Modern Environmental Science and Engineering (ISSN 2333-2581)
May 2020, Volume 6, No. 5, pp. 598-603
Doi: 10.15341/mese(2333-2581)/05.06.2020/009
Academic Star Publishing Company, 2020
www.academicstar.us

Innovation with Hybrid Tecnologies: Nafta/Etanol Cases

Rivaldo Souza Bôto
EFBôto Consultoria Ltda, Brazil

Abstract: The traditional petrochemical processes that use naphtha have little perspective of discovering new products or enhancing operational performance. On the other hand, the processes used in the sugar alcohol industry in Brazil to produce hydrocarbons or other petroleum products using ethanol are always more expensive than those that use naphtha, due to necessary additional processes and loss of atomic efficiency. In petrochemical processes, a polymer grade for raw materials is usually required because other hydrocarbons, especially those with unsaturated chains, are impurities of high and low speed to reaction with catalysts, occasioning an increase in consumption and interfering with the characteristics of the final product. The polymer grade is characterized for the requirement of its purity as above 99.9%, while the chemical grade requires the raw material to have a purity of 95.0%. However, the energy consumption to go from chemical grade to polymer grade is significant, having an impact on the production costs. This paper presents case studies in which hybrid naphtha/ethanol technologies using chemical grade raw materials were shown to be more efficient on the final product.
This paper refers to two case studies of naphtha/ethanol hybrid technologies using chemical grade raw materials. The first case shows the advantage of ethanol impurity in the production of a traditional petrochemical product. The second case shows the advantage of petrochemical impurity in the production of a product traditionally of the alcohol industry.

Key words: polymers, alcohol, ethanol

1. Introduction

The Companhia Pernambucana de Borracha Sintética (COPERBO), located on km 99 of BR 101, Cabo de Santo Agostinho County, Pernambuco State, Brazil, was established in the 1960's to use ethanol as the raw material to produce polybutadiene homopolymer, a type of synthetic rubber widely used in tire manufacturing.

COPERBO had two units: one for butadiene monomer production and another for polybutadiene production with many specifications. In the butadiene unit, with Union Carbide technology, the ethanol was turned into butadiene in fixed bed reactors, whose catalyst was chrome and copper supported on silica gel, as can be seen in reactions (a) and (b).

$$C_2H_6O \rightarrow C_2H_4O + H_2 \quad \text{(a)}$$
ethanol acetaldehyde hydrogen

$$C_2H_6O + C_2H_4O \rightarrow C_4H_6 + 2H_2O \quad \text{(b)}$$
ethanol acetaldehyde butadiene water

These two are endothermic reactions, and the energy needed by the reactors is supplied by the circulation of thermal fluid. Fig. 1 shows a photograph of COPERBO's butadiene unit.

In the polymerization unit, using *Firestone Tire Company* (currently Bridgestone) technology, the butadiene was turned into polybutadiene in reactors operating on continuous polymerization. The main reaction is the following:

$$C_4H_6 \rightarrow n[C_2H_6] \quad \text{(c)}$$
butadiene polibutadiene

The technology acquired from Firestone was for the production of polymers with medium content of the cis isomer (around 30 to 40%) and low content of vinyl isomer.

In the 1970's, the COPERBO started producing the copolymers butadiene-styrene, initially with the same Firestone technology and, later, with their own technology, the result of research and development

Corresponding author: Rivaldo Souza Bôto, MBA, MSC, PMP; research areas/interests: technologies for the use of naphtha and ethanol as feedstock. E-mail: rboto19@gmail.com.

programs, implemented by the directors at that time. The main reaction was the following:

C_4H_6 $+C_8H_8$ $\rightarrow$ n[C4H6-C8H8] (d)
butadiene + styrene copolymers butadiene-styrene

These were exothermic reactions, and the energy was removed from the reactors by means of circulation with refrigeration water.

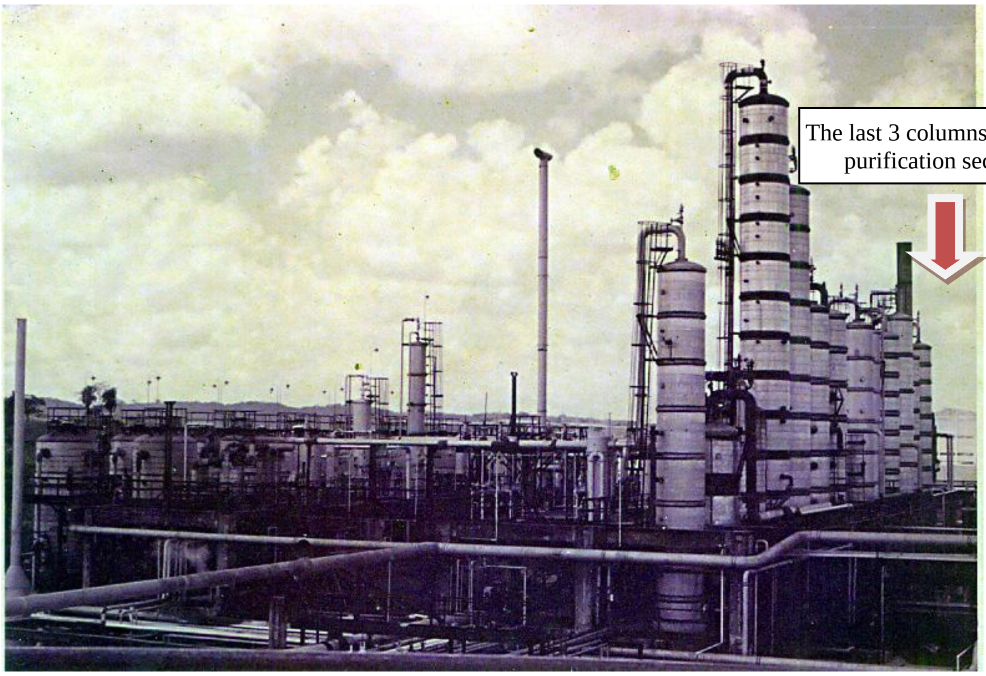

Fig. 1 COPERBO's Butadiene Unit. Photograph courtesy of Carlos Roberto Campos.

COPERBO changed hands many times over the years. At first, it belonged to the government of the State of Pernambuco then in the 1970s is was run by Petrobrás Química SA (PETROQUISA), and was subsequently privatized and successively acquired by several others. Currently, as a new company, it belongs to a joint venture between a company from German and another from Saudi Arabia. The butadiene unit no longer exists, and this polymer is now being supplied by Braskem, located at the Petrochemical Complex of Camaçari. At the moment, the polymerization process uses other technologies from the current shareholders.

The Companhia Alcoolquímica Nacional (ALCOOLQUÍMICA), also located in Cabo de Santo Agostinho County, Pernambuco State, Brazil, next to COPERBO at km 100 of BR 101, was established in the 1980s, using tax breaks from the Alcohol National Plan.

ALCOOLQUÍMICA was a subsidiary of COPERBO established with the purpose of producing vinyl acetate, a product widely used in the manufacturing of PVA (vinyl polyacetate), a raw material for paint manufacturing. The ALCOOLQUÍMICA project was elaborated as part of COPERBO's research and development program in the late 1970s. The vinyl acetate production was characterized by the following main reactions:

$C_2H_6O \rightarrow C_2H_4 + H_2O$ (e)
ethanol ethene water

$C_2H_6O \rightarrow C_2H_4O + H_2$ (f)
ethanol acetaldehyde hydrogen

$C_2H_4O + O_2 \rightarrow C_2H_4O_2 + H_2O$ (g)
acetaldehyde oxygen acetic acid water

$C_2H_4 + C_2H_4O_2 + ½ O_2 \rightarrow C_4H_6O_2 + H_2O$ (h)
ethene acetic acid oxygen vinyl acetate water

The technology needed for ethene production via ethanol (reaction e) used the isothermal process, whose patent was already in the public domain at the time. COPERBO installed pilot reactors to research the best catalyst for dehydration to take advantage of the old reactors from butadiene production for ethene production. The chosen catalyst was activated alumina.

The technology used for production of acetic acid (reaction g) was developed inside COPERBO itself, initially in a lab and then in a semi automatized pilot unit with reactors, absorption and distillation columns, besides other equipment on a smaller scale. The reactors were tubular and used a solution of manganese acetate as the catalyst.

The reactions (e) and (f) took place in units inside COPERBO, which sent the ethene and the acetaldehyde to ALCOOLQUÍMICA, where there were two units. One of the units produced the acetic acid from the acetaldehyde (reaction g), and another unit produced the vinyl acetate, using technology by National Distillers, according to reaction (h). These two reactions were exothermic, and the energy from reaction (g) was removed through the circulation of cooling water, while the energy from reaction (h) was removed through demineralized water, taking advantage of the heat to generate steam. Fig. 2 shows the vinyl acetate unit.

In early 1990s, ALCOOLQUÍMICA ceased being a subsidiary of COPERBO and was privatized. It was successively controlled by several other owners. Currently, ALCOOLQUIMICA has been deactivated and its assets belong to a group of mill owners from Pernambuco State.

Vinyl acetate purification column. At the bottom of this column, the byproducts were concentrated ethyl acetate and butyl acetate.

Fig. 2 ALCOOLQUIMICA's vinyl acetate unit. Photograph courtesy of Carlos Abdenor Neiva Nunes.

2. Cases

2.1 COPERBO Case

At COPERBO's butadiene unit, besides reactions (a) and (b), there we also the formation of several byproducts, the main ones being: ethyl ether, ethyl acetate and butenes. All these byproducts were removed from the process and used in boilers to complement the necessary fuel to generate steam sent to the process.

To meet the specifications of Firestone, the holder of the technology of the polymerization unit, the butadiene to be produced passed through many stages of distillation and absorption to be purified to polymer grade. In the 1970s, preceding export, the butadiene purification system, made up of three columns of series distillation, presented signals of tray obstruction, causing operational problems at the unit. These columns had to be withdrawn from operation to be cleaned, but the unit continued operating, leaving ethyl ether present in the composition of the monomer and, because of that, the butadiene could only reach chemical grade. It was thought that there would be a negative effect of the ethyl ether on the use of the client's rubber. However, surprisingly, it was observed that, instead of being considered out of specification, the rubber sent became a more fitting product for the client, who required that it be made similarly in the following lots.

Posteriorly, it was observed that the oxygen contained in ethyl ether induces an increase in vinyl configuration in the polybutadiene, as is demonstrated by Zeni in the masters dissertation published in 1982 “Reações Fotoquímicas do Polibutadieno com Compostos Carbonílicos” [1]. Given its small installed capacity, compared to other plants outside Brazil, COPERBO has always faced difficulties to export because of its production costs. The discovery that byproducts from the sugar alcohol industry in the composition of butadiene gave other qualities to the rubber, conferred COPERBO greater competitive power in recognition for its added value. For that reason, COPERBO not only managed to reduce production costs with less energy consumption in butadiene manufacturing, but it also started to produce better rubber for some clients.

2.2 ALCOOLQUÍMICA Case

Traditionally ethene is obtained from petrochemical naphtha, the acetic acid from natural gas, whilst oxygen is obtained by fractionation of air. For ALCOOLQUÍMICA, ethene sugar alcohol, with polymer grade purity was planned. The ethene produced from ethanol contains butene, ethyl ether, hydrogen and CO_2 as main byproducts.

The greatest selectivity temperature for the formation of ethene, for the kind of catalyst used, was 360°C. A lower temperature would favor the butene and ethyl ether formation, while a higher temperature would favor the formation of CO_2 and hydrogen. To obtain the polymer grade purity, besides the section of reaction, the ethene unit had a purifying section with distillation towers. At COPERBO, as the isothermal process ensured stability in the reactor temperature, with almost no hydrogen or CO_2 formation, the non-installation of the purifying section was chosen. It was observed that the reactor temperature control handled the presence of butene in the ethene, and that there was formation of ethyl acetate and butyl acetate in the vinyl acetate reactor, products that are still imported to complement the national consumption in Brazil.

Vinyl acetate production, along with the ethyl acetate and butyl acetate, enabled the operational improvement of ALCOOLQUÍMICA.

3. Technological Scenario

COPERBO and ALCOOLQUÍMICA, like many others sugar alcohol industries in Brazil, had difficulties competing in the market because of high production costs. In 1972, COPERBO altered its process route, as reported by Dantas R, in his article “Por que a COPERBO mudou sua rota”, published at Química e Derivados magazine, in August 1983, 600 number, pages 5 to 10 [2]. In 1990, ALCOOLQUÍMICA abandoned the use of ethene and acetic acid, locally produced from sugar alcohol, to ethene via naphtha from BRASKEM, and importing acetic acid.

The wide range of passive, obtainable products, not only from ethanol, but from a general sucrochemical source, is large, as shown in Fig. 3, taken from the book Química Verde no Brasil 2010-2030, p. 197 [3].

In the books “Bioetanol de Cana de Açúcar, Energia para o Desenvolvimento Sustentável” [4] and “Etanol, a Revolução Verde e Amarela” [5], various alternative products of sugar alcohol sources are mentioned.

In our understanding, the use of ethanol as a raw material, simply producing hydrocarbons such as ethene (see reaction e), or butadiene (reaction b), due to the need for an OH^- radical in the form of H_2O, which is discarded in the process, makes little sense. When it happens, there is a loss of approximately 39% of the raw material mass, which, associated to the small integration that exists in the chain of the sugar alcohol industry, generates a decrease in the competitive power for the final products in Brazil.

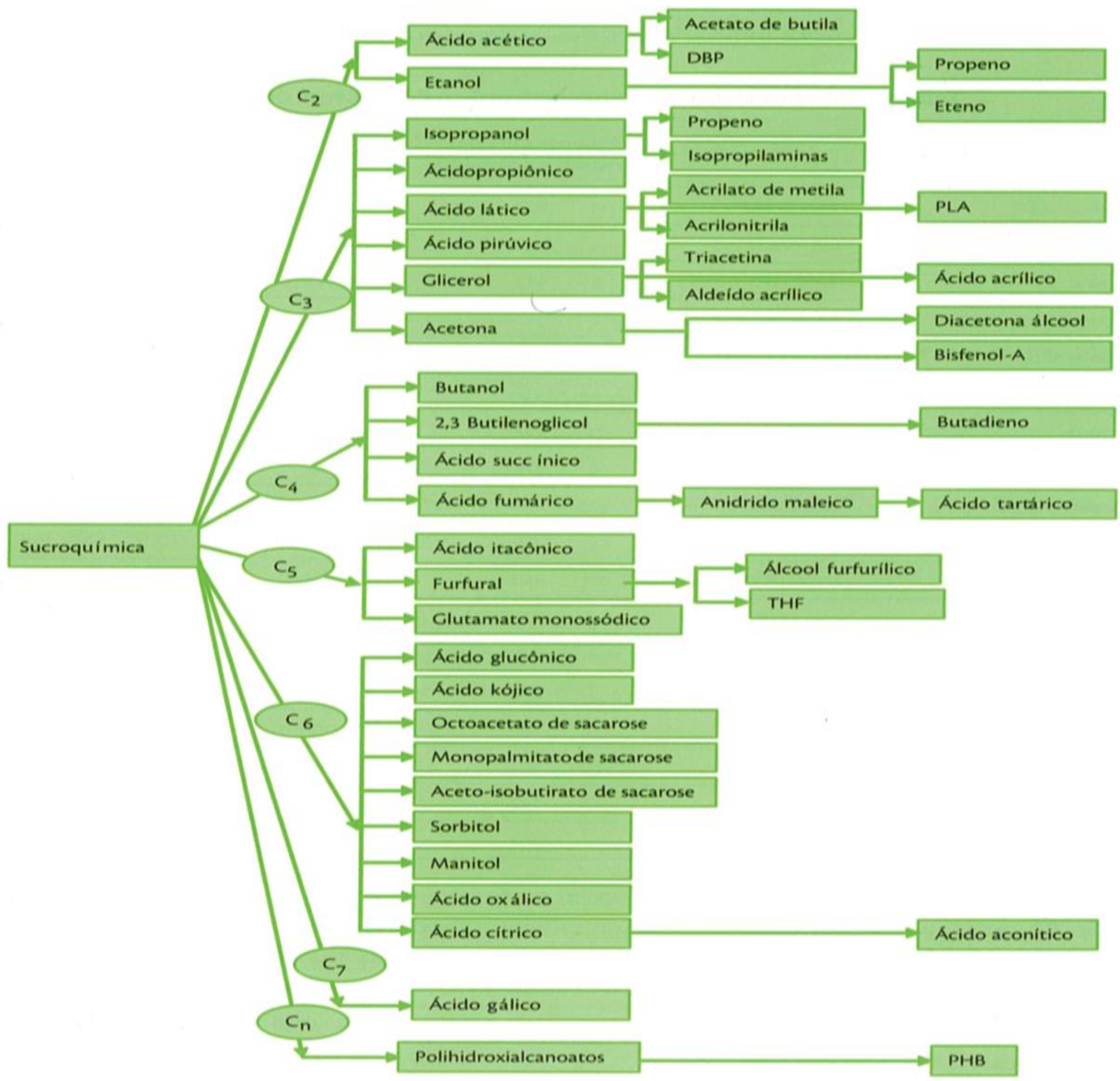

Fig. 3 Products by sucrochemicals. Book Química Verde no Brasil 2010-2030, p. 197.

On the other hand, according to the Química e Derivados magazine, number 600, April 2019, page 6 [6], it can be seen that many sugar alcohol products have reasonable commercial value and require importation to complement national goods, creating opportunities for the Brazilian industries to enhance profits and support the Brazilian Trade Balance.

According to the Anuário Estatístico Brasileiro do Petróleo, Gás Natural and Biocombustíveis 2018, pages 107, 127, 131, published by Agência Nacional do Petróleo (ANP) Brazil [7] does not produce enough naphtha to supply the national industry. In 2017 Brazil imported 10,412 thousand m^3, which corresponded to 77.1% of apparent consumption. This import, whose value in FOB was U$ 3.4 billion, represented 26.4% of the Brazilian spending on petroleum derivatives.

4. Conclusions

We understand that the most adequate model would be a hydrocarbon integrated production of petrochemicals and alcoholic routes. This would give Brazilian industry would have greater competitive power. In Bôto's masters dissertation (2014), "Etanol e Demais Derivados da Cana de Açúcar para Produção de Polímeros Plásticos" [8], examples are given.

Sadly, as shown in pages 126 and 128 of the book Química Verde no Brasil 2010 to 2030 [3], Brazil has a very limited research into the alcohol route and without the vision of hybrid tecnhologies.

Brazil needs to develop research to apply hybrid technologies, as successfully happened during the National Alcohol Program in the 1970s and 1980s. Therefore, a government program to establish goals with incentives for further education and the private initiative is necessary.

References

[1] M. Zeni, Dissertação de Mestrado: Reações Fotoquímicas do Polibutadieno, 1982.

[2] Com Compostos Orgânicos, Instituto de Química da Universidade Estadual de Campinas, SP.

[3] R. Dantas, Por Que a Coperbo Alterou Sua Rota, Revista Química e Derivados, Número 203, Agosto 1983, pp. 5-10.

[4] Banco Nacional de Desenvolvimento Econômico e Social, Química Verde No Brasil 2010-2030, Centro de Gestão e Estudos Estratégicos, Brasília, DF. (2010),

[5] Banco Nacional de Desenvolvimento Econômico e Social, Bioetanol de Cana de Açúcar - Energia para o Desenvolvimento Sustentável, Editora do Departamento de Divulgação do BNDES, Rio de Janeiro. (2008),

[6] O. Fischetti, A Revolução Verde e Amarela, Editora Bizz Comunicação e Produções, 2008.

[7] Revista Química e Derivados, Número 600, Ano LIV, Abril 2019, p. 6.

[8] Agência Nacional do Petróleo, Anuário Estatístico Brasileiro do Petróleo, Gás Natural e Biocombustíveis 2018, pp. 107, 127, 131, Rio de Janeiro RJ.

[9] R. Bôto, Dissertação de Mestrado Profissional: Etanol e Demais Derivados da Cana de Açúcar Como Matérias Primas na Indústria de Polímeros Plásticos, Universidade Federal da Bahia, BA, 2014.