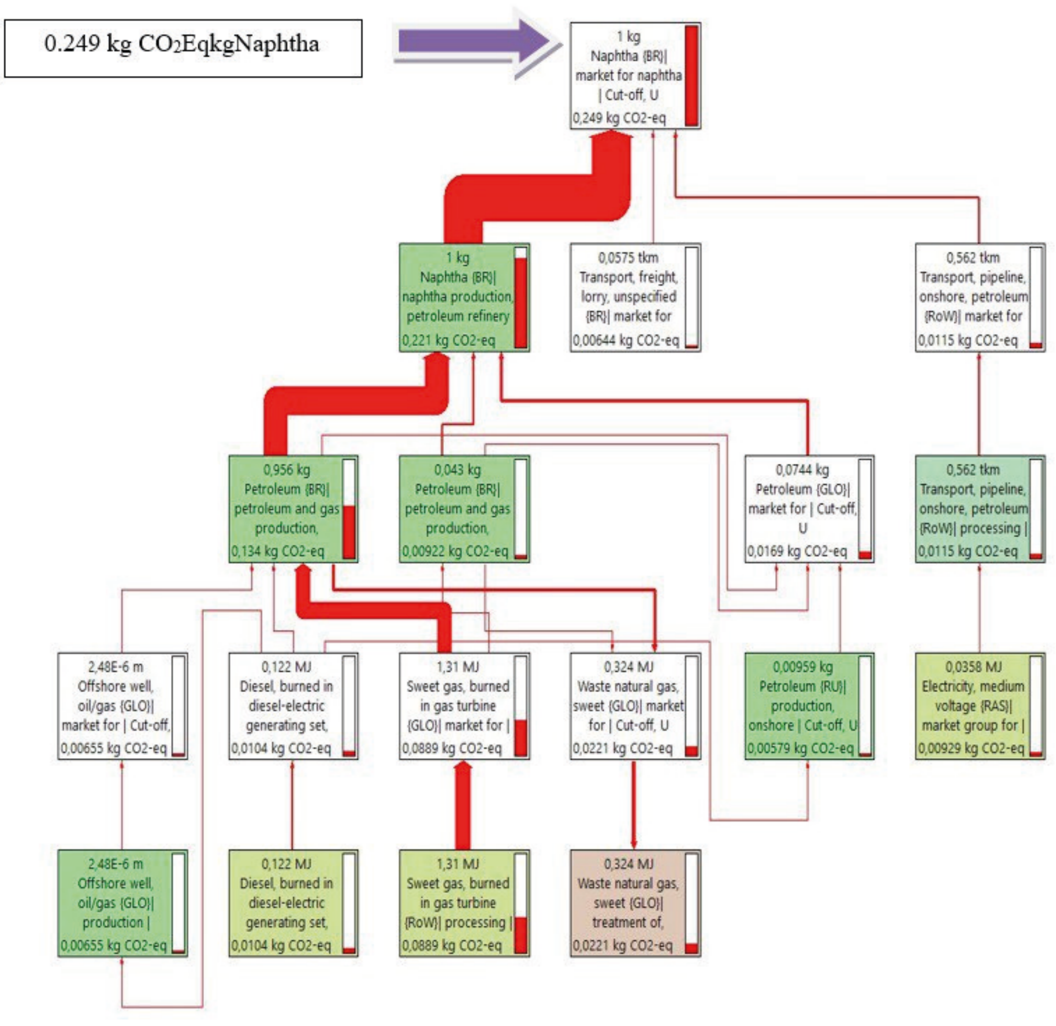

Figure 5 - CO_2 Emissions in Naphtha Production

Source: SimaPro *software* version 9.3.

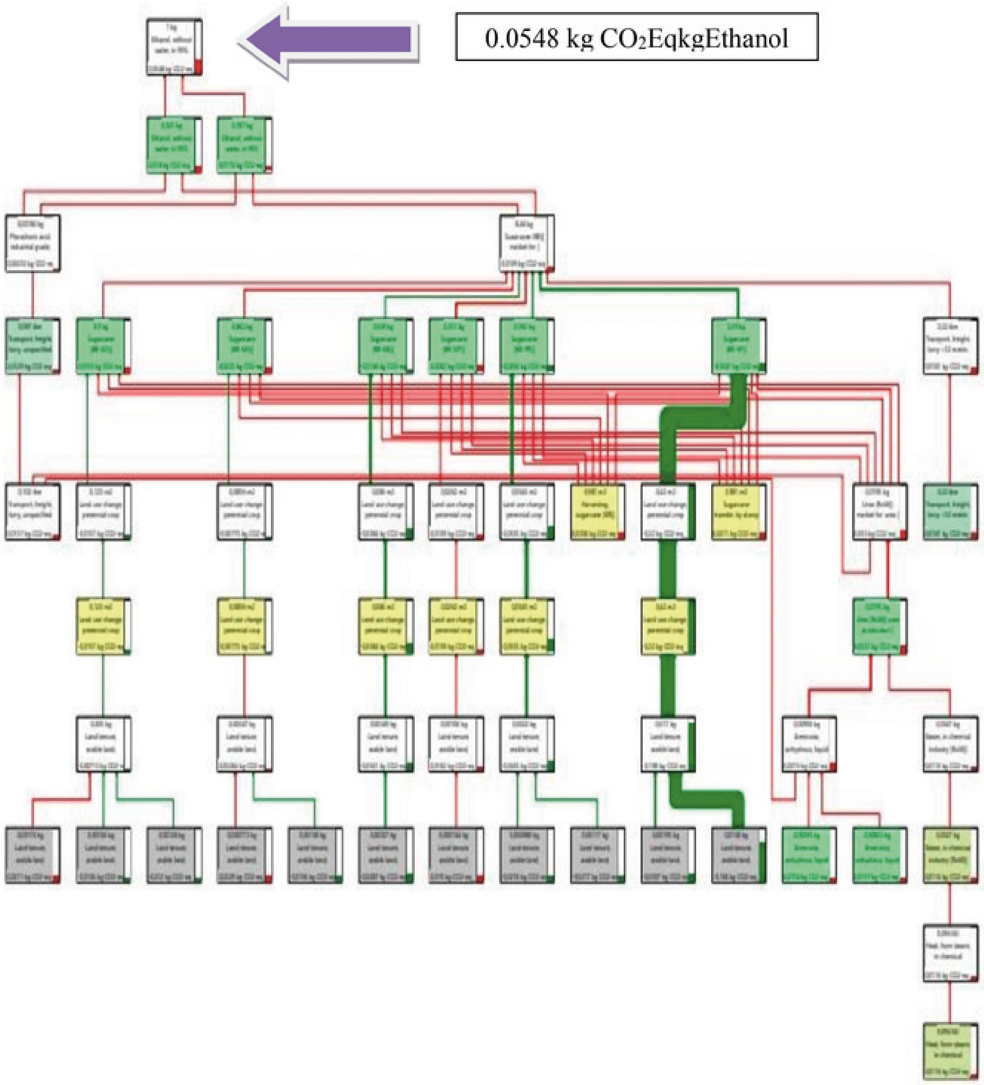

Figure 6 - CO_2 emissions in ethanol production

Source: SimaPro *software* version 9.3.03

As shown in figures (5) and (6), the carbon balance shows that ethanol production releases 0.0548kgCO_2Eq/kg ethanol and naphtha releases 0.249kgCO_2Eq/kg naphtha. The carbon balance for ethanol is controversial because it depends on the assumptions made in the simulation. In order to determine the kgCO_2Eq/kg ethanol index, we considered a mill in the southern region of Brazil, as it is the largest producing region, and also the carbon credits from using CO_2 from the fermentation vats, from generating electricity with excess sugarcane bagasse, and that the sugarcane harvest would be done entirely mechanized without burning the straw. If we consider the worst-case scenarios for ethanol in the simulation, we get a figure of 0.109kgCO_2Eq/kg for ethanol. In other words, ethanol production emits between 43.7% and 220% less CO_2 than naphtha

Although the figures themselves are debatable, because they are based on a mathematical model, and all modeling has assumptions that are sometimes debatable, as the criteria were the same for both cases, we can say that even in the worst case scenario, ethanol production releases less CO_2Eq than naphtha production. In other words,

$(CO_2)_{1x} + (CO_2)_{2x} > (CO_2)_{0y} + (CO_2)_{1y} + (CO_2)_{2y}$

CO_2 emission naphtha > CO_2 emission ethanol

CO_2 emitted in the production of monomers via ethanol

Most of the processes for transforming ethanol into other chemical products are highly selective compared to processes that use naphtha as a raw material. For example, while the yields for converting naphtha into ethylene and propene are between 25 and 30%, the yields for transforming ethanol into ethylene are around 95% and for transforming it into butadiene 1,3 around 60%.

According to the author's experience, acetaldehydes, alcohols, acids, acetates and 1.3 butadiene are produced in yields of over 60%. In addition, because they are more selective, chemical processes based on ethanol are also efficient for low production capacities, and plants can be installed close to the sources of raw materials, facilitating the logistics of receiving them and reducing the use of fuels for transportation.

This means that while obtaining basic products from naphtha to obtain macromolecules, after being polymerized, has relatively low energy yields, obtaining similar products through the alcohol-chemical route has higher energy yields.

We can therefore say

$(CO_2)_{3x}$	>	$(CO_2)_{3y}$
CO_2 emission monomer via naphtha	>	CO_2 emission monomer via ethanol

CO_2 emitted in the production of polymers via ethanol monomers

Considering that the release of CO_2 in polymerization processes for the same monomer is independent of its origin, the production of the polymer will emit the same amount of CO_2, i.e. $(CO_2)_{4x} = (CO_2)_{4y}$.

This shows that the hypothesis in inequality 7 is true, and that the use of ethanol as a raw material to replace naphtha will help reduce carbon emissions in Brazilian industry

NAPHTHA PRODUCTION AND IMPORTS IN BRAZIL

As well as needing to reduce carbon emissions, Brazil could reduce its external dependence on naphtha. The naphtha produced in Brazil has been insufficient to supply the Petrochemical Plants. According to the Brazilian Statistical Yearbook 2021, published by the National Petroleum Agency, pages 107 and 126, the average percentage of naphtha imports in Brazil over the last ten years has been 59.39%. Imports of oil and oil products jeopardize Brazil's trade balance, with naphtha imports being the second largest item among non-energy oil products. In other words, replacing naphtha with ethanol, either partially or totally, would contribute to a better performance of our trade balance.

ECONOMIC VIABILITY OF ETHANOL AS A RAW MATERIAL

The alcohol-chemical route could be economically viable if there were economies of scale and the derivatives obtained were used commercially. The temperature of reactions (1), (2) and (3) in the production of butadiene 1.3 and ethylene from ethanol are the same (around 360°C), and can be obtained from the same heat source, as well as sharing utilities (cooling systems, water and effluent treatment, etc.) and infrastructure. The generation of the various by-products (hydrogen, ethyl ether, acetates, etc.) will have to be commercialized rather than used as fuel, as was the case in the past. In addition, the chain of by-products in the alcohol-chemical route (sugar cane, ethanol, monomers, etc.) would need to be taxed in the same way as the by-products in the petrochemical route (oil, naphtha, monomers, etc.).

Journal of Engineering Research ISSN 2764-1317 DOI https://doi.org/10.22533/at.ed.317552529045

If there is integrated production, with a consequent increase in economies of scale, the use of ethanol as a raw material will be economically viable.

FINAL CONSIDERATIONS

According to the BNDES Center Strategic Studies - Green Chemistry in Brazil 2010-2030 on pages 117 to 137, the global panorama of the theme "biorefineries in the biochemical route" shows a significant growth in the number of publications and patents. However, while there were 1,004 publications in the United States between 1998 and 2009, only 132 were registered in Brazil in the same period. According to the same source, only a small number of Brazilian universities carry out research on the subject of biorefineries. Only fourteen Brazilian universities have demonstrated that they have this focus, four in São Paulo, three in Paraná, two in Minas Gerais, two in Rio Grande do Sul, and one university each in the states of Santa Catarina, Pernambuco and the Federal District. In other words, although Brazil has demonstrated its capacity for technological development, the potential for using ethanol as a raw material is not being properly researched.

As has been shown, the use of ethanol as a raw material to replace naphtha is nothing new in Brazil. It has also been shown that the production of ethanol from sugar cane releases less CO_2 than naphtha. There is evidence that ethanol, as well as sugarcane derivatives, because they have the hydroxyl radical, can easily reach the carbonyl radical, presenting ample conditions for biodegradable products. It's time for Brazil to have the alcohol-chemical route as a technological development target for biodegradable products, as a contribution to decarbonization, or even for products with hybrid technology, as reported.

THANKS

The author would like to thank the Federal University of Bahia - UFBA in the person of Dr. Emerson Andrade Sales, professor and researcher in bioenergy and catalysis, Diego Lima Medeiros, researcher at POSPETRO at IGEO-UFBA and the company ACV Brasil, on behalf of Pré Sustainability, for the permission and support to use the academic license of the Simapro software, without which it would not have been possible to prepare this article.

REFERENCES

AGÊNCIA NACIONAL DO PETRÓLEO GÁS NATURAL E BIOCOMBUSTÍVEIS. Anuário Estatístico 2021, pgs 107 e 126.

ARUTCHELVI, et al. **Biodegradation of Polyethylene and Polypropypene.** Indian Journal of Biotechnology. v.7, p. 9-22, 2008.

BÔTO, R. S. **Etanol e Demais Derivados da Cana-de-Açúcar como Matérias-Primas na Indústria de Polímeros Plásticos**. Dissertação de Mestrado Profissional. Universidade Federal da Bahia. Salvador. p. 69. 2014.

BÔTO, R. S. **Innovation with Hybrid Tecnhologies Naphta / Ethanol – Cases**. E-book Modern Environmental Science and Engineering, v. 6, n. 5, pg. 84-110. New York, USA DOI 10.34188/bjaerv4n2-055. Disponível em htpp://www.academicstar.us/onlineupload.asp? 2020

CENTRO DE GESTÃO E ESTUDOS ESTRATÉGICOS - BNDES. **Química Verde no BRASIL 2010 – 2030**. ed. BNDES. Brasília, 2010

SILVA. O. **Etanol a revolução Verde e Amarela.** ed. Bizz. Rio de Janeiro, pg 65-74, 2008.