

Overview of the CRYOCAP Studies

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The purpose of this paper is to analyze the technological innovations of Air Liquide's CRYOCAP process on an in-depth level to help people with varying scientific backgrounds understand the inner workings of this carbon capture solution. Air Liquide's carbon capture technology centers around the pre-concentration of power plant flue gas in a cold membrane followed by a partial liquefaction step that produces a gaseous stream of CO₂ that meets Enhanced Oil Recovery standards.^{1,2} The 0.3 MWe field test unit was used to assess the performance of hollow fiber, polyimide (PI) bundles in cold membrane operations.^{1,2} The first study focused on testing commercial bundles fabricated from PI-1 fibers, and the re-commissioned study served to validate the superior performance of bundles made from PI-2 material.^{1,2} These studies confirmed that the hybrid membrane and liquefaction process developed by Air Liquide enables greater than 90% CO₂ recovery from pretreated flue gas, greater than 98% CO₂ purity in the gaseous, product stream, and a capture cost lower than \$40/tonne.²

Membrane Bundle

Polyimide Material

Membrane bundles made from PI-1 and PI-2 fibers were studied to quantify CO₂/N₂ selectivity and gas permeability, factors that are instrumental to the gas separations approach of carbon capture. It is important to first understand the basics of the chemistry behind polyimides before diving into the fibers' properties behind the membrane's success. Polyimides are a type of polymer that belong to a class of high performance plastics.³ A polymer is a substance that consists of large molecules composed of monomers which are the multiple repeating subunits.³ As the name suggests, polyimides are composed of imide monomers comprising two acyl groups, composed of a carbon that has a double bond with oxygen, bound to nitrogen.³

Aromatic polyimides tend to be defined by their rigid backbones and strong intermolecular interactions that can limit the range of applications.⁴ These aromatic polyimides are notable for their increased stability due to the cyclic, usually planar molecular structures.⁵ The ring shaped structures are typically composed of alternating single and double bonds which allows for the delocalization of electrons around the ring.⁵ The positioning of these electron orbitals outside of the atomic plane is responsible for the "sharing" of electrons by all carbon atoms in the ring.⁵ These shared electrons serve to equally strengthen all bonds formed in the ring which is the primary mechanism behind the increased stability of aromatic molecules.⁵

Despite the rigidity of most aromatic polyimides, research efforts have introduced flexible linkages and bulky substituents into the backbone of polyimides like PI-1 and PI-2 to overcome the limitations in applicability and to preserve notable properties like high thermal stability, good solvent resistance, excellent light stability, and mechanical strength.⁶ The addition of linkages like ether, isopropylidene, and phosphine oxide are responsible for increased mobility in the polyimide chains, and hindered molecular packing similarly reduces interchain interactions.⁴ These linkages and reduced interchain interactions enable PI-1 and PI-2's enhanced solubility in organic solvents compared to purely aromatic polyimides.⁴ Both polyimide's high thermal stabilities are indicative of their ability to maintain their physical properties at temperatures reaching as low as -50 °C and exceeding that of 200 °C.^{4,7} Not only are PI-1 and PI-2 resistant to the influence of heat or lack thereof, both polyimides are resistant to degradation when exposed to solvents which are chemicals used to dissolve, dilute, or disperse other compounds.⁸ This resistance to degradation is important in the carbon capture process as it prevents the microscopic polyimide fibers in the cold membrane from degrading when exposed to contaminants that bypass the pretreatment filtration steps of the system. As shown in Figure 1, PI-1 and PI-2 also exhibit superior CO₂/N₂ selectivity at lower temperatures compared to other polymer membranes.

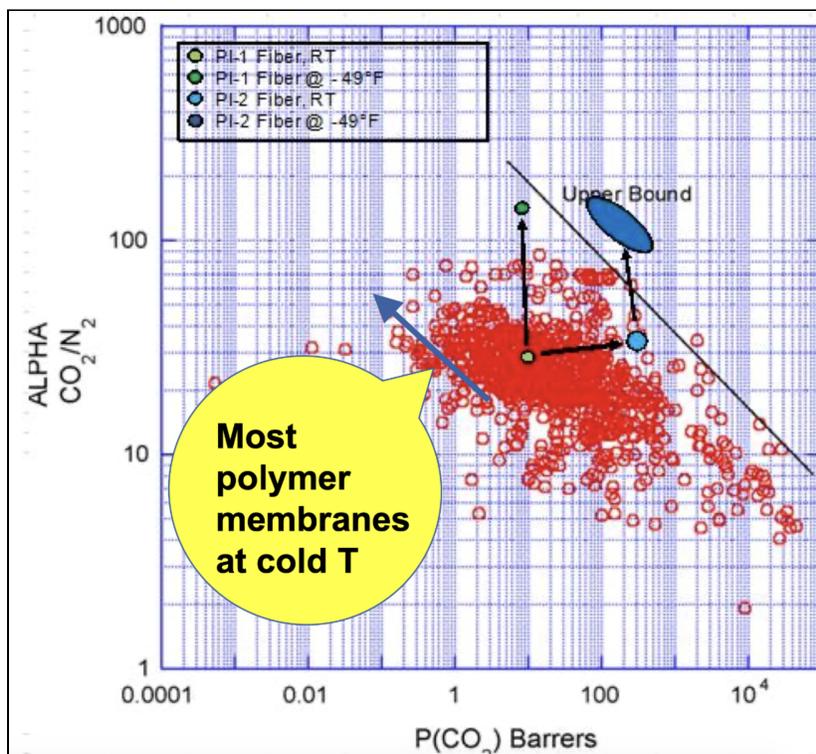


Figure 1. PI-1 and PI-2's superior CO₂ selectivity at cold temperatures. Reprinted from "CO₂ Capture by Cold Membrane Operation with Actual Power Plant Flue Gas and Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules," by A. Augustine, T. Chaubey, R. Gagliano, S. Kulkarni, S. Fu, D. Hasse, T. Li, D. Kratzer, R. Warwick, W. Wheeler, R.

Hutchinson, M. J.-M. Gauthier, and M. Bennett, *2017 NETL CO2 Capture Technology Project Review Meeting*, Pittsburgh, Pennsylvania.

Though PI-1 and PI-2 are analogous compounds, there are key structural differences that translate to PI-2 having a four to five times higher bundle productivity than PI-1.¹ Measurements related to the polyimides' thermal stability have been taken in a laboratory setting that determined PI-1 to have a glass transition temperature of 229 °C and PI-2 to have a lower glass transition temperature of 215 °C.⁴ The glass transition temperature marks the temperature at which an amorphous material, one defined by a lack of long-range order, transitions from a glassy state to a rubbery state.⁹ Below the glass transition temperature, the polyimide's glassy state is marked by molecules "frozen" in place which is responsible for the rigidity of the material in this phase.⁹ Above the glass transition temperature, the rubbery state is marked by increased molecular mobility, still short of complete free flow, which increases the material's flexibility.⁹ There is no change to the chemical structure associated with this transition, rather a shift from the rubbery to the glassy state marks a "physical aging" of the compound.¹⁰ PI-2's slightly lower glass transition temperature and increased thermal stability is attributed to the addition of the phosphine oxide unit in the PI-2 chain, as shown in Figure 2, which increased the flexibility of the chain compared to that of PI-1.⁴ These slight differences in chemical structure between PI-1 and PI-2 are responsible for the quantifiably better performance of membrane bundles formed from PI-2 fibers.

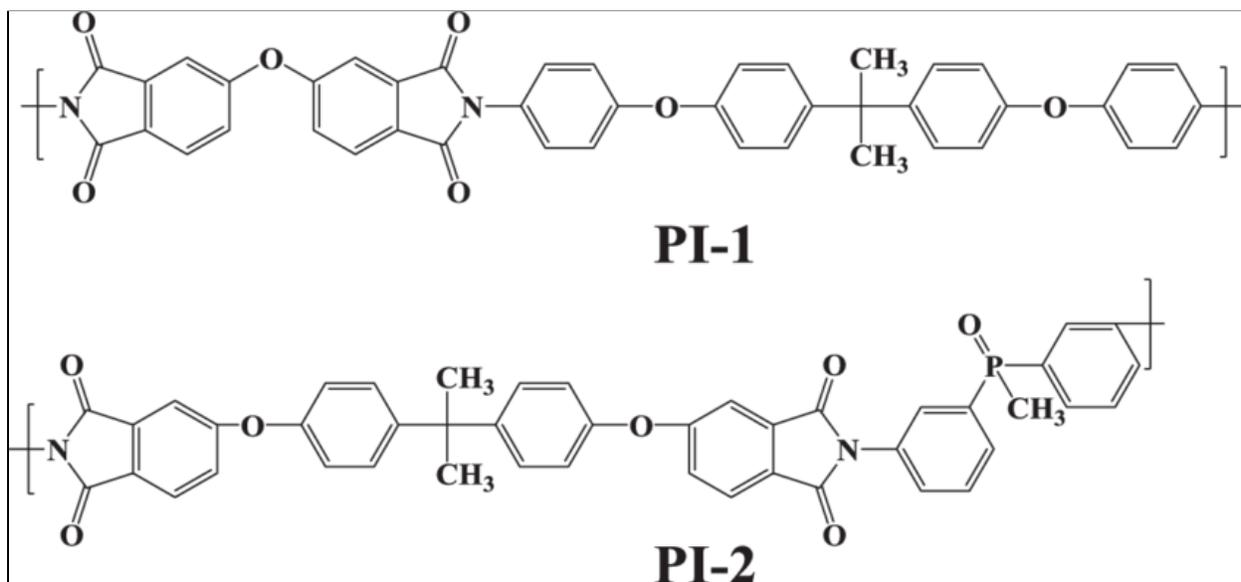


Figure 2. Chemical structures of PI-1 and PI-2. Reprinted from "Physical and thermal properties of poly(ethylene terephthalate) fabric coated with electrospun polyimide fibers," by I. Butnaru (former Bacosca), D. Serbezeanu, M. Bruma, I. Sava, G. Sabyasachi, and G. Fortunato, 2015, *High Performance Polymers*, 27, 616-624. Copyright 2015 by SAGE Publishing.

Manufacturing Technique

Though there is limited information about the specific manufacturing technique employed by Air Liquide as it's likely proprietary information, it is reasonable to assume that electrospinning was utilized to create the polyimide fibers for the membrane. The electrospinning process uses the electrohydrodynamic phenomena to create a thin string of fiber from a liquid polymer solution.¹¹ This phenomena dictates the behavior of electrically charged fluids, and the basic configuration for electrospinning typically involves a syringe-like reservoir that contains the liquid polymer solution and has a needle tip, a pump, a power source, and a collector.¹¹ A voltage is applied to the needle tip and the collector to create an electric field between the two surfaces.¹¹ As the polymer solution is pumped through the needle tip, the generated electric field creates electrostatic repulsions on the surface and exerts a Coulombic force that induces an electric charge on the liquid surface.¹¹ Once the droplet's surface tension is weaker than the electrostatic repulsions, a conical shape is formed, and the polymer stream is ejected to the collector's surface.¹¹ As the solution travels from the needle to the collector, the whipping motion that occurs during the material's flight causes the solvent to evaporate, leaving solid fibers to form on the collector's surface.¹¹ This process produces a non-woven, nanofibrous mat that is deposited on the collector's surface.¹¹ A diagram depicting this general process is shown below in Figure 3.

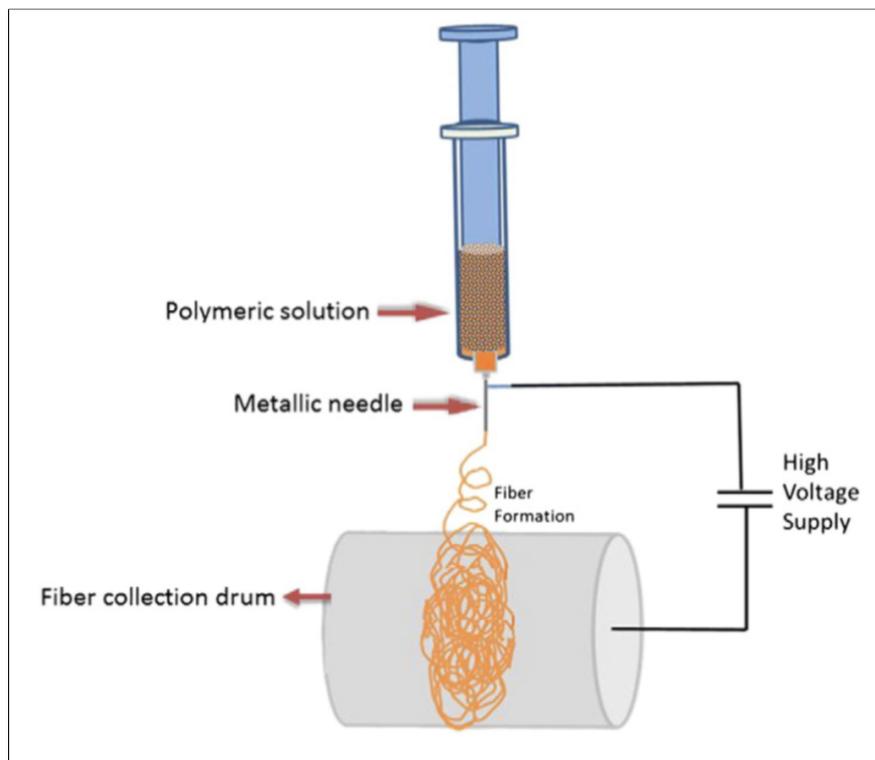


Figure 3. Simplified electrospinning process for fiber production. Reprinted from “A review on electrospinning for membrane fabrication: Challenges and applications,” by F. E. Ahmed, B. S. Lalia, and R. Hashaikeh, 2015, *Desalination*, 356, 15-30. Copyright 2022 by Elsevier B.V.

After being deposited on the container, the fibers go through a washing, drying, and bobbin winding process to prepare for bundle manufacturing.¹² Although Air Liquide's specific manufacturing approach is largely obscure, there is related information in a patented manufacturing technique to produce hollow fiber membranes that details the necessary steps. The washing and drying steps are used to strip the fibers of any contaminants and evaporate any remaining solvent while preserving the pore structure of the fibers, a crucial step as it determines the characteristics of the final membrane.¹³ Once the fibers are dried, they are wound around a bobbin to create a spool of polyimide fiber that is ready to use in the forming process.¹² Using machinery, the polyimide fibers are arranged in a parallel fashion around the bundle core with a tubesheet of the same material at each end of the membrane.¹³ This produces hollow fiber, polyimide membrane whose length can be tailored to fit the process' applications.

This electrospinning technique offers an inexpensive, commercial production of nonwoven, hollow fiber membranes that exhibit low resistance and mechanical stability during the gas separations process.¹⁴ The simplicity and reliability of this technique allows for the preparation of smooth nanofibers with controllable structures from a wide range of polymers.¹⁵

How It Works

The CRYOCAP membrane utilizes a solution-diffusion transport mechanism to produce a CO₂ rich, low pressure permeate stream and an N₂ rich, high pressure retentate stream.^{1,15} In a simplified, step-by-step description of the mechanism, CO₂ first dissolves into the polyimide matrix, then moves along the polyimide chains to free volume areas, which is dictated by the concentration gradient, and finally evaporates on the other side of the membrane.¹⁶ The microscopic pores of the polyimide membrane are responsible for the free volume areas, and this interconnected pore structure enables higher flux to be maintained, and thus a more efficient membrane, by creating shorter paths for molecular diffusion.¹⁵ Additionally, the introduction of polar groups into the polyimide increases the solubility of CO₂ relative to N₂ because of CO₂'s strongly polar bonds, and this increases CO₂ permeance as well as CO₂/N₂ selectivity, ultimately leading to superior membrane performance.¹⁷ Ultimately, the PI-1 and PI-2 membranes exhibited high productivities due to the polyimides' high CO₂ fluxes, high CO₂/N₂ selectivities, thermal, chemical, and mechanical stabilities, resistance to plasticization, cost effective production, and ability to be manufactured in different size/shape membrane modules.¹⁶

It is helpful to visualize and understand the set-up of the membrane in order to comprehend the mechanics of the overall gas separations process. Though there are no diagrams of the membrane officially released by Air Liquide, it is useful to use diagrams of conventional membrane modules, such as Figure 4 below, to visualize the gas separation process.

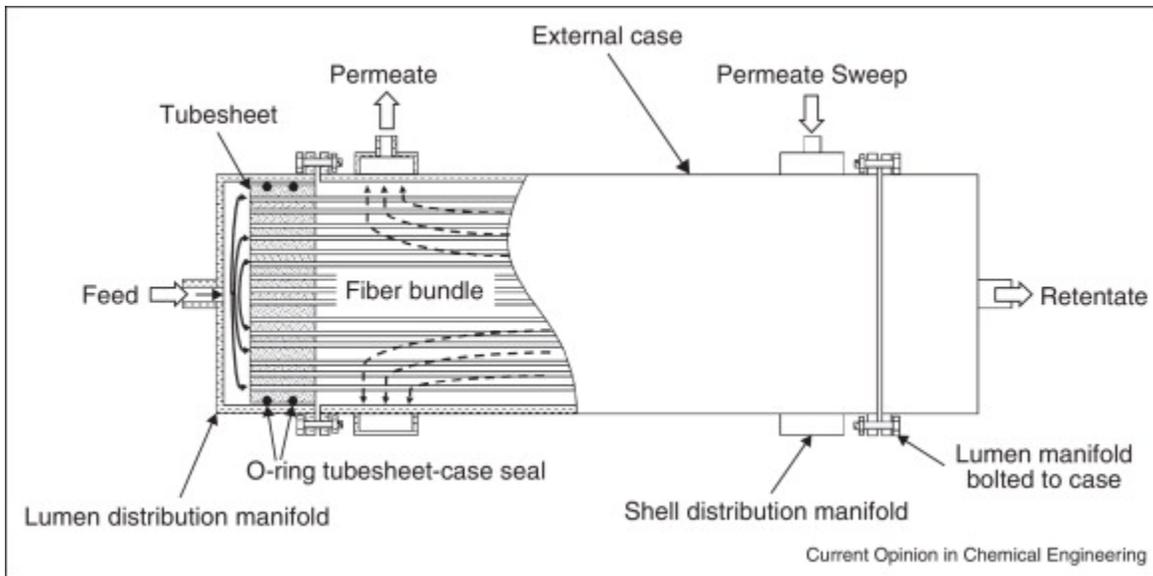


Figure 4. Conventional membrane model for gas separations. Reprinted from “Hollow fiber membrane modules,” by N. C. Mat, Y. Liu, and G. G. Lipscomb, 2014, *Current Opinion in Chemical Engineering*, 4, 18-24. Copyright 2022 by Elsevier B.V.

The feed stream enters from one side of the membrane module. As the pretreated flue gas travels through the membrane module, the CO_2 molecules interact with the polar chains of the polyimide and travel perpendicularly to the feed stream. The nonpolar N_2 molecules, uninfluenced by the polar groups in the polyimide chains, continue in the direction of the feed stream to the opposite end of the membrane. There is also a sweep stream, containing three to five percent of the retentate gas stream, that enters on the permeate side of the membrane to lower the partial pressure of the permeate species, CO_2 , which increases the pressure gradient and thus the driving force.¹ The membrane is operated at a low temperature of around $-45\text{ }^\circ\text{C}$.¹ Importantly, at temperatures below $-20\text{ }^\circ\text{C}$, CO_2 's solubility increases by roughly three-fold and its diffusion coefficient drops by about two-fold.¹⁸ Meanwhile, the opposite property changes occur with N_2 , leading to an increase in the CO_2/N_2 selectivity.¹⁸ This process produces a low pressure, CO_2 rich permeate stream with a CO_2 purity greater than 62% and a high pressure, N_2 rich retentate stream.¹ The membrane can be run continuously for long periods of time as it does not show fast decay in performance when the risk of moisture contamination is reduced and because the flue gas feed stream doesn't chemically react with the membrane, the membrane does not get saturated and avoids frequent shutdown and start-up.¹⁹ The cold membrane is the first major step in producing an almost 100% pure stream of CO_2 .

CRYOCAP Schematic

Simplified Process Diagram

A simplified process diagram can be useful to summarize the main steps such that the general process can be understood at a glance. The trademarked CRYOCAP technology here is specifically tailored to the reduction of CO₂ emissions from flue gas, though Air Liquide has developed similar innovations for steel production, hydrogen production, and oxycombustion.²⁰ Walking through a simplified flow diagram, as shown in Figure 5, can help establish the scientific foundations of the successful capture technique.

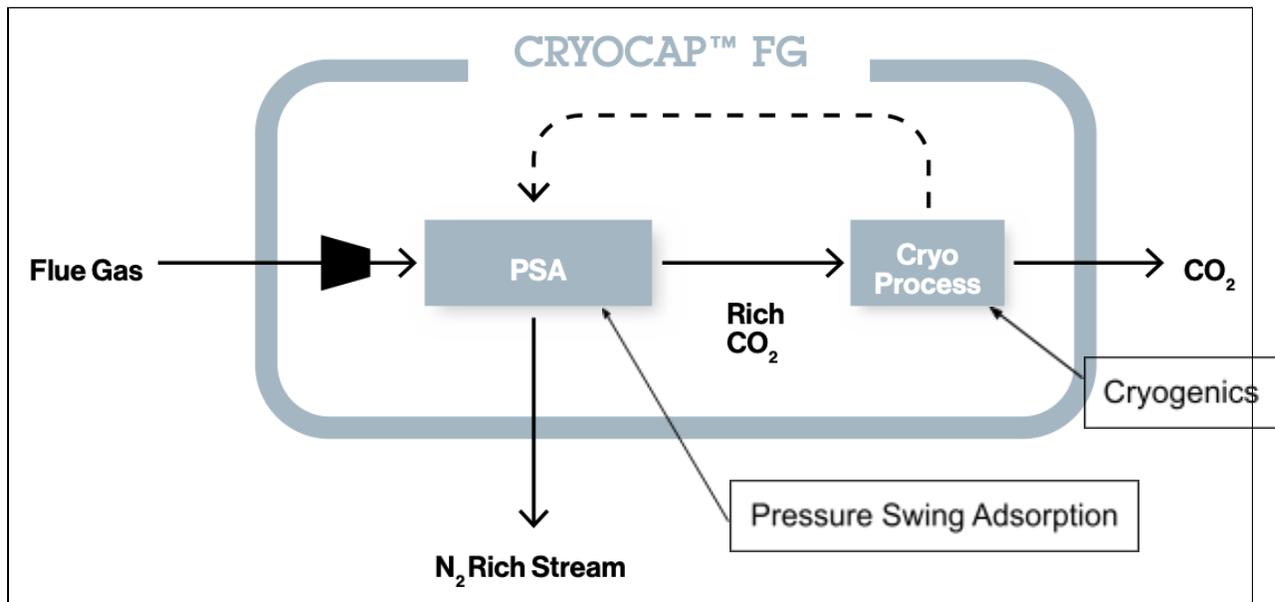


Figure 5. A simplified flow diagram that depicts the CRYOCAP set-up. Reprinted from “CRYOCAP Carbon Capture Technologies,” 2021, *Air Liquide*. Copyright 2022 by Air Liquide.

Walking through the elementary steps of the schematic greatly simplifies an initially daunting process. After fossil fuel combustion, the flue gas is compressed, as shown by the black trapezoid in the diagram, and enters the polyimide membrane which is where pressure swing adsorption occurs.²⁰ Here, pressure swing adsorption is used to separate CO₂ from the flue gas stream by incurring a pressure gradient between the high pressure feed stream and low pressure regeneration and by utilizing CO₂'s affinity for the polyimide material.²¹ This membrane step produces a CO₂ rich stream and an N₂ rich stream.²⁰ The gaseous, CO₂ rich stream then moves to the cryogenics, liquefaction step.²⁰ In the cold box, the cold temperature is used to partially liquefy the CO₂ rich stream which acts as a secondary purification step.²⁰ The gaseous CO₂ is recycled back to the membrane to increase the overall percent of CO₂ captured by the process, and the liquid stream of essentially pure CO₂ is the final product.²⁰

Detailed Process Diagram

Having established the foundations for the carbon capture technique, delving into the details is important to understand how the unique techniques Air Liquide capitalizes on create a cost-competitive capture process that could potentially expand to the commercial scale. The figure below, Figure 6, was created to illustrate the conditions at each step of the process.

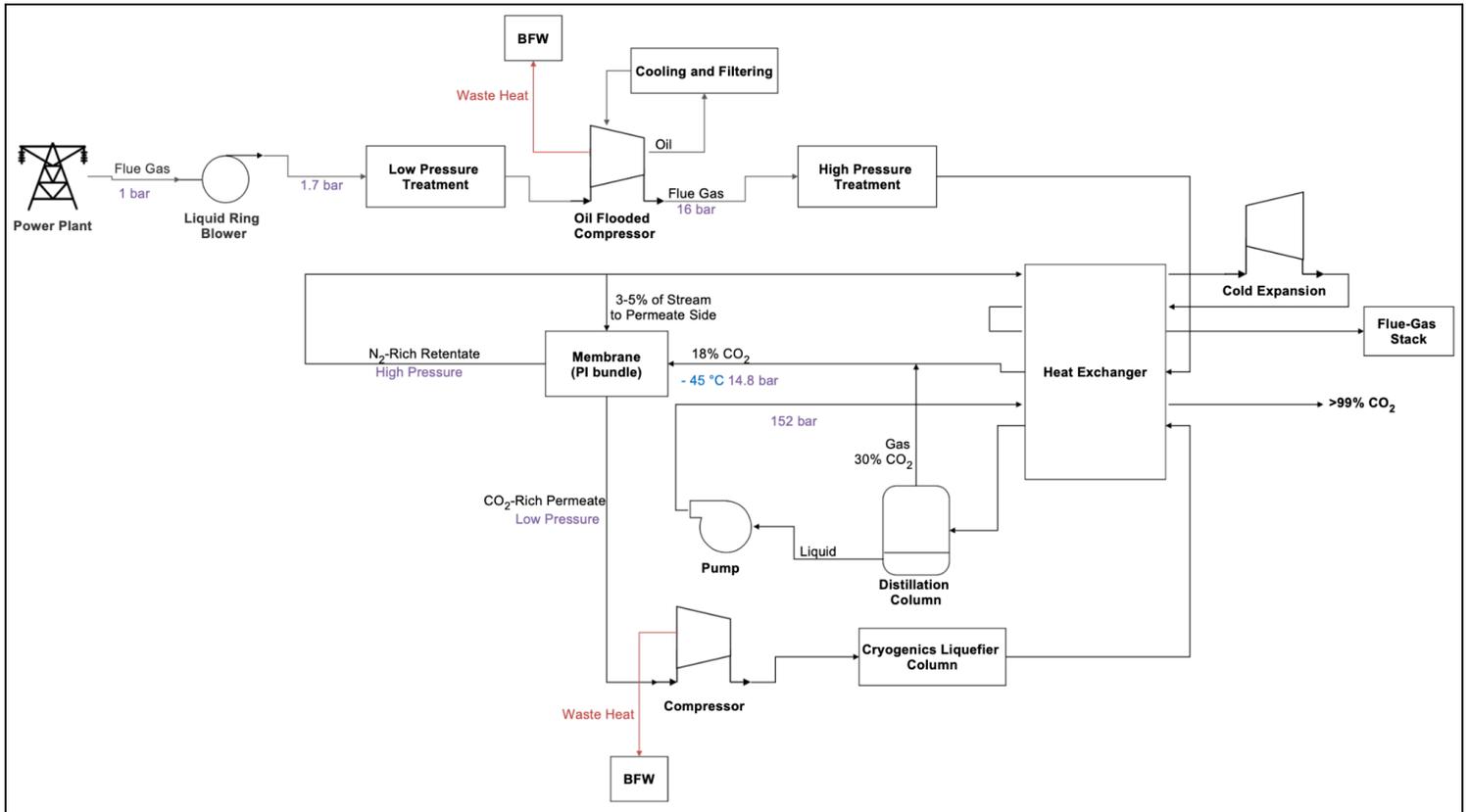


Figure 6. An in-depth schematic of the CRYOCAP carbon capture process.

The same walkthrough approach as done previously in the simplified schematic can be used to understand the CRYOCAP process on a deeper level. Flue gas emitted from the power plant after combustion is sent through the blower to slightly raise the pressure of the flue gas stream from a pressure of 1 bar to 1.7 bar.¹ Following the blower, the stream is sent through low-pressure treatment.¹ This step is used to remove water in a knock-out vessel and particulates in a dust filter to prevent the formation of ice and reduce the risk of moisture and particulate contamination ruining the membrane.¹ The stream is then sent through an oil flooded compressor to increase the pressure of the semi-treated flue gas stream to 16 bar.¹ This unit recycles the oil used to lubricate the spaces between the compressor's rotors, and the waste heat generated from the compression process is used to generate boiler feed water that can be supplied to boilers for hot water and steam production.¹ The pressurized stream is sent to a unit for high pressure treatment.¹ This step is used to remove moisture in a dryer bed, oil residue in

an alumina bed, and small particulates from a fine dust filter, acting as a secondary treatment step to further reduce the risk of contamination.¹

The fully treated flue gas stream is then sent through a brazed-aluminum heat exchanger to cool the gaseous feed down to a temperature between -35 and -45 °C.¹ This heat exchanger is extremely efficient as virtually all of the exchanger's material is used to transfer heat which enables heat transfer across the smallest temperature differences, and the lack of gaskets or supporting equipment enable stable thermodynamic and hydraulic performance.¹ The cooled, pressurized stream is sent to the membrane, which was discussed in depth in the previous section, which produces a high pressure, N₂ rich stream and a low pressure, CO₂ rich stream with a purity upwards of 60% CO₂.¹ The N₂ rich stream is sent back through the heat exchanger, with the exception of 3-5% of the stream that is sent to the permeate side of the membrane to drive the pressure gradient, to aid in the cooling of the pretreated flue gas stream.¹ Finally, after going through a cold expansion step to further cool the nitrogen rich stream and an additional trip through the heat exchanger, the stream is released through the flue gas stack.¹

In comparison, the CO₂ rich stream is sent through a compressor to raise the pressure prior to liquefaction, and this step again produces waste heat which can be used for boiler feed water.¹ Once compressed, the CO₂ rich stream is sent to a cryogenics liquefier column that uses cryogenic temperatures and dew point temperature differences to liquefy a portion of the gaseous stream.¹ A mixture of liquid and gaseous CO₂ that is generated from this process is sent through the heat exchanger for further cooling.¹ The stream is then sent to a distillation column for further purification to meet Enhanced Oil Recovery standards.¹ The liquid stream from this step is pumped to a pressure of 152 bar and is composed of >99% CO₂, and the off-gas from this process, which contains 30% CO₂, is recycled back to the membrane to increase the CO₂ capture rate.¹ This detailed process creates a stream of >99% CO₂ and enables the recovery of 90% of the CO₂ from flue gas.

This schematic describes Air Liquide's experimental CRYOCAP set-up at the bench scale, and the researchers note that the liquid ring blower, oil flooded compressor, and joule thomson valve have low efficiencies at the commercial scale and should be replaced by oil free compressors and turbines.¹

Current Limitations

- Unable to operate below 90% recovery or maintain design of 1.1 bar permeate pressure to explore bundle behavior at different capture rates as they were limited by compressor capacity and blower capacity¹
 - *Improve* by fabricating a bundle with less fiber such that a lower productivity is targeted to test over wider range of CO₂ recovery and understand non-ideal flows¹
- Certain sized bundles experienced a decline in permeance and CO₂/N₂ selectivity with increasing CO₂ capture rate from significant non-ideal flow in the bundle¹

- *Improve* bundle performance through manufacturing technique and using a bundle with a higher length/diameter ratio¹
- Certain bundles experienced a 20% decline in membrane performance from contamination arising from overfilling of oil in the compressor¹
 - *Improve* at large scale by using oil-free compressor¹
- A bundle experienced a 40% loss in CO₂ permeance during cool down phase attributed to moisture breakthrough during start up or insufficient bundle purge time¹
 - *Improve* efficiency of dryer and pretreatment to remove potential moisture by modifying piping for effective drainage of all low points where water can collect¹

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