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PROTON PIONEERS

Anhydrous Ethanol Production Using Membrane Technology

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- INTRODUCTION -

Background

Fuels are an essential, irreplaceable energy source known for their reliability and energy density that have allowed us to thrive in colder climates and expand our traveling capabilities. With the impending impacts of climate change and goal to limit global warming to 1.5 degrees C, it has become crucial to reduce our reliance on fossil fuels and adopt renewable energy sources.

The transportation sector accounts for approximately 30% of global greenhouse gas (GHG)emissions. A current common practice to tackle this significant issue is to blend anhydrous ethanol (>99.5 wt%) into gasoline to increase its octane content resulting in a cleaner combustion. This alone has resulted in a reduction by around 30% in carbon monoxide CO emissions and 20% in smog or hydrocarbon (HC) emissions at the tailpipe.

The Issue

Ethanol-water mixtures form an azeotrope at 95 wt%. making it difficult to further purify using conventional distillation to reach the desired purity and produce anhydrous ethanol. The most widely used method to dehydrate ethanol in Brazil is azeotropic distillation using cyclohexane as an entrainer, an energy intensive process with major safety and environmental concerns, due to concerns of toxicity and adverse human health effects from cyclohexane exposure.

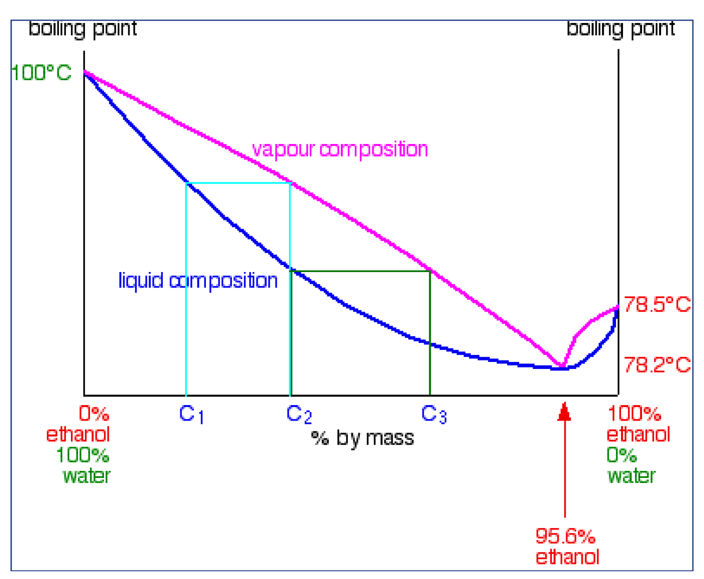


Figure 1. Graph of ethanol-water azeotropic point
https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Equilibria/Physical_Equilibria/Fractional_Distillation_of_Non-ideal_Mixtures_(Azeotropes)

Our Solution

To design a process that completely replaces azeotropic distillation that is more energy-efficient, safer and environmentally responsible. The process utilizes Whitefox membranes to produce anhydrous ethanol at 99.3 wt%. The distillation unit in our process uses vapor injection from the sugar pre-evaporation process instead of reboiler steam, and the stripper column in our dehydration unit utilizes bagasse, instead of conventional natural gas, for steam generation.

Project Drivers

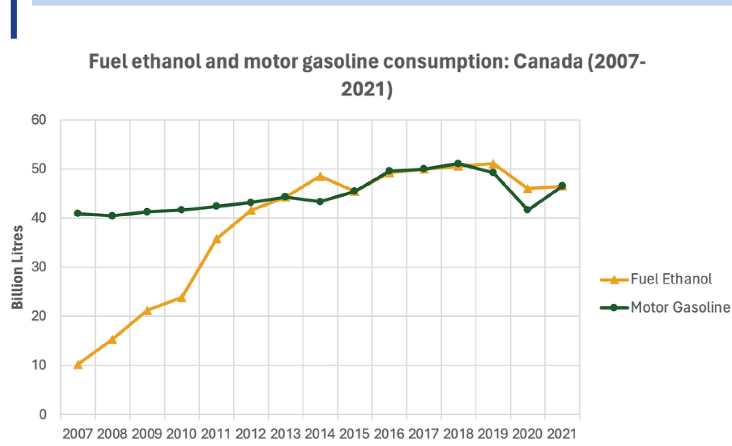


Figure 2. Fuel ethanol consumption 2007-2021
https://www.iea.org/data-and-statistics/charts/ethanol-and-gasoline-prices-2019-to-april-2022

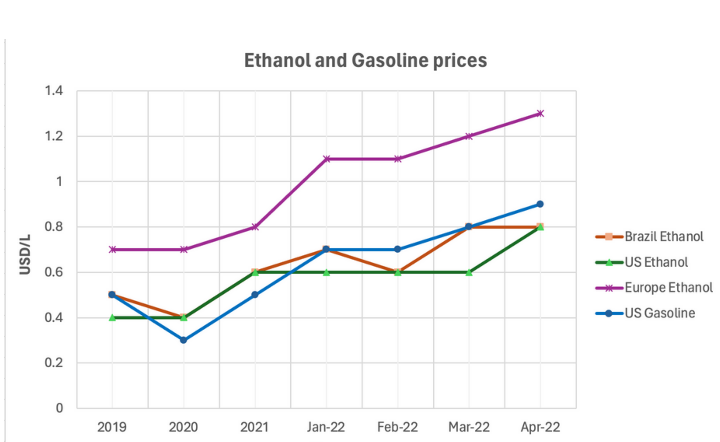


Figure 3. Ethanol fuel price over the years (Santos, Brazil)
https://grains.org/ethanol_report/ethanol-market-and-pricing-data-january-18-2023/

The main incentive to dive into the anhydrous ethanol market is mostly the increasing worldwide demand. Figure 1 outlines the increasing fuel ethanol consumption, while Figure 2 highlights the volatile but increasing fuel ethanol price in Brazil. In summary:

- Ethanol consumption in Brazil (2022) was 30.4 billion L.
- Ethanol production in Brazil (2023) projected to be 32.95 billion L.

These Ethanol market trends observed are caused by various social and legislative acts implemented in the past and recently. Notably:

- Canadian Net-Zero Emissions Accountability Act - passed in 2021
- Brazilian mandate to blend Ethanol into fuel supply - passed in 1930s

- PROCESS OVERVIEW -

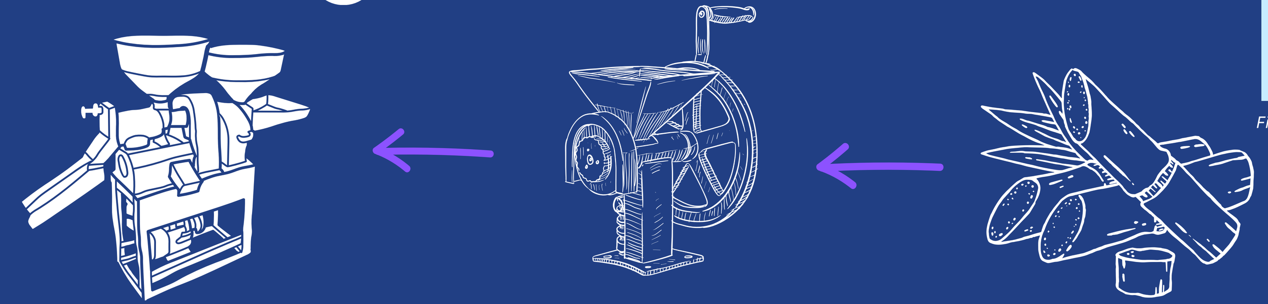
Plant Location: São Paulo State, Brazil

Operational: 180 days/year, May-October

Production Capacity: 230 m³/day anhydrous ethanol

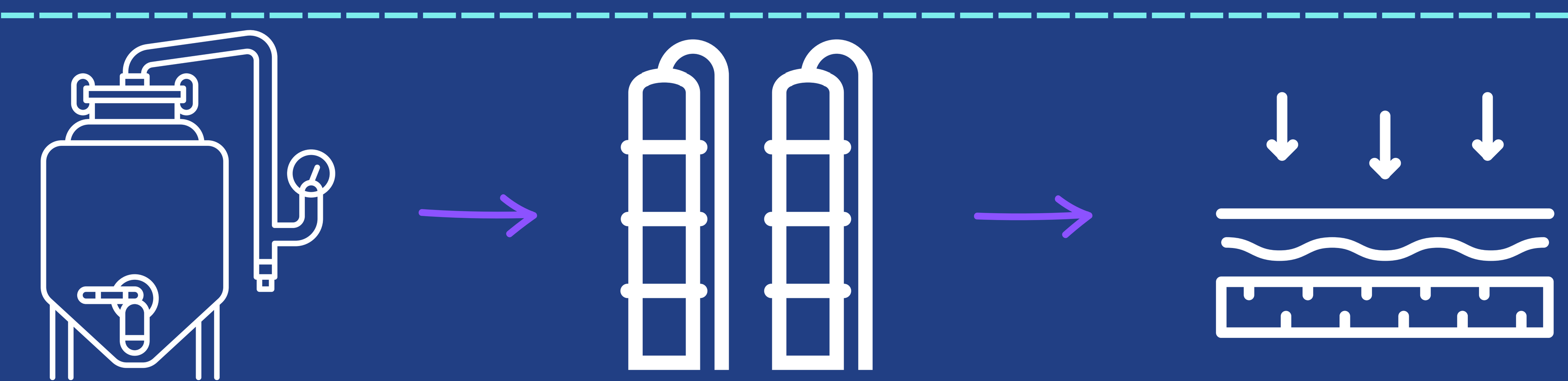
Figure 4. Proton Pioneers' plant location, São Paulo State

1. Freshly harvested sugarcane arrives at plant for treatment and milling



2. Extracted sugarcane juice, at a concentration of ~200g/L sucrose, is diverted to distillery for ethanol production

Distillery



3 Fermentation

~ 40 Degrees C. — Atmospheric Pressure

- Ethanol Fermentation: A biological process whereby microorganisms metabolize sugars producing ethanol and carbon dioxide (CO_2) as by-products.
- It is the initial step to producing ethanol, conducted under anaerobic conditions.
- The solution collected at the conclusion of the fermentation cycle is referred to as *wine* composed of 10-12 wt% ethanol, ~86 wt% water, and trace amounts of solids and non-condensables such as CO_2
- Two main reaction mechanisms:

1. Hydrolysis - $C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$
2. Glycolysis - $C_6H_{12}O_6 \rightarrow C_2H_5OH + 2CO_2$

Residence Time: 10-12 Hours

Yeast Strain: *S. Cerevisiae*

4 Distillation

of Sieve Trays - Column 1: 24 Trays; Column 2: 54 Trays

Tray Efficiency of 60%

- Simulated with SLB's Symmetry process simulation software.
- Both columns use direct vapour injection to drive the process and pressure gradient. On average, 3.5 kg of vapour is consumed per kg of ethanol produced.
- The wine enters the first column in tray 1 pre-heated to 85 degrees C, just below the bubble point using the bottoms at 112 degrees C and 150 kPa. The bottoms are referred to as vinasse which is primarily water rich in organic matter such as phosphorus, potassium, and nitrogen.
- A side-stream vapour draw is taken from the 4th tray with a composition of ~50 wt% ethanol injected into the 8th tray of column 2. Hydrous ethanol (93 wt% ethanol) is recovered in the overhead product and sent to the dehydration unit.

5 Dehydration

Tubular Hollow Fiber, Vapour Permetation Membrane

Medium Selectivity

- Dehydration consists of two main units: the Whitefox stripper column and anhydrous ethanol membrane separator.
- Whitefox membranes are modular and scalable allowing great flexibility over their configuration and operation.
- The membrane is hydrophilic allowing the water to permeate through at a concentration of ~30 wt% ethanol, retaining anhyrdrous ethanol at a purity of 99.3 wt% which is condensed and sent to storage.
- Operating pressure on the permeate side is 500kPa with a 50 kPa drop across the membrane, while the retentate is maintained at a moderate plant vacuum of 30 kPa.
- The stripper tower is used to vaporize and pressurize the hydrous ethanol feed entering the membrane. It is also used to recover ethanol from the permeate/recycle stream.

ACKNOWLEDGEMENTS

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- SAFETY & ENVIRONMENT -

Safety Risks

- Ethanol's High Flammability
- High Pressure Membrane
- High Temperature Distillation
- Leakage
- Human Error
- Fluctuating Wine Impurities

Safety Mitigations

- Proper Ventilation
- Pressure Rated Membrane Casing
- Frequent Equipment Maintenance
- Control System
- Sensors & Alarms
- Operator Training and PPE

Environmental Concerns

Land Use

- Indirect land-use changes need to be addressed to avoid unintended harmful consequences.
- Sugarcane cultivation can lead to soil erosion, degradation, and conflict with food production.
- Increasing crop yield and utilizing marginal land can improve sustainability efforts.

Water Consumption

- Significant cooling water consumption requirements however, a majority of it is recovered throughout the process.
- Vinasse commonly used for fertigation purposes.
- To prevent thermal pollution, cooling water return temperature is limited to 45 degrees C.

Emissions

- Approximately 200 t/d CO_2 produced during fermentation
- High purity (>95%), will be captured and utilized in industry
- Bio-ethanol production can be considered net-zero as CO_2 emissions are negated by CO_2 sequestered during sugarcane cultivation

- FINDINGS -

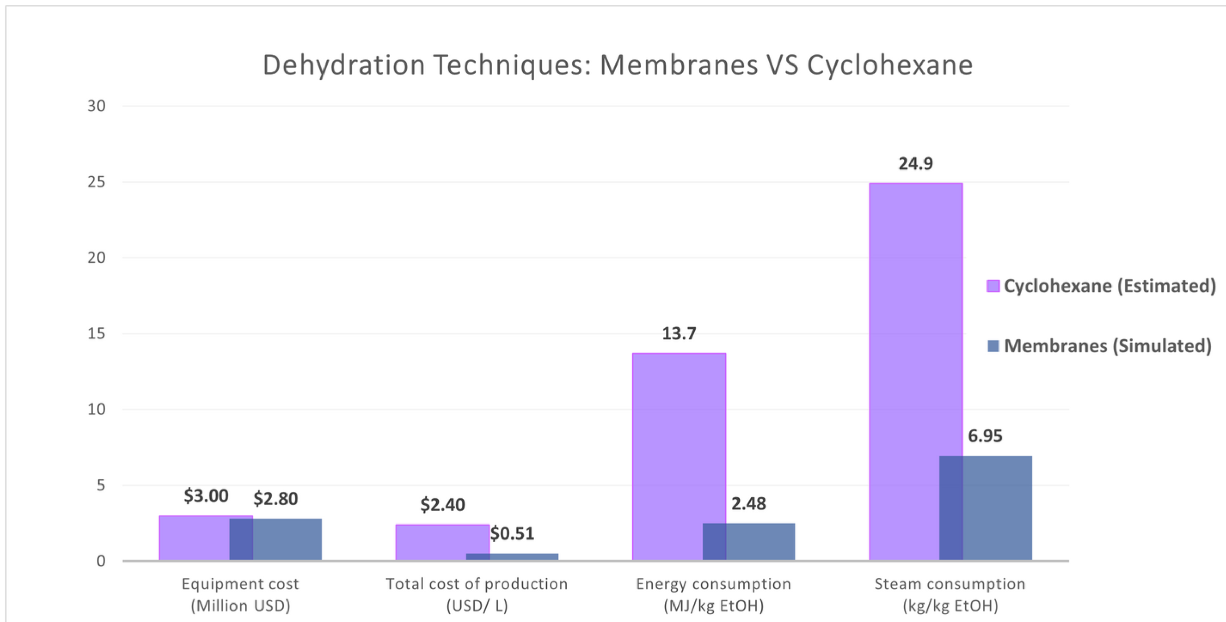

Figure 5. Advantages of Membrane Dehydration Compared to Cyclohexane

As summarized, the Whitefox membranes show extended benefits in terms of economics, safety and operability. This is due to multiple factors:

- The higher equipment cost for dehydration using cyclohexane entrainer (**~$3 million USD**) can be attributed towards the material of equipment required due to the toxic properties of cyclohexane. Additionally, cyclohexane entrainer systems call for a more complex plant layout with additional equipment (distillation columns, recovery columns, etc.) in comparison to the Proton Pioneers' plant that utilizes membrane dehydration technology (equipment cost of **$2.8 million USD**)
- Membrane dehydration shows lower cost of production (**$0.51 USD/L**) mainly due to the evident difference in energy and steam consumptions. Moreover, membrane dehydration systems are shown to require less maintenance than cyclohexane entrainer systems (cost of production **~$2.40 USD/L**). This is due to the comparatively simplistic design and fewer equipment in membrane dehydration systems.
- Dehydration using cyclohexane entrainer has higher energy and steam consumption (**13.7 MJ/ Kg EtOH, 24.9 Kg steam/kg EtOH**) than the membrane unit (**2.48 MJ/ Kg EtOH, 6.95 Kg steam/kg EtOH**). This difference is due to the high thermal energy requirement in the distillation process and the additional energy needed for the recovery and recycling for the entrainer.
- Membrane separation is safer than dehydration using cyclohexane because it minimizes the risk of chemical exposure and environmental emissions of volatile organic compounds.