Review

Insights on Cryogenic Distillation Technology for Simultaneous CO$_2$ and H$_2$S Removal for Sour Gas Fields

Tengku Nur Adibah Tengku Hassan$^{1,2,*}$, Azmi Mohd Shariff$^{1,2,*}$, Mohd Mu’izzuddin Mohd Pauzi$^{1,2}$, Mai Syadiah Khidzir$^{1,2}$ and Amiza Surmi$^{2,3}$

$^1$ CO$_2$ Research Centre (CO$_2$ RES), Institute of Contaminant Management, Universiti Teknologi PETRONAS, Bandar Seri Iskandar 32610, Malaysia; tengku_19000950@utp.edu.my (T.N.A.T.H.); mohd.muizz@utp.edu.my (M.M.M.P.); msysadiah.khidzir@utp.edu.my (M.S.K.)
$^2$ Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar 32610, Malaysia; amiza_surmi@petronas.com.my
$^3$ Group Research & Technology, Petrolam Nasional Berhad (PETRONAS), Lot 3288 & 3289, off Jalan Ayer Itam, Kawasan Institusi Bangi, Kajang 43000, Malaysia

* Correspondence: azzmish@utp.edu.my; Tel.: +60-5-3687530

Abstract: Natural gas demand has dramatically increased due to the emerging growth of the world economy and industry. Presently, CO$_2$ and H$_2$S content in gas fields accounts for up to 90% and 15%, respectively. Apart from fulfilling the market demand, CO$_2$ and H$_2$S removal from natural gas is critical due to their corrosive natures, the low heating value of natural gas and the greenhouse gas effect. To date, several gas fields have remained unexplored due to limited technologies to monetize the highly sour natural gas. A variety of conventional technologies have been implemented to purify natural gas such as absorption, adsorption and membrane and cryogenic separation. The application of these technologies in natural gas upgrading are also presented. Among these commercial technologies, cryogenic technology has advanced rapidly in gas separation and proven ideally suitable for bulk CO$_2$ removal due to its independence from absorbents or adsorbents, which require a larger footprint, weight and energy. Present work comprehensively reviews the mechanisms and potential of the advanced nonconventional cryogenic separation technologies for processing of natural gas streams with high CO$_2$ and H$_2$S content. Moreover, the prospects of emerging cryogenic technologies for future commercialization exploitation are highlighted.

Keywords: natural gas; high CO$_2$ separation; H$_2$S removal; conventional cryogenic technology; unconventional cryogenic technology

1. Introduction

In 2020, BP reported the sharp decline in global natural gas consumption by 81 billion cubic meters (bcm), or 2.3%, due to the unprecedented impact of the COVID-19 outbreak and oil crisis leading to economic downturn worldwide [1]. Despite the persistent impact of the crisis, the U.S. Energy Information Administration (EIA) projected a growth of natural gas utilization by 30% between 2020 and 2050 with the uplifting of economic activity and travel restrictions [2]. In fact, the outlook for natural gas demand seems to be more resilient compared to oil demand. The natural gas demand is expected to recover and robustly increase to approximately 5300 bcm by 2050 [3]. The rising demand of natural gas is mainly driven by progressive economic activities and industrialization in developing Asian countries, such as China and India, with the transition from coal to low-carbon fuels. Hence, the utilization of natural gas is anticipated to continue outperforming the consumption of fossil fuels for power generation and transportation fuel in the future, as it has a lower price and carbon footprint [1,4–7]. Natural gas, however, is a fossil fuel that is extracted from deep beneath the earth’s surface and primarily consists of hydrocarbons or higher alkanes such as ethane, propane, butanes and pentanes. It also contains trace...
amounts of nonhydrocarbons or impurities, including sulfur, helium, nitrogen, hydrogen sulphide and carbon dioxide, and it must be retained as sweet gas for market sale. Natural gas with hydrogen sulphide, having a H$_2$S content of more than 4 parts per million (ppm), is considered sour gas. Sour gas obtains its name from the fact that it smells like rotten eggs and can be found naturally in sewers, crude, hot springs and volcanoes rather than being created by industrial processes such crude oil and gas refining, wastewater treatment and pulp and paper manufacturing. As a result, some underdeveloped gas resources have remained unknown. China has developed the majority of sour gas reservoirs, with about 60% of gas fields containing 20,000 to 40,000 ppm H$_2$S and some containing more than 100,000 ppm [8]. It was stated that the higher the level of H$_2$S, the deeper the reservoir, subsequently leading to a higher temperature, which encourages thermochemical reaction [9]. With the deposition of sulfur, the formation of these gases in natural gas can clog and damage pipelines. During the industrial process, any leakage or blowout of this gas will severely harm the well site and pollute the environment. Furthermore, most of the research solely focuses on CO$_2$ removal to overcome the challenges mentioned before. However, there are only a few studies available that study simultaneous CO$_2$ and H$_2$S removal.

As a result, to solve the pipeline problem, this sour gas must go through a sweetening process to remove H$_2$S and CO$_2$. Absorption, adsorption, membrane separation and cryogenic distillation are the existing technologies for natural gas sweetening. The process that has been widely used for natural gas sweetening is absorption. The absorption process can be classified into two types, which are chemical absorption and physical absorption. These processes are explained in detail in Section 2.1. Amine gas treatment is one of the examples of chemical absorption technology that is widely used in the pretreatment unit of LNG plants and other gas processing plants to sweeten the gas. This process uses amines or other solvents to absorb the acid gases to remove the sour gases from the natural gas. However, this process is not economically viable for high concentrations of gas, as it requires a large footprint and complex offshore facilities. It also requires solvent transportation in order to operate at offshore facilities.

Nevertheless, there are still other technologies that have been developed and implemented in the industry which are more economical and practical. Instead of implementing the absorption process, the adsorption process is applied at industrial scale for a more cost-effective removal [10]. However, Cherif [11] stated that the dominating market share of the adsorption process started to decrease in 2008 due to the development of other technologies. This is because this technology requires a treatment process for the final product. In addition, the operation and expense increase significantly as the supply of fossil fuels decrease [1]. The adsorption technology is reviewed in more detail in Section 2.2. Apart from adsorption, membrane separation can be used to separate the majority of CO$_2$ quickly, but it has many drawbacks in terms of operating costs, heat and chemical resistance and long-term process stability [12]. To obtain less than 2% CO$_2$ in gas sales, this technology necessarily requires gas staging and recycling [13]. This technology is explained in more detail in Section 2.3.

Out of these technologies, cryogenic distillation technology is in a mature stage of its life cycle and has been routinely used in medium to large-scale plants to produce nitrogen, oxygen and argon. This technology is preferred, as it is the most cost-effective technology for high CO$_2$ concentrations and high production rate plants to purify a very high content of oxygen and nitrogen. By reducing the temperature to lower than 73.3 °C using a refrigeration system, cryogenic distillation converts H$_2$S and CO$_2$ from the gas phase to the liquid or solid phase and then valorizes the product [11]. The main advantage of this process is it can produce liquid CO$_2$ that is ready for transportation. One feature of this technique is that it does not involve any water or solvent, which would raise the expense of the removal process.

Overall, natural gas consumption will continue to rise significantly in the coming decades, outpacing that of other fossil fuels. The growth demands are likely to turn into the
exploitation of more sour gas fields and the development of new technologies to separate H2S and CO2 gas from natural gas. Therefore, this paper critically reviews the conventional separation technologies that are applied in industries, focusing more on the insights into cryogenic separation. Cryogenic distillation technologies give more competitive benefits compared to other technologies such as amine gas treatment and membrane separation. Cryogenic distillation has low energy consumption and low CO2 content in the feed stream when compared to amine treatment [11]. The insights of this technology for future removal of sour gas from natural gas are reviewed in more detail in Section 3. The important insights of the review on the conventional separation technologies and advanced cryogenic process for CO2 and H2S removal from sour natural gas are summarized in Table 1.

Table 1. Important insights of the review.

| Category                                      | Insights                                                                 |
|----------------------------------------------|--------------------------------------------------------------------------|
| Conventional CO2 and H2S separation technologies | Gas separation mechanisms of the conventional technologies—absorption, adsorption and membranes and cryogenic separation. Research and development of technologies for sour natural gas treatment Challenges or limitations of conventional separation technologies |
| Advanced cryogenic distillation process       | Modifications or advancements in the conventional cryogenic process—cryogenic packed bed, anti-sublimation, controlled freeze zone (CFZ) and CryoCell The extent of the capability of the processes to handle bulk CO2 and H2S in sour natural gas State-of-the-art and perspective of the advanced cryogenic process for natural gas upgrading application |

2. CO2 and H2S Separation Technologies

2.1. Absorption

At the beginning of the 21st century, the first solvent that was used for the absorption process was a carbonate solution that was applied in dry ice plants to separate CO2 from flue gas [14]. Sodium carbonate solutions were rapidly phased out after the introduction of alkanolamine, as this solvent absorbs CO2 faster and can attain extremely high CO2 removal efficiency [14]. Starting in 1930, primary generation alkanolamine solvents such as diethanolamine (DEA), (MEA) and diglycolamine (DGA) were developed for the CO2 removal process [14–16]. Then, secondary alkanolamine solvents such as diethanolamine (DEA) and diisopropanolamine (DIPA) were invented as alternatives to MEA [17]. The difference between primary and secondary is that the primary alkanolamines contain hydrogen atoms directly bonded to nitrogen [17]. A tertiary alkanolamine solvent, which is methyltriethanolamine (MDEA), was proposed by Frazier and Kohl to promote the selectivity of H2S [17]. In 1983, 2-amino-2-methyl-1-propanol (AMP), which hindered amines, was developed at Exxon Research and Engineering Company [18]. From 1995 to now, there has been a lot of research into sterically hindered amines as potential alkanol amine absorbents. There are also lots of studies that report the promoters, such as piperazine, potassium carbonate, mono ethanol amine (MEA) and diethanolamine (DEA), that can be blended with amine solvent, such as MDEA, to enhance the reaction rates of the absorption process [17]. Starting in 2005, the interest in the usage of amino acid for acid gas removal started to develop in using the sodium or potassium salt glycine (NaGly), which is the simplest primary amino acid, for CO2 capture [19]. Recently, in 2003, ionic liquids, ILs, were branded as “solvents of the future”, as they have the potential as alternative solvents for acid gas removal [20,21].

The absorption process is the process where a gas mixture comes into contact with a liquid (solvent). The gas phase is transported into the liquid phase in the absorption process. This process has been used in the natural gas industry for 100 years for the gas sweetening...
process to separate sour gas from natural gas. It is used to remove any impurities or contaminants in gas mixtures to recover valuable products. This process can be classified into two types of solvents, which are chemical solvents and physical solvents. In chemical solvent processes, alkanolamines or alkaline salts with weak acids, such as sodium or carbonates, are used as solvents for the absorption process. The sweetening of sour gas via absorption is referred to in Figure 1 by using alkanolamines. The sour gas is injected through a tower and makes contact with alkanolamine solutions for the absorption process to happen. The solvent absorbs sulfur compounds from H$_2$S and release the effluent gas. Then, the desorption process, or regeneration process, is performed to strip the acid gases from the solvent at low pressure or high temperature.

Figure 1. Schematic diagram of the amine sweetening process [22]. Reprinted with permission from Speight, J.G. (2015). Copyright 2021 Elsevier.

In physical solvent processes, organic solvents such as methanol, N-Methyl-2-Pyrrolidone, Poly(Ethylene Glycol) Dimethyl Ether, Sulfolane and Diisopropanolamine are used to absorb H$_2$S and CO$_2$ depending on the partial pressure. The performance of the absorption is increased at high partial pressure and low temperature. This process does not have any corrosive effects and also does not require the addition of heat in the stripping process. In addition, physical solvents can strip off impurities without any additional heat. However, this process is not suitable for bulk absorption of CO$_2$ gas, as it requires high pressure and low temperature [23]. Figure 2 shows the flow diagram for the physical absorption process.
In chemical absorption, an aqueous solution of alkanolamines is one of the most effective absorbents that is still widely used for the absorption process for natural gas purification. Nevertheless, this solvent has many drawbacks, including foaming, high cost, high energy consumption for regeneration, high toxicity and high corrosivity. The drawbacks faced by amine-based solvents can be catered back by using aqueous amino acids, as they have the same functional group. Amino acids are one of the alternative solvents that have many advantages, such as high stability towards oxidative degradation, high chemical reactivity with carbon dioxide and low vapor pressure [26]. Due to their physical properties, amino acid solvents have high reactivity towards CO\textsubscript{2} compared to conventional solvents such as MEA and MDEA [27]. Hu G et al. stated that amino acids such as lysine, proline and sarcosine have a larger reaction than monoethanolamine (MEA) for the absorption of CO\textsubscript{2} [26]. The absorption of CO\textsubscript{2} is influenced by the ionic strength, pH and cations of weak bases such as sodium and potassium for the amino acid to react with the CO\textsubscript{2} gas [26]. It was also reported that the use of amino acids blended with amine shows better absorption of CO\textsubscript{2} than the neutralization of amino acids with potassium hydroxide [28]. Nevertheless, the combination of these solvents for large-scale absorption application is not economical because it requires higher regeneration temperature, as stated in Erga et al. [29]. Knuutila et al. [14] found that the use of sarcosine requires a higher energy cost compared to MEA.

Ionic liquids (ILs), particularly functional ILs, are known as unique absorbents for the removal of H\textsubscript{2}S from gas mixtures because they can absorb a large amount of H\textsubscript{2}S at high pressure. Ionic liquids (ILs) have been widely studied for CO\textsubscript{2} and H\textsubscript{2}S absorption, as they have several advantages, such as environmentally friendliness, extremely low vapor pressure, tuneable structure and high thermal and chemical stability [30]. Most of the research found that functionalized ILs can act as catalysts or substitutes for amine-based, metal-based, substituted benzoate-based and pyridinium-based solvents for H\textsubscript{2}S removal. However, the major drawbacks of IL-based solvents are high cost, high viscosity, complicated synthesis process and that they cannot be applied to a large-scale industry. In addition, most industries still prefer gas–liquid systems because this process requires low cost and low energy consumption during solvent regeneration. Overall, the previous literature reviews show that CO\textsubscript{2} and H\textsubscript{2}S removal using green solvents such as amino
acid and ionic liquid are not economical for commercial application due to high cost and energy consumption during operation and regeneration. Moreover, most of the studies for green solvents such as amino acid only focus on CO$_2$ removal, whereas there are only a few literature studies about H$_2$S removal [30].

2.2. Adsorption

The first systematic research on adsorption application began in 1773, conducted by Scheele to observe the adsorption of air by using charcoal via a volumetric apparatus [31]. The first commercial application of the adsorption process was purifying white sugar. Back in 1783, charcoal had been used as the adsorbent to remove impurities and contaminants from sugar [32]. However, during that era, people were not concentrating on the improvement of adsorbent properties and only relied on the natural adsorbent properties such as charcoal, clay and peanut hull [33]. In the 19th century, the study to improve the properties of adsorbent started along with the industrial revolution. The researchers concentrated on the surface area and the porosity of the adsorbent [34,35]. The idea to improve the adsorbent based on the porosity and the surface area began after Chappius measured the isotherm from the adsorbent layers [36].

Adsorption has had numerous applications in industry in the past 30 years, such as in the purification of gas mixtures, mainly in petrochemical, environmental, electronic and medical industries, due to its unique characteristics [37]. There are many types of adsorbents available with different pore sizes and selectivity that create flexible designs to separate and purify gas mixtures for particular desired goals. The impurities removal application includes organic and inorganic impurities removal, electronic gas purification, air pollution control, gas drying, solvent vapour recovery and nuclear waste management. Moreover, the gas separation application includes methane and carbon dioxide separation, hydrogen recovery, air separation, alcohol dehydration, production of ammonia synthesis gas and isoparaffin separation [38]. The well-known technologies commercially used are pressure swing adsorption (PSA), temperature swing adsorption (TSA), vacuum swing adsorption (VSA) and electric swing adsorption (ESA) [39,40]. For NG application, TSA is used for gas purification, whereas bulk gas separation often uses the PSA process [37].

PSA technology was first patented in 1932 by Charles Skarkstrom for oxygen enrichment, in which the cyclic adsorption process was employed using four main steps that included feed, blowdown, purge and pressurization [41]. In PSA, the acid gas stream that contains high CO$_2$ makes contact with spherical adsorbents packed in the column which are typically arranged in parallel to maximize the energy efficiency [42]. The feed gas is initially fed into the column and pressurized to a pressure higher than atmospheric pressure. CO$_2$ is selectively bound and adsorbed on the surface of the adsorbent at high pressure and low temperature until equilibrium is achieved. The adsorbent is saturated with adsorbed CO$_2$. Hence, the regeneration of the adsorbent takes place by restricting the gas flow and depressurizing the column to liberate the CO$_2$ from the surface of the adsorbent [43]. In contrast, the regeneration of adsorbent in VSA is performed at vacuum condition by reducing the pressure below atmospheric pressure, whereas in TSA, CO$_2$ is liberated by increasing the temperature at a constant pressure [44–46]. Meanwhile, ESA is named due to the low-voltage electric current being introduced to heat the adsorbent by the direct Joule effect [47]. The difference between TSA and ESA is that ESA heats the adsorbent by using electric power while TSA heats the adsorbent by using waste heat from noncondensable gas [48].

There are a wide range of adsorbents that have been utilized according to their level of selectivity attraction towards contaminants to be removed. Furthermore, adsorbent enhancement could be achieved by synthesizing and impregnating other compounds onto the surface of the adsorbent. There are two types of adsorption approaches, either physisorption or chemisorption. The physisorption process is a physical process directed by weak Van Der Waals bonds between the adsorbent and adsorbate [49]. On the other hand, chemisorption is governed by the bond formation between the functional groups that attach
at the surface of the adsorbent and the adsorbate [49]. Due to the attached functional groups, chemisorption is generally more efficient than physisorption, specifically when using basic and oxygen-containing groups, as CO$_2$ is acidic in nature; hence, these functional groups play a major role in the removal of CO$_2$ from natural gas [30]. The specific surface area of the adsorbent also has a major effect on the adsorption process. It is well-known that the higher the specific surface area, the higher the adsorption capacity. The major disadvantage of the adsorption system is waste generation. One of the solutions to overcome this issue is introducing the regeneration process to the adsorbent. However, regeneration may not be effective in the long run. The highest number of regeneration cycles obtained in the literature is 5 cycles, after which removal efficiency starts to decrease [51].

The interest in H$_2$S removal in natural gas processing units enhanced several studies to develop regenerable solid sorbents. However, the low adsorption capacity of commercial solid adsorbents needs a large amount of adsorbent bed while frequent disposal of saturated adsorbents is one of the major environmental concerns. The adsorbent-filled fixed bed reactors for H$_2$S capture may operate according to two different mechanisms, either physisorption or chemisorption [52]. Zinc and copper oxides supported on porous adsorbent silica have attracted recent attention for H$_2$S capture due to the potential for the combination of sulfidation thermodynamics and active metal oxides [53,54]. The porous adsorbent is generally synthesized from various composite materials based on metal foams [55], zeolites [56], laterites [57], kaolin [58], silica [59], carbon of miscellaneous sources [60] and other solid phases impregnated with metal salts and their mixtures in order to enhance the adsorption capability of the fixed bed. Bahman Elyasis et al. stated that Cu-ZnO nanoparticles impregnated with mesoporous silica show a significant impact on H$_2$S removal. The amount of H$_2$S captured is 75 mg/g$_{sorbent}$, while the commercial ZnO only captures about 34 mg/g$_{sorbent}$ [61].

NG often contains significant amounts of CO$_2$ and H$_2$S that have to be reduced to less than 1% for CO$_2$ and 4 ppm for H$_2$S to meet the fuel gas specifications for pipeline transportation [62]. Adsorption also has been recognized to be an energy-efficient technology for CO$_2$ and H$_2$S removal, provided that the material exhibits high and stable adsorption capacity along with excellent selectivity toward acid gases. The early work for simultaneous adsorption separation of CO$_2$ and H$_2$S from methane was performed by Huang et al. by using amine impregnated on silica xerogel. They found that the excellent performance in terms of CO$_2$ and H$_2$S adsorption by amine-modified silica is due to large amounts of amine groups on the surface resulting from their high surface areas [63]. However, the CO$_2$ and H$_2$S selectivity was not mentioned. Recently, Ma et al. reported that polyethylenimine (PEI) impregnated with silica is capable of selective adsorption of both CO$_2$ and H$_2$S. However, it was stated that not only is the adsorption of CO$_2$ diffusion limited, but also the optimum temperature for CO$_2$ adsorption is 75 °C, whereas the H$_2$S is 25 °C. Moreover, CO$_2$ seems to strongly inhibit the H$_2$S adsorption at room temperature [64].

The usage of amines as activators for the adsorbent demonstrates certain limitations to CO$_2$ and H$_2$S separation because by nature the CO$_2$ has higher acidity than H$_2$S. Due to both CO$_2$ and H$_2$S being electron acceptors, they have a strong effect on the amines group which leads to reactive and nonreactive adsorption, hence restricting the efficiency of CO$_2$ and H$_2$S separation. This phenomenon occurs due to the adsorbent being more selective toward H$_2$S than CO$_2$ [10]. Most of the commercial gases used in industries consist of both acid gases, such as CO$_2$ and H$_2$S, and polar species, such as H$_2$O or CO. A study performed by Billow et al. investigated the reaction of CO$_2$ and H$_2$S adsorption on LTA and FAU zeolite. They found that H$_2$O was the highest preferred by the adsorbent, followed by H$_2$S and CO$_2$ [65]. Hence, a proper study needs to be conducted to investigate the selectivity ratio of H$_2$O, CO$_2$ and H$_2$S for better separation efficiency.

2.3. Membrane

Over the past few decades, membrane technology emerged as a sustainable process in various applications such as wastewater treatment, food technology, medicine, pharma-
Molecular systems offer several advantages compared to traditional separation techniques, such as low energy consumption, flexibility for scale-up, small footprint, and high energy efficiency. In recent years, membrane technology has made significant progress in the purification of natural gas, with a particular focus on CO₂ and H₂S removal. The demand for CO₂ separation from natural gas has increased due to the growing awareness of environmental issues and the need for CO₂ capture and storage (CCS) to mitigate climate change. CO₂ removal from gas streams is crucial for the successful implementation of CCS projects and to meet the ever-tightening greenhouse gas emission standards.

CO₂ is a major component in sour natural gas, which contains high concentrations of impurities such as H₂S and other hydrocarbons. The presence of these impurities can cause corrosion and fouling of downstream equipment, leading to increased operational costs and environmental issues. Membrane-based acid gas removal technology has emerged as a promising candidate for sour gas treatment, offering a more economical and environmentally friendly solution compared to traditional absorption technologies.

Membrane separation is driven by the pressure and concentration gradient, with the gas molecules diffusing through the semi-permeable membrane barrier. The types of membrane material and properties of the permeants, such as condensability, influence gas transport across the membrane. In addition, the molecular size of the gas molecules significantly affects the gas diffusion rate, with larger molecules diffusing more slowly than smaller ones. This selectivity is crucial for efficient CO₂ separation.

Membrane technology offers several advantages over traditional separation methods, including lower energy consumption, smaller footprint, and higher energy efficiency. Moreover, membrane separation is more economical and environmentally friendly, as it does not require the utilization of any chemical solvent, which eliminates the need for compression to regenerate solvent.

Membranes are generally classified based on material (e.g., glassy or rubbery polymers) and configuration (e.g., flat sheet, hollow fiber or spiral wound). Gas separation is achieved through selective gas transport across the semi-permeable barrier. Figure 3 shows the selective separation of CO₂ and H₂S from natural gas using a hollow fibre membrane system. Gas transport in membrane separation is driven by the pressure and concentration gradient. Theoretically, gas transport behavior in membrane separation is governed by the solution–diffusion mechanism where solubility (S) and diffusivity (D) play important roles to determine gas permeability. The types of membrane material and properties of the permeants, such as condensability, influence gas transport across the membrane. In addition, the molecular size of the gas molecules significantly affects the gas diffusion rate in the order of C₃H₆ > C₂H₆ > CH₄ > N₂ > O₂ > CO₂ > H₂S > H₂ [72]. Membrane separation also requires sufficiently high pressure to drive gas separation. In addition, the pretreatment process is required prior to gas separation to remove any water or heavy hydrocarbons from the feed gas to avoid membrane fouling [73].

![Illustration of selective separation of CO₂ and H₂S from natural gas using hollow-fibre membrane module](image)

**Figure 3.** Illustration of selective separation of CO₂ and H₂S from natural gas using hollow-fibre membrane module [74]. Reprinted with permission from Sanghani, P. et al. (2020). Copyright 2021 Society of Petroleum Engineers (SPE).
Commercial membranes such as cellulose acetate [75], polyimide [76,77] and polyamide are the leading materials used in membrane gas separation due to their robustness, superior permeability and selectivity, as well as excellent durability. Glassy membranes such as cellulose acetate are typically effective for CO\(_2\) separation, while rubbery membranes are typically effective for H\(_2\)S separation. Cyanara-NATCO [75] developed a cellulose triacetate (CTA)-based hollow fiber membrane system for natural gas sweetening in the offshore processing facility at the Cakerawala platform located in the Gulf of Thailand. The membrane system is capable of handling 228.89 m\(^3\)/s process gas and successfully reduces the CO\(_2\) content from 37% to 15%. Recently, Nafisi et al. discovered the potential of fluorinated polyimides (6FDA) for CO\(_2\) separation, where CO\(_2\) permeability attained as high as 1468 Barrer with CO\(_2\)/CH\(_4\) selectivity of 22.6 [78]. Besides polymeric membranes, zeolite membranes such as silicalite-1 [79], SAPO-34 [80,81] and DDR [82,83] also demonstrated a promising performance for separation of CO\(_2\) from CH\(_4\). Zeolite membranes are known for their high selectivity, which is attributed to the uniform pore structures. Poshuta et al. reported a separation factor of 36 with CO\(_2\) permeance of \(2 \times 10^{-8}\) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\) by using SAPO-34 membrane [84]. Furthermore, Cui et al. demonstrated higher performance of zeolite T membrane, where CO\(_2\) permeance and CO\(_2\)/CH\(_4\) selectivity was found to be \(4.6 \times 10^{-8}\) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\) and 400, respectively [85]. The application of zeolite membrane is presently confined to lab-scale study due to its brittle nature and complex fabrication procedure which hamper its commercial opportunity.

On the other hand, some membrane materials also demonstrate promising capability to handle contaminants other than CO\(_2\), such as H\(_2\)S. Currently, the studies on H\(_2\)S removal using membrane separation are usually confined to low H\(_2\)S concentration due to high toxicity and stringent safety requirement during handling. Moreover, the simultaneous existence of these impurities also leads to competitive sorption that consequently minimizes membrane separation performance [86]. Recently, polymers with an etheric oxide (EO) unit, such as commercial PEBAX\(^\text{®}\), appear as promising membranes that offer high H\(_2\)S/CH\(_4\) selectivity ascribed to their high specific interaction with polar molecules such as H\(_2\)S [87]. Previous studies demonstrated that PEBAX\(^\text{®}\) exhibit H\(_2\)S/CH\(_4\) selectivity up to 80 [88,89]. Moreover, some membrane materials also have inherent copermeation properties of CO\(_2\) and H\(_2\)S with relatively high selectivity over CH\(_4\). Cellulose acetate (CA) membrane was the first commercialized polymeric membrane since the 1980s and is presently used in the industry for acid gas removal [86]. Achoundoung et al. [90] reported the equivalent CO\(_2\)/CH\(_4\) and H\(_2\)S/CH\(_4\) selectivity of CA membranes up to 30 under feed pressure of 3447 kPa. However, CA membranes suffer loss of selectivity under aggressive feed conditions.

In 2017, Schlumberger in collaboration with PETRONAS successfully installed and commissioned the CYANARA PN-1 acid gas removal membrane system at onshore gas processing facilities in Terengganu Gas Terminal (TGAST), Malaysia [91,92]. The dual-zoned cellulose acetate-based hollow fibre membrane system efficiently processed 228.89 m\(^3\)/s and produced a gas stream containing 12 mol% to 25 mol% of CO\(_2\) and H\(_2\)S to meet product specifications of <8 mol% CO\(_2\). Compared to the conventional absorption process, the CYANARA PN-1 membrane offers economic advantages through 60% reduction in footprint and 50% installation cost savings. In addition, the installation of the membrane system also is anticipated to reduce operational expenditure (OPEX) by USD 180 million for 20 years of estimated operating cost [91]. Evonik recently launched a high-performance polyimide-based hollow fibre membrane (SEPURAN NG\(^\text{®}\)) in 2018 for selective separation of CO\(_2\) and H\(_2\)S from natural gas. However, the application of SEPURAN NG\(^\text{®}\) is yet to be reported elsewhere.

The application of membrane separation is usually limited to moderate gas flow rate, as performance may deteriorate at high volumes of gas processing. Multistage membrane separation may be necessary to achieve high product purity, which creates additional expenditure. Plasticization and compaction of membranes over a long operation period are the major drawbacks which may impede the excellent progress of membrane gas separation.
technology. The presence of impurities such as CO$_2$, H$_2$S and other heavy hydrocarbons may degrade the integrity of the membrane and thereby result in poor separation performance. Research methods are underway to cater these limitations through the crosslinking of polymer chains, modification of polymer properties and thermal treatment. Mixed matrix membrane (MMM) paved a new avenue in membrane development to improve their separation performance by synergistically combining the processability of polymeric membrane and high selectivity of inorganic filler.

On the other hand, the growing interest in the development of hybrid processes, which combine membrane and other conventional separation technologies, creates opportunity in gas separation. Bhide et al. [93] developed a process design study and economic assessment of hybrid processes by combining membrane separation and amine absorption, which aimed to purify natural gas that contains up to 40 mol% CO$_2$ and 1 mol% H$_2$S. The simulation showed that the hybrid process yielded lower operating costs, costing 1.516 MM USD/year, compared to the independent amine process, costing 2.853 MM USD/year. Furthermore, the total capital investment (TCI) of the hybrid process was estimated to be USD 4.196 MM, which was significantly cheaper than the amine process, which had a TCI of USD 6.226 MM. The cost benefits are due to the fact that the membrane removed approximately 78% of CO$_2$ from the feed stream and thereby minimized the solvent circulation rate as well as the design capacity required for absorption and the solvent regeneration process. Rezakazemi et al. [94] suggested that the hybrid process is feasible for industrial gas separation with feed flow rate more than 8.17 m$^3$/s and CO$_2$ content higher than 12%. Moving forward, the progress of membrane technology in natural gas sweetening will focus on the development of high-performance membranes with an active layer in the order of 0.1 µm to enhance their competitiveness as a sustainable separation process.

2.4. Cryogenic Distillation

Numerous distillation applications were applied in the 19th and 20th centuries, particularly for the alcohol separation process [95]. In 1945, F. Taylor invented the first concept of distillation using laboratory apparatus consisting of three main pieces of equipment: a vessel, a condensing apparatus and a receiver [96]. Then, John M. Chambers (1953) established a more structured distillation column concept to purify the fermented alcohol and remove impurities from the feed stream to obtain high-purity ethanol considering the optimum reflux ratio and heat input in a more stable operation [97]. The demand for distillation technology is increasing rapidly, and the concept is growing and evolving very fast with increased opening of oil refineries and petrochemical plants around the world. Nowadays, most refineries or petrochemical plants have distillation columns in the process, and the application is not just at atmospheric pressure. Still, distillation has been expanded and upgraded for more challenging environmental conditions such as high pressure, low-temperature and high-temperature process, cryogenic temperature, vacuum condition, etc.

The distillation column is designed to separate two or more components from the feed gas stream. The concept of separation is based on differences in boiling point or relative volatility of the component. The low boiling point component is left as a top product, while the higher boiling point component is at the bottom of the column as a liquid product. The operating temperature and pressure are critical parameters in achieving the separation performance [98,99]. Typically, the distillation column operates at a two-phase region where the vapor and liquid contact plays an important role in mass transfer. The liquid will flow from top to bottom of the column, while the vapor will flow counter-currently to the top, and the vapor–liquid interaction is where the mass transfer for the separation occurs [100].

The internal design of the distillation column, including the selection of trays or packing, is key for mass transfers to meet the performance. The selection of the internals will depend on the purpose of the separation, physical properties, service or system,
operating conditions, etc. Typically, the designer will conduct the process simulation to evaluate the feasibility of the design before proceeding with the detailed engineering design of the column [99–106]. The design and operation of the distillation column are challenging and require good process control to have stable operation, since it involves changes in phase inside the distillation column due to different temperature profiles in each theoretical stage. Furthermore, maintaining the operating pressure and controlling the cooling and heating rate at the condenser and reboiler are important to achieve the separation target [105,107]. Cryogenic separation is one of the most efficient methods to separate high CO$_2$ concentration together with H$_2$S. Cryogenic separation is widely used commercially to separate CO$_2$ content to meet the pipeline specification [108].

Despite the bright potential of the technology, the operation of the distillation column is highly energy-intensive, and it consumes almost 40% of energy in the chemical industry to meet the separation performance of the process [109]. Therefore, a lot of optimization and improvement of the distillation column is currently ongoing by researchers to minimize the project’s overall cost. More advanced cryogenic technology for the process separation is further discussed in the following section.

3. Advancement of Cryogenic Distillation

The modifications on the conventional cryogenic distillation are further discussed in the following section.

3.1. Cryogenic Packed Bed

A packed bed separator is one of the examples of nonconventional methods because the component will desublimate and turn into solid phase throughout the process [110]. In the CO$_2$ and H$_2$S capture, cold bed material is used as the heat transfer surface between the CO$_2$ and the cryogenic conditions. The cryogenic separation process starts with precooling the bed material to −120 °C as a cooling step by using cold nitrogen gas that feeds into the packed bed column. After this precooling process is completed, the cold nitrogen gas is stopped from being injected into the column and switched with the flue gas containing sour gas. The CO$_2$ and H$_2$S sublimate and water condenses on the bed to form crystals after sufficient cooling of the bed material. These CO$_2$ and H$_2$S crystals continue to form on the bed material until the bed material becomes concentrated. The process of crystal formation continues on the fresh bed material further into the column. This process leads to front frost that spreads through the packed column. The rate of the front frost is called front frost velocity, and the regeneration of the packed column is required once the packed column is concentrated with the crystal [108]. In the regeneration process, CO$_2$ is recycled for CO$_2$ recovery while air is recycled for water recovery. The regeneration process is compatible with the low flow rate gas and needs to be performed on at least three beds in parallel. Figure 4 shows the schematic process flow for the cryogenic packed bed for CO$_2$ removal [111].

The advantage of the packed bed cryogenic separation is that CO$_2$, water and other impurities such as H$_2$S can be simultaneously removed from the sour gas based on the differences of their dew and sublimation points [110]. In addition, the issues of pressure drop and clogging can be prevented [112]. Tuineir et al. stated that the packed bed cryogenic process has an advantage in that it does not require chemical sorbent and elevated pressure to be performed [113]. The chemical sorbent contributes to the increase in capital expenditure (CAPEX) when the chemical sorbent needs to be replaced due to the degradation effect [16]. The elevated pressure is not required on the cryogenic process due to the crystallization of CO$_2$, water and H$_2$S, which is determined by the cold energy in the bed material packing [113]. In addition, the packed bed cryogenic separation has better purity of the main product compared to the pressure swing adsorption process (PSA). Tuinier et al. performed a study on the effect of packed bed cryogenic separation on the quality of the methane compared to the PSA. They found that methane recovery improved to 94.3% and methane productivity improved to 350.2 kg CH$_4$ h$^{-1}$ m$_{packing}^3$, compared to
the PSA process, where methane recovery and productivity were only about 79.7% and 43.1 kg CH$_4$ h$^{-1}$ m$^{3}$packing$^{3}$, respectively [114].

![Diagram of cryogenic packed bed](image)

**Figure 4.** Process flow for cryogenic packed column with (above) counter current and (below) cocurrent flow configuration [111]. Reprinted with permission from Ali, A. et al. (2014). Copyright 2021 John Wiley and Sons.

The energy requirements for the conventional and nonconventional cryogenic methods have been questioned recently. Energy minimization is very important for technology to be economically reliable. Abulhassan et al. studied the comparison of energy requirements between the conventional method and the packed bed method, which is the nonconventional cryogenic method using gas mixture with CO$_2$ concentration of 70% [111]. They found that the cryogenic packed bed used less energy, about 810 kJ/kg CO$_2$, compared to the conventional cryogenic method, which used about 1472 kJ/kg CO$_2$, to separate the CO$_2$ from the gas mixture. In addition, a study from Tuinier et al. stated that the energy consumption for the packed bed cryogenic process was 22% lower than the PSA process [114]. The energy required for the packed bed cryogenic separation was 2.9 MJ/kg CH$_4$, whereas the PSA separation process required 3.7 MJ/kg CH$_4$ [114]. The CAPEX of the cryogenic process can be reduced if the methane needs to be liquefied since the methane leaving the cryogenic packed bed is already at a very low temperature; hence, the cost of the additional part to install the liquefied process system can be prevented [110].

The cryogenic packed bed faces several limitations and challenges, even though this technology has potential compared to chemical absorption and PSA. The main issue of the cryogenic packed bed is that the current thermal insulator available commercially is not good enough to maintain a low temperature during the process. The cold energy loss to the environment leads to cold energy supply increasing, along with time. Hence, the technology of the thermal insulator needs to be improved to avoid sensible and latent heat loss [115]. In addition, the simultaneous purification of CO$_2$ and H$_2$S requires high energy consumption, as the dew point of H$_2$S is around $-150^\circ$C. For obtaining a high H$_2$S removal efficiency, the process needs to be performed at a very low temperature for a long period. The process will lead to an increase in operation expenditure (OPEX) [116]. The cold energy exchange or heat integration from the liquefied natural gas (LNG) production and air separation unit (ASU) is recommended to cover any loss during the purification process [117].
3.2. Anti-Sublimation (AnSU)

Anti-sublimation (AnSU) is a phrase referring to the reverse phase change from gas to solid, where the initial term sublimation is defined as the phase change from solid to gas. CO₂ removal using AnSU is a post-treatment method that utilizes the thermodynamics of CO₂ anti-sublimation at atmospheric pressure [118]. CO₂ is directly converted from gas to solid phase at a point when the pressure is lower than the triple point pressure. Figure 5 shows the phase diagram for pure CO₂ that illustrates the CO₂ phase change with respect to pressure and temperature.

![CO₂ phase diagram](image)

**Figure 5.** CO₂ phase diagram [119]. Reprinted with permission from Pan, X., Clodic, D. and Toubassy, J. (2013). Copyright 2021 John Wiley and Sons.

The sublimation temperature of CO₂ also depends on its concentration inside the flue gas. The flue gas needs to further cool down to bring the CO₂ into the solid phase if the CO₂ pressure is lower than its triple point. Figure 6 shows the phase envelope for the CO₂ and CH₄ mixture with variation of the CO₂ concentration. The triple point for every CO₂ and CH₄ mixture varies depending on the CO₂ concentration. For instance, the triple point of 80% of CO₂ has been found at −65 °C and 30 bar of pressure. Based on Figure 6, the anti-sublimation process needs to maintain pressure between 1 bar and 40 bar and temperature between −60 °C and −150 °C for obtaining the solid–vapour phase, depending on the CO₂ concentration [120]. Consequently, the CH₄ which is still in vapour form can be separated and commercialised.

![CO₂-Ch₄ mixture phase envelope](image)

**Figure 6.** Phase envelope of CO₂-CH₄ mixture [120]. Reprinted with permission from Maqsood, K. et al. (2015). Copyright 2021 Walter de Gruyter and Company.
There are five stages in the AnSU process for CO\textsubscript{2} removal as illustrated in Figure 7. The first stage is mainly for moisture removal and cooling by lowering the temperature down to $-40$ °C. The removal of water in this stage is crucial to avoid any hydrates in the main process line later. There are three loops of water removal set in series which consist of a condensing unit (CU) and evaporating unit (EU) for each loop. The rich flue gas (RFG) is fed into CU1, CU2 and CU3 and cooled by the sprayed solution during these three stages of condensing units. Meanwhile, the poor flue gas (PFG) goes to three evaporation units (EU), which are EU1, EU2 and EU 3. The solution loops are heated by RFG in CU and cooled by PFG in EU. This solution mainly consists of CaCl\textsubscript{2} to capture the water. The temperature of the flue gas after CU1 is about 20 °C and 0 °C after CU2 with a water content of 6500 ppm. After CU3, the sprayed CaCl\textsubscript{2} reduces the temperature down to $-40$ °C with a water content of 160 ppm.

![Figure 7. Schematic diagram of anti-sublimation process mechanism](image-url)

The second stage of AnSU is mainly to reduce the water content down to 1 ppm level. The heat exchanger (FFX) is installed after CU3 and PFG goes to EU3 to recover the coldness of PFG coming from the low-temperature CFX. RFG is cooled down to $-100$ °C in FFX. The defrosting approach at FFX is important, as the water content at the RFD inlet is 160 ppm and targeted to obtain 1 ppm at the RFG outlet. The third stage of AnSU is to provide a low temperature for CFX to convert CO\textsubscript{2} from gas to solid. The RIC consists of several cooling stages.

The fourth stage is the CO\textsubscript{2} freezing in the CFX heat exchanger. RFG enters CFX at $-100$ °C and the CO\textsubscript{2} will antisublimate, where the CO\textsubscript{2} phase directly converts into solid from gas. CFX is designed to present a temperature glide along the section since the CO\textsubscript{2} partial pressure of 12 kPa will solidify at $-101$ °C and $-119$ °C at 1.5 kPa. The final stage of the AnSU process is CO\textsubscript{2} recovery. The CO\textsubscript{2} is not only covered in liquid but also gas from the RIC evaporator enclosure. The major advantage of this AnSU technology is that high purity of CO\textsubscript{2} captured (99.9% purity) is obtained without having any contamination [119,121–123].

A few studies show that AnSU technologies could provide less energy consumption compared to the typical absorption technology in terms of CO\textsubscript{2} removal. A study performed
by D. Clodic et al. stated that the energy consumption for CO₂ removal is only high at a low CO₂ concentration and becomes lower as the concentration of CO₂ is increased [123]. Hence, the AnSU can be implemented either in low or high CO₂ concentrations, as the energy consumption for CO₂ concentration above 10% is significantly low.

Schach et al. studied and compared AnSU and adsorption technology in terms of electrical energy consumption using ASPEN HYSYS for the same 90% of CO₂ removal efficiency [124]. They found that AnSU technology is better at reducing electrical energy demand compared to the adsorption of CO₂ using MEA. The total electrical power required for AnSU, which is 178 MW, is much lower, while the adsorption is 209 MW. Moreover, the specific electrical energy required per kg of CO₂ captured in AnSU technology is also lower compared to the adsorption, with values of 0.286 kWh/kg CO₂ and 0.391 kWh/kg CO₂ respectively, which reduces the total operation expenditure (OPEX) for the treatment plant [124]. Table 2 illustrates the summary of the comparison between AnSU and adsorption technologies performed by Schach et al.

Table 2. Power plant efficiency loss, total power required and specific electric required comparison between adsorption and AnSU [124]. Adapted with permission from Schach, M. et al. (2011). Copyright 2021 Elsevier.

| Technology Used          | Adsorption | AnSU   |
|--------------------------|------------|--------|
| Power plant efficiency loss | 12.5%      | 10.7%  |
| Total electrical power required | 209 MW     | 178 MW |
| Specific electric required | 0.391 kWh/kg CO₂ | 0.286 kWh/kg CO₂ |

Even though AnSU is a great technology for high efficiency and as an alternative for CO₂ removal, this technology faces several limitations and challenges in terms of operation and maintenance. The major drawback for AnSU is the usage of several compression systems in the process which require regular maintenance due to involvement of rotating parts. This compression system is essential to provide the expansion condition that will be used for obtaining the lower temperature due to Joule–Thomson effect. The regular maintenance for this compression system will increase the operation expenditure from time to time. In addition, the capital expenditure for AnSU is also relatively higher due to its complexity to operate, which was discussed previously in the mechanism of AnSU. AnSU consists of five stages of process mechanisms in which each stage has its own special required equipment. However, there is no study yet on simultaneous CO₂ and H₂S removal that utilises AnSU as one of the removal techniques. To overcome the limitations and challenges faced by AnSU, it is proposed to integrate cooling energy from other sources to the heat exchanger inside the AnSU process. A good supply of cooling energy could replace the complexity of the compression and expansion systems in providing a low temperature for the system.

3.3. Controlled Freeze Zone (CFZ)

The application of the conventional cryogenic distillation process in gas separation, particularly involving CO₂, was often subjected to CO₂ solidification at low temperatures [125]. Intensive efforts have been devoted to valorize the solidified CO₂ obtained from the cryogenic separation for geo-sequestration of CO₂. In 1985, ExxonMobil Upstream Research Company introduced and patented a nonconventional cryogenic technology of controlled freeze zone (CFZ™) technology to separate CO₂ and H₂S from natural gas [125,126]. CFZ™ technology is usually used for bulk CO₂ removal from natural gas. This technology offers an integrated solution to overcome the bottlenecks of cryogenic technology through a single-step cryogenic distillation process to treat sour gas resources with high contaminants such as CO₂. Compared to the conventional cryogenic approach, the CFZ™ process allows CO₂ to freeze out under controlled conditions using a unique designed section in the distillation column. A typical CFZ™ process with a modified rectification section is capable of purifying natural gas to meet pipeline specifications with CO₂.
concentration of less than 50 ppm [127]. CFZ™ offers lower capital expenditure (CAPEX) compared to the other conventional separation technologies, owing to its small footprint, less processing equipment and no solvent being required.

CFZ™ usually operates at a constant pressure while the operating temperature is determined by the feed conditions and expected product specifications. The configuration of CFZ™ technology is illustrated in Figure 8. The CFZ™ tower is comprised of three sections: (1) the conventional upper rectifying section, (2) the controlled freeze zone section and (3) the conventional for bottom stripping section [128]. At the upper section, CO₂ content is reduced in the rectifying section via conventional distillation. Entering the solidification area, the liquid from the upper section is sprayed into the unobstructed opening area of the CFZ™ section through nozzles where it encounters a warmer temperature ranging between −90 °C and −85 °C and vaporizes lighter components such as CH₄. Consequently, the liquid droplet is increasingly rich with CO₂ and solidified within the chamber at a solidification temperature of −62 °C to −45 °C. Beyond the solidification condition, the solids CO₂ forms fall onto the liquid layer at the bottom of the CFZ™ section and are directed to the stripping section for CH₄ recovery. CH₄ is stripped off from the bottom liquid stream enriched with CO₂ and other contaminants at the bottom of the CFZ™ chamber via conventional distillation. Besides CO₂, the bottom liquid stream may also contain other contaminants such as H₂S, mercaptans and heavy hydrocarbons. As a result, the top product exiting the column is significantly concentrated with CH₄.

**Figure 8.** Process flow for controlled freeze zone (CFZ™) cryogenic distillation technology [125]. Reprinted with permission from Abdulsalam, J. et al. (2018). Copyright 2021 Taylor & Francis.

In 1985, Exxon Production Research built a pilot plant with a capacity of 0.6 MCFD at Clear Lake Gas Plant, Houston to evaluate the capability of this technology to process natural gas containing CO₂ between 15% and 65%. The CFZ™ was operated at pressure ranging from 3447 to 4137 kPa. The pilot plant successfully obtained products that met pipeline quality which approached LNG specification by reducing CO₂ content down to ppm levels along with a minimum CH₄ loss of 0.5%. Following the CDP, ExxonMobil developed a commercial demonstration project (CDP) in 2007 at Shute Creek Gas Treating facility (SCTF), LaBarge, WY, USA to evaluate the commercial readiness of CFZ™ technology. The project aimed to process and sequester CO₂ from sour natural gas for acid gas injection application [129]. The CDP was designed to process 228.89 m³/s natural gas with CO₂ and H₂S content of 65% and 5%, respectively, at the high pressure of 4137 kPa [130]. This process is capable of obtaining the overhead product with CO₂ and H₂S composition of
680 ppm and 1.2 ppm, respectively. Moreover, the bottom liquid product contains 4.1% CO₂ and 0.23% H₂S. The energy requirement of CFZ™ technology is not yet reported elsewhere.

Interestingly, the application of CFZ™ technology is economically viable for highly sour gas separation because it is capable of processing a wide range of CO₂ and H₂S compositions in the feed gas. The overhead product and bottom liquid product, which are discharged at relatively high pressure, significantly reduce the recompression cost for sales gas delivery through pipeline and acid gas reinjection to the reservoir. To date, acid gas injection (AGI) emerged as a common approach to dispose the separated CO₂ and H₂S from natural gas. The combination of CFZ™ and AGI technology facilitates the geo-sequestration of CO₂ for enhanced oil recovery by exploiting the high-pressure liquid stream discharged at the bottom of the column. On the other hand, the CFZ™ process also imposed a less stringent dehydration requirement rendered by the high water-holding capacity of the liquid CO₂ [131]. Valencia et al. [131,132] reported that compared to Ryan Holmes and combined bulk fractionation-Selexol processes, CFZ™ demonstrated lower capital expenditure by 5% and 10%, respectively. Mart [133] cited that the economic advantages offered by CFZ™ are attributed to the simplicity of the process that minimizes the needs of processing equipment. Using CFZ™, a significant operational cost–savings between 12% and 37% was attained, relative to the conventional processes such as Selexol, combined bulk fractionation-Selexol- and Ryan Holmes. Furthermore, a greater sales gas revenue of 4% to 8% can be achieved by exploiting the excellent process efficiency through the integrated configuration of CFZ™ and AGI technologies. However, the application of CFZ™ for simultaneous separation of CO₂ and H₂S remains challenging due to the inhibition of CO₂ solidification with the presence of H₂S [130]. Currently, the demonstration project of CFZ™ has been completed and the technology is ready for scale-up and commercialization to process sour feed gas up to 326.99 m³/s [134].

3.4. CryoCell

CryoCell® is a nonconventional cryogenic technology developed by Cool Energy Ltd. in 2009 to treat high-CO₂ natural gas fields using the similar concept of CO₂ sublimation as applied in CFZ™ process [135]. The portable and compact design of CryoCell® provides the flexibility of this process for offshore applications [136]. Besides separation, this technology also demonstrates great potential for geo-sequestration of CO₂ by reinjecting the liquid CO₂ obtained in the bottom product into the reservoir for geological storage. Compared to the conventional separation technology, CryoCell® offers economic advantages by eliminating the need for water consumption, chemicals or solvents and minimizing the possibilities of corrosion-related issues. These benefits would result in lowering capital cost of CryoCell® by 20% to 40% relative to the conventional LNG purification process. In fact, by taking advantage of the Joule–Thomson effect, the requirement for the refrigeration process can be significantly minimized. The laboratory trials of CryoCell® demonstrated the capability of this process to reduce up to 70% of CO₂ content in natural gas and moisture levels down to less than 200 ppm.

The configuration of the CryoCell® process is illustrated in Figure 9. In the CryoCell® process, the feed gas containing high CO₂ initially undergoes a dehydration process to reduce the moisture level down to 5 ppm [110]. The dried feed gas is then cooled to a temperature higher than the freezing point of CO₂ at a constant pressure, which results in condensation of the feed gas mixture into liquid phase. Next, the liquid mixture expands through the Joule–Thomson valve at a constant enthalpy that leads to phase change of the CO₂ into three phases that include liquid, solid and vapor [137]. The operating condition of CryoCell® is critical to ensure low CO₂ content in the vapor phase while maintaining rich CO₂ in the liquid product. The different phases of CO₂ are separated in the CryoCell® separator. The solid CO₂ collected at the bottom of the separator is melted using external heating sources and combined with the existing liquid product. Besides CO₂, the solids product may also contain heavy hydrocarbons and H₂S. The rich-CO₂ liquid product that exits the bottom of the separator is compressed to meet the required disposal pressure prior
to the reinjection into the reservoir. Meanwhile, the vapor product emerging from the top of the column is compressed to meet sales gas delivery specifications.

In 2006, a commercial demonstration plant (CDP) was developed by Cool Energy Ltd. in collaboration with Shell Global Solutions at Perth Basin, Western Australia to explore the viability of this technology. The plant design of this 2 MMscf/d plant was built based on the process flow scheme for low CO\(_2\)-lean gas as proposed by Hart and Gnanendran [135]. The compact module of CryoCell\(^\circledR\) was designed to process natural gas with CO\(_2\) content up to 60 mol\% at feed pressure ranging between 5500 and 6500 kPag. The feed flow rate also varies between 600 kg/h and 1300 kg/h based on the desired feed stream composition. The CryoCell\(^\circledR\) separator was operated at three different pressures of 1200 kPag, 1600 kPag and 1900 kPag. Meanwhile, the temperature of the reboiler was maintained between \(-50^\circ\)C and \(-60^\circ\)C throughout the testing. The CDP revealed that the CryoCell\(^\circledR\) technology successfully reduced about 81% CO\(_2\) in natural gas.

Hart and Gnanendran [135] performed a benchmark study between CryoCell\(^\circledR\) versus amine process which aimed to treat 16.5 m\(^3\)/s feed gas with CO\(_2\) composition of 20 mol\% and 35 mol\% using Aspen HYSYS. Based on the simulation, CryoCell\(^\circledR\) utilized significantly lower heat duty of less than 0.1 MW compared to the amine process which required process heating between 19 and 35 MW. In view of economics, CryoCell\(^\circledR\) technology demonstrated significant cost savings for plant installation with the total cost of 65.84 AUD/kg of CO\(_2\).
and 90.88 AUD/kg of CO₂ for 20 mol% and 35 mol% of CO₂ content, respectively. Meanwhile, the amine process yielded a total cost of 86.70 AUD/kg of CO₂ and 146.53 AUD/kg of CO₂ for both CO₂ contents. This economic benefit exploits the advantages of the simplified gas treatment process, geo-sequestration of CO₂ and low energy requirement due to elimination of solvent pumping and heat requirement for the reboiler duty. Nonetheless, the compression and refrigeration requirement slightly offset the cost-savings of CryoCell® technology. The simulation data show that CryoCell® technology requires higher compression power, between 4.3 MW and 7.0 MW, than the amine absorption process, which requires between 1.9 MW to 3.8 MW, at increasing CO₂ content in natural gas.

Cool Energy Ltd. is expected to undertake the commercialization of this technology in the future with the successful completion of the first phase of Front-End Engineering and Design (FEED) study for 19.62 m³/s Cryocell® plant at Cooper Basin, South Australia. Provided with the commercial demonstration plant testing and simulation data, CryoCell® shows a huge potential for natural gas treatment with high CO₂ while sequestering the CO₂ for geological storage. Currently, the studies on the application of CryoCell® are still ongoing to overcome the operational challenges to control the CO₂ freezing and handling of solids formation. According to Amin et al. [136], without reliance on any pretreatment system such as amine or membrane process, CryoCell® is capable of handling a wide range of contaminants such as heavy hydrocarbons and H₂S. However, limited literature is available to further understand the application of this technology for H₂S removal. Hence, future work that extends on this application would be beneficial to monetize the underdeveloped sour gas fields by taking advantage of their benefits in terms of energy requirement, economics and compact design.

4. Future Outlooks and Perspectives of Cryogenic Technology

The exploration of sour natural gas fields plays a significant role in ensuring a sustainable energy supply to accommodate the rising energy demand fueled by the growth of population and economy. From the viewpoint of economics, cryogenic technology is well-suited for bulk CO₂ removal to monetize the subquality gas fields. In fact, the technology also demonstrates a great potential towards achieving the Net Zero Carbon Emission 2050 aspiration. Despite the excellent advancement of the cryogenic process, the current application of cryogenic separation is usually limited to CO₂ separation, while removal of H₂S is still rarely reported. The removal of H₂S through the cryogenic process remains challenging, as it is a highly energy-intensive process which requires a very low operating temperature, leading to dramatic increases in operating expenditure [110]. Hence, future work on the integration between cryogenic process and liquefied natural gas (LNG) production is significantly important to harness cold energy to provide a sufficiently low temperature for the cryogenic separation. Consequently, the operating expenditure of cold utilities and energy consumption can be significantly minimized. Moreover, in terms of thermodynamics, the phase equilibrium data are typically available for CO₂–CH₄ binary gas systems, while the presence of higher hydrocarbons and contaminants are rarely highlighted. Therefore, further research is necessary to develop a thermodynamic model which accounts for the multicomponents present in natural gas [138,139]. The thermodynamic study is crucial to facilitate the design and optimization of an energy-efficient and high-performance cryogenic process. On the other hand, hybrid methods which integrate the cryogenic process and other separation processes, such as membrane separation and absorption, are identified as promising approaches to enhancing the efficiency of natural gas purification. By exploiting the advantage of high CO₂ recovery, hybrid processes are anticipated to produce high-quality LNG that meets market specification with lower energy consumption [140].

5. Conclusions

The criticality of CO₂ and H₂S removal from natural gas which aims to monetize undeveloped sour gas fields is highlighted in this review paper. The application of the
conventional separation technologies for natural gas sweetening such as absorption, adsorption and membrane and cryogenic separation are briefly discussed. However, these conventional technologies are often associated with multiple drawbacks such as energy-intensiveness, corrosion issues, high compression and regeneration cost, as well as degradation of materials’ integrity due to long operation time. In fact, these technologies were also reported less economical for the treatment of highly sour natural gas. Thus, cryogenic separation emerged as an economically attractive technology for natural gas upgrading, particularly for feed gas with high CO\(_2\) content. Multiple benefits are offered by this technology in terms of capital and operational cost, energy requirements, product purity and environment. Until now, several unconventional cryogenic technologies, such as cryogenic packed bed, anti-sublimation (AnSU), Controlled Freeze Zone (CFZ\(^\text{\textregistered}\)) and CryoCell\(^\text{\textregistered}\), are currently explored to enhance the efficiency of the cryogenic separation. In addition, these nonconventional cryogenic technologies also offer huge potential in the sequestration of CO\(_2\) for enhanced oil recovery and minimization of greenhouse gas effects. The commercial readiness of cryogenic technology is also reviewed in the present work. While substantial research and commercial trials of the different cryogenic technologies are currently available for high CO\(_2\) removal, the data for H\(_2\)S removal are still scarce. Thus, future work is necessary to fully comprehend the viability of these technologies for upsampling and commercialization for coremoval of CO\(_2\) and H\(_2\)S application.

**Author Contributions:** Conceptualization, A.M.S., T.N.A.T.H., M.M.M.P., M.S.K. and A.S.; writing—original draft preparation, T.N.A.T.H., M.M.M.P., M.S.K. and A.S.; writing—review and editing, A.M.S., T.N.A.T.H., M.M.M.P., M.S.K. and A.S.; supervision, A.M.S.; funding acquisition, A.M.S., M.M.M.P. and A.S. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by PETRONAS Research Sdn Bhd, grant number 015MD0-055 and Yayasan Universiti Teknologi PETRONAS, grant number 015LC0-136.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors would like to acknowledge Universiti Teknologi PETRONAS for the facilities provided for the CO\(_2\) and H\(_2\)S related research work.

**Conflicts of Interest:** The authors declare no conflict of interest.

**Sample Availability:** Samples of the compounds are not available from the authors.

**References**

1. BP p.l.c. Statistical Review of World Energy 2021. 2021. Available online: https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html (accessed on 13 December 2021).
2. U.S. Energy Information Administration. International Energy Outlook 2021—With Projections to 2050. 2021. Available online: https://www.eia.gov/outlooks/ieo/ (accessed on 13 December 2021).
3. BP p.l.c. Energy Outlook 2020 Edition. 2020. Available online: https://www.bp.com/en/global/corporate/news-and-insights/press-releases/bp-energy-outlook-2020.html (accessed on 13 December 2021).
4. International Energy Agency. Gas 2020. 2020. Available online: https://www.iea.org/reports/gas-2020 (accessed on 13 December 2021).
5. Pellegrini, L.A.; Langé, S. An Innovative Technology for Natural Gas Sweetening by Means an Innovative Technology for Natural Gas Sweetening by Means of Cryogenic Distillation. In Proceedings of the GPA Europe Annual Conference, Florence, Italy, 16–18 September 2015.
6. ExxonMobil. 2019 Outlook for Energy: A Perspective to 2040; 2019; pp. 1–58. Available online: https://corporate.exxonmobil.com/Energy-and-innovation/Outlook-for-Energy (accessed on 22 December 2021).
7. Solutions, S.G. Natural Gas: Providing More and Cleaner Energy. Available online: https://www.shell.com/energy-and-innovation/natural-gas/providing-more-and-cleaner-energy.html (accessed on 29 October 2021).
8. Mao, J.; Yang, X.; Wang, D.; Zhang, Y.; Luo, S.; Smith, G.S.; Li, Y.; Zhao, J. Optimization of effective sulfur solvents for sour gas reservoir. *J. Nat. Gas Sci. Eng.* **2016**, *36*, 463–471. [CrossRef]
9. Lei, D.; Fu, D. Overview: The geological genesis in high sour gas reservoir. In Proceedings of the 2013 International Conference on Computational and Information Sciences (ICCIS ’13), Shiyang, China, 21–23 June 2013; pp. 1220–1222.

10. Georgiadis, A.; Charisiou, N.; Gould, M. Removal of Hydrogen Sulfide From Various Industrial Gases: A Review of The Most Promising Adsorbing Materials. *Catalysts* **2020**, *10*, 521. [CrossRef]

11. Cherif, H. Study and Modeling of Separation Methods H2S from Methane, Selection of a Method Favoring H2S Valorization. Ph.D. Thesis, PSL Research University, Paris, France, 2016.

12. Narayan, R.S.; Patton, C.J. Bulk CO2 Removal Achieved Through Membrane Separation. In Proceedings of the SPE Annual Technical Conference and Exhibition, Houston, TX, USA, 16–19 September 1984.

13. Burr, B.; Lyddon, D. A Comparison of Physical Solvents for Acid Gas Removal. *Water*. 1998. Available online: https://www.bre.com/PDF/A-Comparison-of-Physical-Solvents-for-Acid-Gas-Removal-REVISED.pdf (accessed on 29 October 2021).

14. Knuutila, H.; Svendsen, H.F.; Juliussen, O. Kinetics of carbonate based CO2 capture systems. *Energy Procedia* **2009**, *1*, 1011–1018. [CrossRef]

15. Bottoms, R.R. Process for Separating Acidic Gases. U.S. Patent 1783901A, 7 October 1930. Available online: https://patents.google.com/patent/US1783901A/en (accessed on 29 October 2021).

16. Vega, F.; Sanna, A.; Navarrete, B.; Maroto-Valer, M.; Cortés, V. Degradation of amine-based solvents in CO2 capture process by chemical absorption. *Gamm. Gases Sci. Technol.* **2014**, *4*, 707–733. [CrossRef]

17. Vega, F.; Cano, M.; Camino, S.; Fernández, L.M.G.; Portillo, E.; Navarrete, B. Solvents for Carbon Dioxide Capture. In *Capture and Oil Recovery, Karam*, I., Shaya, J., Srou, H., Eds.; IntechOpen: Rijeka, Croatia, 2018; p. 8.

18. Shah, M.S.; Tsapatsis, M.; Siepmann, J. Hydrogen Sulfide Capture: From Absorption in Polar Liquids to Oxide, Zeolite, and Metal-Organic Framework Adsorbents and Membranes. *Chem. Rev.* **2017**, *117*, 9755–9803. [CrossRef]

19. Weiland, R.H.; Hatcher, N.A.; Nava, J.L. Post-combustion CO2 Capture with Amino-Acid Salts. *GPA Eur.* **2010**, *22*, 24.

20. Rogers, R.D.; Seddon, K.R. Ionic Liquids—Solvents of the Future? *ISRN Chem. Eng.* **2012**, *2012*, 368381. [CrossRef]

21. Greer, A.J.; Jacquemin, J.; Hardacre, C. Industrial Applications of Ionic Liquids. *Molecules* **2020**, *25*, 5207. [CrossRef]

22. Speight, J.G. Fouling During Gas Cleaning. In *Fouling in Refineries*; Heinemann: Boston, MA, USA, 2011; pp. 251–300.

23. Georgiadis, A.; Charisiou, N.; Goula, M. Removal of Hydrogen Sulfide From Various Industrial Gases: A Review of The Most Promising Adsorbing Materials. *Catalysts* **2020**, *10*, 521. [CrossRef]

24. Miller, B.G. Clean Coal Technologies for Advanced Power Generation. In *Clean Coal Engineering Technology; Rahimpour, M.R., Farsi, M., Makarem, M.A., Eds.; Woodhead Publishing: Sawston, UK, 2020; pp. 479–501.

25. Ghasem, N. Chapter 21—CO2 Capture from Flue Gases Using Pressure Swing Adsorption. In *Advances in Carbon Capture and Sequestration; IntechOpen: Rijeka, Croatia, 2018; p. 8.

26. Bottoms, R.R. Process for Separating Acidic Gases. U.S. Patent 1783901A, 7 October 1930. Available online: https://patents.google.com/patent/US1783901A/en (accessed on 29 October 2021).

27. Ghasem, N. Chapter 21—CO2 Capture from Flue Gases Using Pressure Swing Adsorption. In *Advances in Carbon Capture and Sequestration; IntechOpen: Rijeka, Croatia, 2018; p. 8.

28. Bottoms, R.R. Process for Separating Acidic Gases. U.S. Patent 1783901A, 7 October 1930. Available online: https://patents.google.com/patent/US1783901A/en (accessed on 29 October 2021).

29. Wang, B.; Zhang, K.; Ren, S.; Hou, Y.; Wu, W. Efficient capture of low partial pressure H2S by tetraethyl ammonium amino acid liquidics with absorption-promoted solvents. *RSC Adv.* **2016**, *6*, 101462–101469. [CrossRef]

30. Rouquerol, J.; Avnir, D.; Yetter, D.H.; Dischler, C.; Haynes, M.; Pernicone, N.; Ramsay, J.D.F.; Sing, K.S.W.; Unger, K.K. Guidelines for the Characterization of Porous Solids. *Stud. Surf. Sci. Catal.* **2000**, *134–143*. [CrossRef]

31. Knuutila, H.; Svendsen, H.F.; Juliussen, O. Kinetics of carbonate based CO2 capture systems. *Energy Procedia* **2009**, *1*, 1011–1018. [CrossRef]
72. Jariwala, A. High H2S Gas Field Monetization: A Novel Approach. In Proceedings of the Offshore Technology Conference, Houston, TX, USA, 6–9 May 2019.

73. Lin, H.; White, L.S.; Lokhandwala, K.; Baker, R.W. Natural Gas Purification. In Encyclopedia of Membrane Science and Technology; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2013; pp. 1–25. [CrossRef]

74. Sanghani, P.; Kumar, H.; Ghorbani, N.; Morisato, A.; Mahley, G. Sour Gas Has A Sweeter Future-Bulk H2S Removal Using Polymeric Cellulose Triacetate Based Membranes. In Proceedings of the Abu Dhabi International Petroleum Exhibition & Conference 2020, Abu Dhabi, United Arab Emirates, 11 November 2020.

75. Callison, A.; Davidson, G. Offshore processing plant uses membranes for CO2 removal. Oil Gas J. 2007, 105, 56–65.

76. Jusoh, N.; Lau, K.K.; Shariat, A.M.; Yeong, Y.F. Capture of bulk CO2 from methane with the presence of heavy hydrocarbon using membrane process. Int. J. Greenh. Gas Control 2014, 22, 213–222. [CrossRef]

77. Jusoh, N.; Lau, K.K.; Shariat, A.M. Removal of Bulk CO2 from Methane with the Presence of Heavy Hydrocarbon using Polyimide Membrane. J. Teknol. 2014, 69, 41–46. [CrossRef]

78. Nafisi, V.; Hägg, M.B. Gas separation properties of ZIF-8/6FDA-durene diamine mixed matrix membrane. Sep. Purif. Technol. 2014, 128, 31–38. [CrossRef]

79. Zhu, W.; Habranek, P.; Gora, L.; Kapteijn, F.; Mouljin, J.A. Role of Adsorption in the Permeation of CH4 and CO2 through a Silicalite-1 Membrane. Ind. Eng. Chem. Res. 2006, 45, 767–776. [CrossRef]

80. Li, S.; Martinek, J.G.; Falconer, J.L.; Noble, R.D.; Gardner, T.Q. High-Pressure CO2/CH4 Separation Using SAPO-34 Membranes. Ind. Eng. Chem. Res. 2005, 44, 3220–3228. [CrossRef]

81. Li, S.; Falconer, J.L.; Noble, R.D. Improved SAPO-34 membranes for CO2/CH4 separations. Adv. Mater. 2006, 18, 2601–2603. [CrossRef]

82. Himeno, S.; Tomita, T.; Suzuki, K.; Nakayama, K.; Yajima, K.; Yoshida, S. Synthesis and permeation properties of a DDR-type zeolite membrane for separation of CO2/CH4 gaseous mixtures. Ind. Eng. Chem. Res. 2007, 46, 6989–6997. [CrossRef]

83. Mobashir, M.; Fong, Y.Y.; Keong, L.K.; Shariat, M.A.B. Synthesis and performance of deca-dodecasil 3 rhombohedral (ddr)-type zeolite membrane in CO2 separation—A review. ASEAN J. Chem. Eng. 2015, 14, 48–57. [CrossRef]

84. Poshusta, J.C.; Tuan, V.A.; Pape, E.A.; Noble, R.D.; Falconer, J.L. Separation of light gas mixtures using SAPO-34 membranes. AIChE J. 2000, 46, 779–789. [CrossRef]

85. Cui, Y.; Kita, H.; Okamoto, K.-I. Preparation and gas separation performance of zeolite T membrane. J. Mater. Chem. 2006, 16, 4902–4908. [CrossRef]

86. Lu, H.T. The Impact of Impurities on the Performance of Cellulose Triacetate Membranes for CO2 Separation. Ph.D. Thesis, Chemical Engineering Department, School of Chemical and Biomedical Engineering, The University of Melbourne, Melbourne, Australia, 2018.

87. Chatterjee, G.; Houde, A.; Stern, S. Poly(ether urethane) and poly(ether urethane urea) membranes with high H2S/CH4 selectivity. J. Membr. Sci. 1997, 135, 99–106. [CrossRef]

88. Sadeghi, M.; Talakesh, M.M.; Shamsabadi, A.A.; Soroush, M. Novel Application of a Polyurethane Membrane for Efficient Separation of Hydrogen Sulfide from Binary and Ternary Gas Mixtures. Chem. Select. 2018, 3, 3302–3308. [CrossRef]

89. Harrigan, D.J.; Yang, J.; Sundell, B.J.; Lawrence III, J.A.; O’Brien, J.T.; Ostraat, M.L. Sour gas transport in poly (ether-b-amide) membranes for natural gas separations. J. Membr. Sci. 2020, 595, 117497. [CrossRef]

90. Achoundong, C.S.K.; Bhuwania, N.; Burgess, S.K.; Karvan, O.; Johnson, J.R.; Koros, W.J. Silane Modification of Cellulose Acetate Dense Films as Materials for Acid Gas Removal. Macromolecules 2013, 46, 5584–5594. [CrossRef]

91. Schlumberger. Petronas Gas Plant Reduces Costs with Dual-Core Acid Gas Removal Membranes. 2018. Available online: https://www.slb.com/resource-library/case-study/osf/cynara-acid-gas-removal-membrane-systems (accessed on 25 October 2021).

92. Schlumberger. CYNARA-Acid Gas Removal Membrane Systems. 2016. Available online: https://www.slb.com/well-production/processing-and-separation/gas-treatment/cynara-acid-gas-removal-membrane-systems (accessed on 25 October 2021).

93. Bhide, B.; Voskeriyan, A.; Stern, S. Hybrid processes for the removal of acid gases from natural gas. J. Membr. Sci. 1998, 140, 27–49. [CrossRef]

94. Rezkazemi, M.; Heydari, I.; Zhang, Z. Hybrid systems: Combining membrane and absorption technologies leads to more efficient acid gases (CO2 and H2S) removal from natural gas. J. CO2 Util. 2017, 18, 362–369. [CrossRef]

95. Liebmann, A.J. History of distillation. J. Chem. Educ. 1956, 33, 166. [CrossRef]

96. Taylor, F.S. The evolution of the still. Sci. Am. 1945, 5, 185–202. [CrossRef]

97. Chambers, J.M. Alcohol Distillation Process. U.S. Patent 2647078, 17 December 1949. Available online: https://patents.google.com/patent/US2647078A/en (accessed on 27 October 2021).

98. Kaymak, D.B.; Luyben, W.L.; Smith IV, O.J. Effect of relative volatility on the quantitative comparison of reactive distillation and conventional multi-unit systems. Ind. Eng. Chem. Res. 2004, 43, 3151–3162. [CrossRef]

99. Department of Chemical and Environmental Process Engineering. Packaged Distillation Columns; Budapest University of Technology and Economics: Budapest, Hungary, 2016; pp. 1–7.

100. Blahuisik, M.; Kiss, A.; Kersten, S.; Schuur, B. Quick assessment of binary distillation efficiency using a heat engine perspective. Energy 2016, 116, 20–31. [CrossRef]

101. Pilling, M.; Holden, B.S. Choosing trays and packings for distillation. Am. Inst. Chem. Eng. CEP 2009, 105, 44–50.

102. Spiegel, L.; Duss, M. Structured Packings; Elsevier Inc.: Amsterdam, The Netherlands, 2014.
103. Patil, K.; Choudhary, P.; Bhatia, T. Distillation Operations: Methods, Operational Dynamics and Design Issues. In Proceedings of the National Conference on Advances in Heat & Mass Transfer, FAMT, Ratnagiri, India, 30–31 December 2009; pp. 1–9.

104. Agarwal, S.; Taylor, R. Distillation Column Design Calculations Using a Nonequilibrium Model. Ind. Eng. Chem. Res. 1994, 33, 2631–2636. [CrossRef]

105. Kolmetz, K.; Ng, W.K.; Lee, S.H.; Lim, T.Y.; Summers, D.R.; Soyza, C.A. Optimize distillation column design for improved reliability in operation and maintenance. Asia-Pac. J. Chem. Eng. 2007, 2, 294–307. [CrossRef]

106. Kolmetz, K.; Jaya, A. Distillation Column Reboiler Selection, Sizing, and Troubleshooting. In Kolmetz Handbook of Process Equipment Design; KLM Technology Group: Johor Bahru, Malaysia, 2013; Available online: https://www.klmtechgroup.com/PDF/EDG-SYS/ENGINEERING-DESIGN-GUIDELINES-reboiler-Rev1.3web.pdf (accessed on 27 October 2021).

107. Taqvi, S.A.; Tufa, L.D.; Muhadizir, S. Optimization and Dynamics of Distillation Column Using Aspen Plus®. Procedia Eng. 2016, 148, 978–984. [CrossRef]

108. Font-Palma, C.; Carun, D.; Udemu, C. Review of Cryogenic Carbon Capture Innovations and Their Potential Applications. J. Carbon Res. 2021, 7, 58. [CrossRef]

109. Fitzmorris, R.E.; Mah, R.S.H. Improving distillation column design using thermodynamic availability analysis. AIChE J. 1980, 26, 265–273. [CrossRef]

110. Song, C.; Liu, Q.; Deng, S.; Li, H.; Kitamura, Y. Cryogenic-based CO2 capture technologies: State-of-the-art developments and current challenges. Renew. Sustain. Energy Rev. 2019, 101, 265–278. [CrossRef]

111. Ali, A.; Maqsood, K.; Syahera, N.; Shariff, A.B.; Ganguly, S. Energy minimization in cryogenic packed beds during purification of natural gas with high CO2 content. Chem. Eng. Technol. 2014, 37, 1675–1685. [CrossRef]

112. Tuinier, M.; Annaland, M.V.S.; Kramer, G.; Kuipers, H. Cryogenic CO2 capture using dynamically operated packed beds. Chem. Eng. Sci. 2010, 65, 114–119. [CrossRef]

113. Tuinier, M.; Annaland, M.V.S.; Kuipers, H. A novel process for cryogenic CO2 capture using dynamically operated packed beds—An experimental and numerical study. Int. J. Greenh. Gas Control 2011, 5, 694–701. [CrossRef]

114. Tuinier, M.J.; Annaland, M.V.S. Biogas Purification Using Cryogenic Packed-Bed Technology. Ind. Eng. Chem. Res. 2012, 51, 5552–5558. [CrossRef]

115. Demko, J.; Fesmire, J.E.; Johnson, W.L.; Swanger, A.M. Cryogenic Insulation Standard Data And Methodologies. AIP Conf. Proc. 2014, 1573, 463–470.

116. Baxter, L.; Baxter, A.; Burt, S. Cryogenic CO2 capture as a cost-effective CO2 capture process. In Proceedings of the 26th Annual International Pittsburgh Coal Conference 2009, PCC 2009, Pittsburgh, PA, USA, 20–23 September 2009.

117. Fu, Q.; Kansha, Y.; Song, C.; Liu, Y.; Ishizuka, M.; Tsutsumi, A. An Advanced Cryogenic Air Separation Process Based on Self-heat Recovery for CO2 Separation. Energy Procedia 2014, 61, 1673–1676. [CrossRef]

118. Berstad, D.; Anantharaman, R.; Nekså, P. Low-temperature CO2 capture technologies—Applications and potential. Int. J. Refrig. 2013, 36, 1403–1416. [CrossRef]

119. Pan, X.; Clodic, D.; Touabassi, J. CO2 capture by antisublimation process and its technical economic analysis. Greenh. Gases Sci. Technol. 2013, 3, 8–20. [CrossRef]

120. Maqsood, K.; Mullick, A.; Ali, A.; Kargupta, K.; Ganguly, S. Cryogenic carbon dioxide separation from natural gas: A review based on conventional and novel emerging technologies. Rev. Chem. Eng. 2014, 30, 453–477. [CrossRef]

121. Clodic, D.; Younes, M. A new method for CO2 capture: Frosting CO2 at atmospheric pressure. In Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies, Kyoto, Japan, 1–4 October 2002; pp. 155–160.

122. Clodic, D.; Younes, M.; Bill, A. Test results of CO2 capture by anti-sublimation Capture efficiency and energy consumption for Boiler plants. In Greenhouse Gas Control Technologies 7; Elsevier Science Ltd.: Amsterdam, The Netherlands, 2005; pp. 1175–1780.

123. Clodic, D.; Hitti, R.; Younes, M.; Bill, A.; Casier, F. CO2 capture by anti-sublimation Thermo-economic process evaluation. In Proceedings of the Fourth Annual Conference on Carbon Capture and Sequestration, Alexandria, VA, USA, 2–5 May 2005.

124. Schach, M.-O.; Oyazuzu, B.; Schramm, H.; Schneider, R.; Repke, J.-U. Feasibility study of CO2 capture by anti-sublimation. Energy Procedia 2011, 4, 1403–1410. [CrossRef]

125. Abdulsalam, J.; Mulopo, J.; Amosa, M.; Bada, S.; Falcon, R.; Oboirien, B.O. Towards a cleaner natural gas production: Recent developments on purification technologies. Sep. Sci. Technol. 2018, 54, 2461–2497. [CrossRef]

126. Haut, R.C.; Denton, R.D.; Thomas, E.R. Development and application of the controlled-freeze-zone process. SPE Prod. Eng. 1989, 4, 265–271. [CrossRef]

127. Nichols, J.L.V.; Friedman, B.M.; Nold, A.L.; McCutcheon, S.; Goethe, A. Processing technologies for CO2 rich gas. In Proceedings of the 88th Annual Convention of the Gas Processors Association, San Antonio, TX, USA, 8–11 March 2009.

128. Rufford, T.E.; Smart, S.; Watson, G.C.; Graham, B.F.; Boxall, J.; Da Costa, J.D.; May, E.F. The removal of CO2 and N2 from natural gas: A review of conventional and emerging process technologies. J. Pet. Sci. Eng. 2012, 94, 123–154. [CrossRef]

129. Valencia, J.; Northrop, P.; Mart, C. Controlled Freeze Zone™ Technology for Enabling Processing of High CO2 and H2S Gas Reserves. In Proceedings of the IPTC 2008: International Petroleum Technology Conference, Kuala Lumpur, Malaysia, 3–5 December 2008.

130. Northrop, P.S.; Valencia, J.A. The CFZ™ process: A cryogenic method for handling high-CO2 and H2S gas reserves and facilitating geosequestration of CO2 and acid gases. Energy Procedia 2009, 1, 171–177. [CrossRef]
131. Valencia, J.A.; Kelman, S.D. The Controlled Freeze Zone™ Technology for the Development of Sour Gas Resources. In Proceedings of the International Petroleum Technology Conference 2013, Beijing, China, 26–28 March 2013.

132. Valencia, J.A.; Denton, R.D.; Northrop, P.S.; Mart, C.J.; Smith, R.K. Controlled freeze zone technology for the commercialization of Australian high CO₂ natural gas. In Proceedings of the Society of Petroleum Engineers-SPE Asia Pacific Oil and Gas Conference Exhibition APOGCE 2014-Changing the Game: Opportunities, Challenges and Solutions, Adelaide, Australia, 14–16 October 2014; Volume 2, pp. 951–961.

133. Mart, C.J.C. Controlled Freeze Zone™ Technology–An Integrated Solution for Processing Sour Natural Gas. *Glob. Clim. Energy Proj. Res. Symp. 2009*. Available online: https://gcep.stanford.edu/events/symposium2009/presentations.html (accessed on 27 October 2021).

134. Northrop, S.; Seagraves, J.; Ramkumar, S.; Cullinane, T. Exxonmobil’s experience with sour gas treating and acid gas handling. In Proceedings of the Abu Dhabi International Petroleum Exhibition & Conference ADIP 2019, Abu Dhabi, United Arab Emirates, 11–14 November 2019.

135. Hart, A.; Gnanendran, N. Cryogenic CO₂ capture in natural gas. *Energy Procedia 2009*, 1, 697–706. [CrossRef]

136. Amin, R.; Jackson, A.; Kennaird, T. The Cryocell: An Advanced Gas-Sweetening Technology. In Proceedings of the International Petroleum Technology Conference This, Doha, Qatar, 21–23 November 2005; pp. 1–5.

137. Park, J.; Yoon, S.; Oh, S.Y.; Kim, Y.; Kim, J.K. Improving energy efficiency for a low-temperature CO₂ separation process in natural gas processing. *Energy 2021*, 214, 118844. [CrossRef]

138. Babar, M.; Bustam, M.A.; Ali, A.; Maulud, A.S.; Shafiq, U.; Mukhtar, A.; Shah, S.N.; Maqsood, K.; Mellon, N.; Shariff, A.M. Thermodynamic data for cryogenic carbon dioxide capture from natural gas: A review. *Cryogenics 2019*, 102, 85–104. [CrossRef]

139. Babar, M.; Bustam, M.A.; Ali, A.; Maulud, A.S. Identification and Quantification of CO₂ Solidification in Cryogenic CO₂ Capture from Natural Gas. *Int. J. Automot. Mech. Eng. 2018*, 15, 5367–5376. [CrossRef]

140. Liu, B.; Yang, X.; Chiang, P.; Wang, T. Energy Consumption Analysis of Cryogenic-Membrane Hybrid Process for CO₂ Capture from CO₂ EOR Extraction Gas. In *Aerosol and Air Quality Research;* Taiwan Association for Aerosol Research: Taoyuan City, Taiwan, 2020; Volume 20, pp. 820–832.